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Studies on Flame Retardant Finishes for Cellulosic and Polyester Fibers

Shigeko Nakanishi

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Chapter 3 Establishment of Finishing conditions for the Most Favorable Flame Retardance and Physical Properties for Textile End Uses

Chapter 1

Chapter 1 General Introduction

1-1 "Target" of This Study

-is to Maintain the "Safety" in Our Daily Life-

The most important condition for the human life is the "safety". Any natural calamity, such as earthquake, storm or flood, beyond the human capacity, can not be managed by the human power, but for fire, there is a big possibility left over to us to prevent by ourselves.

However, according to the investigations by Tokyo Fire Defense Agency, 6500-7000 cases/year have been occurred in the latest 10 years only in Tokyo and number of dead was 130 cases/year in average. The recent countrywide trend has showed that the latest data is 64,100 cases/year increasing from the previous year by 2% and number of dead was 2000 (2356 in 1995 because of Hanshin earthquake) and that of wounded approximately 8000. Another information has told that an increasing tendency has been found particularly among aged persons and infants who are short in quick action. Therefore, the fire protection is indispensable for the safety of life as well as for the human life protection.

The fire generally occurs by ignition of flammable gases generated from any flammable materials by thermal degradation caused by exposure to high temperatures raised by approaching or contact of any heat source. Once they are ignited, flame flashes over traveling vertically along vertical things e. g. curtains to reach ceiling. If it happens on a carpet, flame will propagate also horizontally. In the case of flammable clothes, ignited flame reaches a chin within 5 sec.

Therefore, in order to prevent such disaster caused by fire, it is highly required to make any flammable materials flame retardant to retard ignition or to extinguish by themselves after ignition rather than fire fighting after outbreak of fire.

However we have been surrounded by too many flammable materials in our environment, specially fiber products are the most ignitable and flammable also from the shape, particularly in the case of clothing materials, flammability or flame retardance could be vital factor dominating life or death.

In our house, at any basic living space, curtain, paper sliding door or screen in Japanese style dwellings can be big media for flash over which is the initiation of fire. It has been informed that about 90% of the dead by building fire which occupy 60% of the total fire is from fire of ordinary dwelling houses, which tells us how many or much flammable materials exist in our dwelling houses. The main ignited goods are beddings, clothes and cloths and heat sources are burning cigarettes or cooking fire. The famous hazardous accident which happened at a hotel in Tokyo in

1982 was originated by a burning cigarette left on bed by a guest who fell into sleep without quenching.

Disasters of fire which have been successively occruing not only at hotels but also at supermarkets, old-age homes and underground cables confirm necessity of the flame retardation of any flammable materials.

Taking the above facts into consideration, the study finally aimed at contributing to the protection from fire to secure the safety in our daily life, i. e., attention was based on specially high flammability of fiber products as materials for clothes used to directly cover the human body and targeted on the flame retardation of these flammable materials to prevent fire for maintaining safety in our daily life, i. e., the investigation was initiated by establishing the most favorable finishing conditions for many kinds of flame retardant finishes for cellulosic, polyethylene terephthalate (PET) as well as cotton/PET blended fabrics and extended to the effects of these flame retardant finishes on the physical properties of fabrics and on the discoloration of dyed fabrics in combination of effect of ultraviolet irradiation as well as to the durability of durable flame retardant finished samples.

Since burning cigarette in fiber assemblies is most significant heat source for fire as mentioned above, next investigation was carried out for the purpose of observing heat propagation behavior in fiber assemblies from burning cigarette by using miniature sleeping Futons to simulate the practical and real conditions.

The purpous was further extended to observe thermal degradation behavior as the origin of fire to see there would be any difference in thermal degradation behavior between flammable samples and flame retardant samples, simultaneously, investigations were performed for another purpose of obtaining very important information about pyrolytic gas production behavior to study how the flame retardant finishing would work effectively to inhibit or reduce the generation of pyrolytic gases including toxic gases and what kind of flame retardant finish would be the most effective.

As mentioned above, the study this time was extended to the wide range.

1-2 Historical Circumstances for Flame Retardation

It is no exaggeration to say that the improvement of the human race was initiated by attaining a means to control fire. Fire is indispensable for maintaining the human life as well as for daily life, and the human race has succeeded in greate improvement by discovery of fire, however, it is extremely dangerous. Therefore, the human race has been utilizing fire and protecting from the danger of fire to reach the present life through a long history of strategy with fire.

1-2-1 Trend in Practical Field

In Japan "Fire in Edo (Tokyo)" was famous from highly frequent fire outbreak in Tokyo, and firemen in this Edo era wore jackets made of thick cotton cloth with stiching. They might have recognized that thick cloths would retard ignition and stiching would make ignition harder by reducing the air content involved in the fiber structure. Moreover, at the time of fire fighting, they wetted by pouring water upon themselves, which is only means of those days to protect themselves from heat and flame with nothing of knowledge and technology for the flame retardation but knowing the flame retardant and quenching effect of water on any flammable materials. Effect of moisture on the flammability of textile materials was studied scientifically by Miller et al.[1] in 1975, and the authors[2] have also investigated on influences of water contents in cotton fiber on flame retardance of flame retardant finished fabric.

It seems that the desire for flame retardation of flammable materials has been considerably long in the history of the human race. Researches on the flame retardation of cotton have been initiated already in 17th century and continued extending over 2 centuries, and evaluated to have reached the approximate completion in the latter half of 1980s. But in the period of 1800-1900, there were all nondurable finishes treated with single or mixed solutions of water soluble inorganic compounds such as boric acid and borax, diammonium hydrogen phosphate or ammonium chloride.

In U. S. A., materials treated with such inorganic compounds were used for tents for the military use or sheets for army trucks or weapon carriers, but loss of flame retardance by exposure to rain was a big problem, which required for developing any water proof durable flame retardant and a durable flame retardant finish called FWWMR finish by US army during the 2nd world war. This is a combination of paraffin chloride and antimony oxide. But it was yet for only for tents not for clothing materials which have been the main use of cotton.

After the 2nd world war, the development for durable flame retardant finishing for cotton has become very active since the mid-twentieth century, i. e., THPC, APO, TRIS, Fyrol FR-2 and Pyrovatex CP came into the market one after another, but of which TRIS, APO and Fyrol FR-2 were banished because of the toxicity.

Thus, when agitated over the toxicity of flame retardants, man-made fibers, such as acrylic and PET have been developed and flame retardant man-made fiber materials for which materials themselves were brought flame retardant were further developed.

However, such actual trend as every year increase in demands for natural fibers represented by cotton and wool in spite of such development of synthetic fibers can not be denied, particularly cotton has been evaluated the most favorable material for underwear etc. which are used for those directly contact with the body skin because of agreeable feeling and high hygroscopicity, and none of synthetic fibers could have such favorable properties. However, cotton indispensable for the human life has such demerit as highly flammable and easily ignited.

Therefore, such flame retardant finishes as to add safety simultaneously with making the most of good properties of cotton have been strongly required even after appearance of many other flame retardant materials, and tremendous efforts have been made continuously for researches centering in Europe and the United States.

As the results of constant researches, tetrakishydroxymethylphosphonium chloride (THPC) was developed as a durable flame retardant for cotton fabrics as mentioned above in U. S. A. in 1953 followed by an improvement such as ammonia cure of THPC by Albright & Wilson Co. (A & W) in U. K. in 1960 and further improvement has been successively achieved in various countries such as Switzerland, Germany, U. S. A. and Japan etc. Some of them were patented also in Japan.

In 1980s, instead of THPC, a new type flame retardant with THP sulfate, THPS, was developed, by which handing was improved and formation of toxic component as well as of formaldehyde was inhibited. Up to present, a flame retardant finish by ammonia cure of THPS has been widely used throughout the world as PROBAN finish together with Pyrovatex finish (Ciba Geigy) which have been representative durable flame retardant finishes.

On the other hand, finishes with inorganic compounds have not been ignored because of easy and handy finishing procedures in spite of lacking in washability. Therefore, nondurable materials treated with water soluble inorganic salts have been employed for indoor goods such as stage curtains in public facilities for entertainment, curtains or interior goods in dwelling houses for which frequent washing is unnecessary.

As for the kinds, flame retardants of the whole world have been universally used simultaneously with the internationalization of the flame retardant goods market. For example, when focused to the U. S. market, mixtures of boric acid and borax with or without addition of ammonium carbonate and ammonium sulfate, diammonium hydrogen phosphate alone or with ammonium sulfate and ammonium chloride or ammonium sulfamate which have been indicated in the circular of NBS (National Bureau of Standard). Therefore these can be recognized as the classics and the origin of flame retardant finish.

In Japan, the initiation of flame retardant finish was brought by the allied forces after the 2nd world war. Some of them were adopted at that time with a guidance that such inorganic precipitations are only applicable to cellulosic fiber products but not to synthetic fibers.

As mentioned above, since synthetic fibers appeared, flame retardant finishes were investigated also for those man-made fibers, of which flame retardant finish was studied preferentially for PET fibers most widely used in the world, Hexabromocyclododecane (HBCD) has been used for PET since Br is effective on PET. According to our studies, addition of a slight amount of phosphorus (P) shows remarkable elevation of flame retardance by the synergistic effect. Nevertheless, such fact has neither been recognized by the industrial field nor been utilized for any practical use, which has been disclosed by the result of the investigation that only 1 company out of 10 has been using P in combination with Br.

At present, the build-in method seems to be applied to man-made fibers for the flame retardation in more cases than the after treatment, and products have appeared in the market as flame retardant man-made fibers with various trade names. The major flame retardant fiber products are PET and acrylic which is a copolymer with modacrylic fiber, and a part of share is occupied by polyvinyl chloride or phenol type polymers. It should not be ignored that the build-in method has been attempted also to regenerated cellulose to manufacture flame retardant polynosic fiber since 1970s.

Concerning cotton/PET blended fabrics, nothing special but the same or similar compounds mentioned above for 100% cotton or simultaneous use with Br compounds for PET and antimony trioxide have been employed. Series of studies on flame retardant finishes for cotton/PET blended fabrics have been published by Nakanishi et al.

Wool is less flammable, yet thin fabrics have been sometimes finished for flame retardance though the recognition of flame retardant for wool was retard until 1990s.

1-2-2 Transition in Research Fields

The first patent for a textile flame retardant was granted in 1735. This fact satisfactorily explains that the necessity of flame retardation for highly flammable textiles has been recognized for such long time as longer than 260 years.

The first systematic study on the flame retardation for textiles was initiated by Gay-Lussac in 1820. Since then, studies on almost all inorganic salts have been carried out so far, of which the above mentioned boric acid and borax or ammonium salts of sulfur (S) and P have been practically used in the world market up to present.

In the first half of 20th century up to 1950s, effects of P on flammability of cellulosic fiber were considerably studied and a fact concerning increase in flammability with insufficient P content was also reported[3].

On the other hand, it has been found already in 1920 that methylol groups in THP salts are extremely reactive with NH_3 to form a water insoluble resinous substance[4], and it was found in 1953 that THPC could be applied to the durable flame retardant finish for cotton fabric followed by the development of ammonia cure for THPC in1960 and further improved by modification of chloride to sulfate in 1980s as mentioned above.

In the last period of 1950s, observations of thermal degradation of cellulose were reported one after another[5-8], and investigations on the thermal degradation behavior, the flame retardation mechanism as well as on the chemical modification of cellulose observed with flame retardation by the thermogravimetry simultaneously with the development of thermobalance. Shift of thermogravimetric (TG) curves to lower temperatures shown by flame retardant cellulose treated with inorganic salts has been reported in 1958[7]. Furthermore, it has been found at about the same time that Br already recognized to be effective for PET showed favorable effect also for cotton and the synergistic effect of Br in combination with P was reported at that time.

In 1960s, studies on flame retardants for thermal degradation of cellulose were carried out[9-18] and extended to analyses of a pyrolytic product, tar[9]. In 1964-1965, Reich et al.[12-19] achieved series of analyses to estimate orders of reactions[13] as well as to obtain parameters and apparent activation energies (Ea)[14-16] of thermal degradations by utilizing TG traces. They attempted investigations also on the thermal degradation of teflon[12]. Ozawa[17] proposed a method to obtain Ea from TG curves and succeeded in establishment of so-called world-wide Ozawa's method. Concerning the effect of P on the thermal degradation of P-containing polymers, the results of series of studies have been reported by Inagaki et al.[19-23] in 1969-1971. On the other hand, a durable flame retardant APO-THP was developed by Berkowitz-Mattuck[11].

In 1970s, simultaneously with the systematization of analytical instruments, investigations on pyrolytic products or effects of flame retardants on the thermal degradation and observations for effects of chemical compositions of materials on combustion behavior were achieved with the aid of combinations of thermogravimetric analysis (TGA), gas chromatography (GC) and mass spectrometry (MS) etc. [24-35] The mechanism of flame retardation with P-containing compounds and the effect of water[1] on the flammability have been also reported and attention has been paid not only to effects of flame retardants but also to that of water contents in materials.

At that time, investigations were aimed at decision of the criterion for the flammability to judge "flammable" or "flame retardant" as well as at the rationalization of test methods for evaluation of flame retardance[36-38]. In this case, attention was paid to determination of self-extinguishability[36] as a criterion and considerable efforts were made for achievement of reasonable test methods and establishment of the methodology[37,38].

Studies on the flame retardation of cotton/PET blended fabrics were started at that time[33,34,39].

Similar investigations were successively carried out also in 1980s, but in the last half, majority of investigations were related to synthetic polymers (plastics)[40-43]. Chang et al[44]. and Willie et al[45]. have proposed the flame retardation mechanism of PET successively.

In 1990s, only a small number of studies have been found except that the authors investigated on durable flame retardant finishes to compare merits and demerits of thermo-fixed finished sample and ammonia cured sample[46-48] as well as on effect of nitrogen (N) and P or halogens on pyrolytic gas generation from cellulosic fibers[49,50] in 1991-1992.

As for the flame retardation of man-made fibers, series of studies on flame retardant finishes of PET and thermal properties and physical properties of flame retardant finished PET were achieved by Nakanishi et al.[51-53]

Since cotton/PET blended fabrics require the most difficult strategy for any sufficient flame retardant finish because of the composition of such blended fabrics with both hydrophilic and hydrophobic properties, the authors also attempted flame retardant finishes of cotton/PET blended fabrics simultaneously with application of electron beam to curing flame retardants[54,55].

The flame retardation of polypropylene was also investigated by Wang et al.[56] who attempted to elucidate the flame retardation mechanism by the spectral analysis using XPS (ESCA). Novel flame retardant materials, polyphosphoramide esters were also synthesized by Kannan et al.[57] These esters were recognized as heat resistant and fire proof materials with high flame retardance as the results of the spectral analysis.

On the other hand, flame retardance, thermal properties or thermal stabilities of chemically modified epoxy-imide resins were investigated successively in 1995-1996 in Republic of China[58-60], as well as in France, and Derouet et al[61]. reported that fire resistibility and thermal stability of thermosetted epoxy-amine resin could be elevated by chemical modification with dialkyl (or aryl) phosphate.

Aluminium hydroxide {$Al(OH_3)$} is an effective flame retardant that has been traditionally used in thermoset and elastomers because of its ease of incorporation at low processing temperatures. Its use as a flame retardant filler for thermoplastics is fairly recent. It was reported in 1995 by Liauw et al.[62] that the result was improved by modifying the surface and the best property was obtained by coating $Al(OH_3)$ with strongly coupling silane.

Dombrowski[63] published a commentary on the flame retardation mechanism about each flame retardant element such as phosphorus, boron, halogens, nitrogen, aluminium and their combinations to make any technical person to develop efficient solutions to his or her flame retardant requirement, which is not an original report but will be useful to get some concepts for the flame retardation.

As mentioned above, the recent trend is to work preferentially for the development of flame retardant synthetic polymer products. In this case, Br has been used very frequently to produce flame retardant PET, not only for PET fiber but also for build-in PET plastics, which is connected with the environmental contamination as one of the most serious world-wide problems that will never been ignored at present.

1-3 A Suggestion to Reduce Br

Since halogens (particularly Br) are effective for the flame retardation of synthesized polymers, HBCD has been most widely used, and attention has been focused on Br. Therefore, the curtailment of Br dose or stop using Br is required from the ecological standpoint.

According to the results of investigation by the authors, PET retains much amounts of Br when treated with Br-containing compounds probably because of high affinity of Br to PET, which may be one of the factors for the remarkable contribution of Br to the flame retardation of PET. But, it might be possible to reduce considerable amount of Br when the synergistic effect with P is taken into consideration. For example, our result showed that about 12.7% of Br is required to obtain sufficient flame retardance exceeding the critical level when added alone, but addition of 0.7% of P enabled to maintain the same level of flame retardance with 1/2 Br dose. The above result is just an example and further reduction of Br will require considerable increase in P. However, since the ratio of P used so far was significantly too lower than that of Br, it is supposed that much room is still left for addition of P, and application of any phosphorus compound with high level of P content will be highly expected as a potential flame retardant having the synergistic effect with Br, which will contribute to gain sufficient flame retardance with much less amount of Br. This involves a possibility of significant further reduction of Br dose.

On the other hand, there is one more necessity left for further consideration. Since synthetic polymers melt when exposed to high temperatures, there is much danger of serious burn if such polymer melts on the skin when we are clothed in any clothes made of any synthetic polymer. Therefore, it is indispensable to give sufficient heat resistibility or fire-proof property to any synthetic clothing material in order to avoid such easy melting on the skin, for which addition of minimum amount of Br may be inevitable.

However, unlike cellulosic materials, there is little fear of flash over at the time of ignition because of melting. Consequently, Br should be applied only to such limited cases as clothing materials which contact directly with the human body and those which are always placed in the vicinity of fire or any heat source, and in the cases for any other purpose, additions of sufficient amount of P alone without any combination with Br or with a trace of Br, making the best of the synergistic effect, as well as with the aid of metallic additives such as antimony oxide will compensate well the reduction or absence of Br. Such strategy will work for the considerable curtailment of Br from the overall viewpoint.

1-4 History of the regulation of the Fire Defense Agency or voluntary rules for the flame retardant products

In U. S. A., the flammable textile law was regulated in July, 1954, which was originated from an accident happened to a little girl sitting by a stove the flame of which caught her negligee to cause her death.

In Japan, the new regulation of the Fire Defense Agency (Article 8-3) was enforced on 1st of April in 1969, 15 years later than that in U. S. A., by which curtain, blind made of fabrics, blackout curtain, drop curtain, proscenium curtain and protective screen used for any place crowded with many and unspecific people, i. e., high buildings, underground centers, theaters, hotels, movie theaters, hospitals, public halls, night clubs, recreation halls, department stores, markets, old-age homes, kindergartens, blind and deaf-and-dumb schools as well as in trains should be under an obligation to be flame retardant products with flame retardance higher than the standard level regulated by the government ordinance. But the difference between the system of U. S. A. and that of Japan is that not only items used for the public institutions but also textile products used for the general houses were regulated in U. S. A., in contrast, only interior goods used in the public institutions, but not any items used in personal dwelling houses were regulated in Japan at that times.

Notifications were issued successively by Fire Defense Agency as follows.

(1) Five years after, the Fire Defense Agency issued the guide-line (recommendation) on 25th in

June 1974 {Notification of the Fire Defense Agency (NFDA below) No. 65}, by which beddings, tentages, carpets and sheets were added, and those recognized to have any oral toxicity, skin irritation or allergic trouble by the medical tests were rejected.

(2) In 1982 (1st April) NFDA No. 69 was issued to add emergency rucksack and protective hood for refuge to protect individuals against fire at the time of earthquake.

(3) NFDA No. 129 was issued on 19th September 1986 to notify that beddings, blankets, towelspreads, tentage, sheets, curtains, emergency rucksack, protective hoods, clothes and upholstered furnitures used for old-age and children homes and any institute for handicapped persons must be flame retardant products for the safety of weaker persons. The reason for this notification was the fire at a social welfare institute which involved 8 persons' death.

(4) On 6th in June 1987, an old-age home was destroyed by fire which caused 17 persons' death and 25 wounded, soon after NFDA No. 160 was issued. As the results of inspections, it was found that sheets, pillow covers and pajamas etc. stored in a linen room were the ignition sources and accelerated the expansion of combustion, which led them to notify that not only beddings but also sleeping goods mentioned above should be flame retardant.

(5) NFDA No. 200 was issued on 30th of September 1991 to notify that not only textile products but also houses should be protected, i. e., residential antidisaster instruments which cleared the standard level for their structures and performances should be recommended by sticking the standardized recommendation mark (residential fireproof security mark) to help residents to choose guaranteed things when they want to purchase these instruments.

(6) NFDA No. 229 issued on 12th in November 1992 to add body covers of cars and motorcycles to be flame retardant because of increase in incendiary fire.

(7) NFDA No. 265 was issued in 1995 for reviewing the flammability test standard for blanket and in 1997 again for protective hoods.

(8) Most recently, NFDA No. 274 was issued on 27th in October 1997 to newly add low partition panel and exhibition panel as well as sliding paper screen to be flame retardant.

1-5 Constitution of This Thesis

This thesis is constituted by the following subjects and the contents which are summarized as follows,

1-5-1 Evaluation Methods for Flame Retardance

It is indispensable for the flame retardant finish to obtain highly reliable information for each sample to decide flammable or flame retardant, which requires accurate measurements and exact evaluation. The test methods for the evaluation of flame retardance have been universally standardized, and on the other hand, regulated by JIS L-1091 and JIS K-7201 in Japan.

Method of JIS L-1091 is practical involves significant difficulty to decide the conclusion with varied and deviated results for each sample to compare detailed differences among a large number of samples. In contrast, LOI Method regulated by JIS K-7201 offers precise numerical value as a measure of flame retardance for each sample, which enables minute comparison among many specimens objectively and is recognized as much better for our studies

Therefore, many kinds of samples were prepared by treating with inorganic or organic compounds and their flame retardances or flammabilities were evaluated by JIS L-1091, LOI Method and Mushroom Method, another method based on Part 1633 for the general clothes regulated by NBS (National Bureau of Standard). The results disclosed that evaluations by these three methods favorably be agreed[64], which permitted us to use LOI values for the evaluation of flame retardance in every case in our studies.

1-5-2 Establishment of Finishing Conditions for the Most Favorable Flame Retardance and Physical Properties for Textile End-Uses

Since it is most important for the flame retardant finish to establish the most favorable condition for each finish, investigations were performed for this purpose for cellulosic, PET and cotton/PET blended textile products (fabrics) as representative textile materials in the worldwide market.

The cellulosic fabrics were finished with both durable flame retardants and nondurable inorganic compounds.

Durable flame retardant finishes were carried out with most worldwide representative flame retardants, Pyrovatex CP (3-dialkylphosphono-N-methylolpropionamide) and THPS (tetrakis hydroxymethyl phosphonium sulfate) in addition to THPS precondensate with urea were adopted, and finishing conditions for each of them were minutely investigated. In this case, the authors improved the process of ammonia cure for THPS precondensate (PROBAN finish) and succeeded in obtaining results better than those from maker's sample. On the other hand, THPS itself was used for the applicability of heat cure to be substituted for ammonia cure, which showed that heat cure was sufficiently applicable.

Moreover, it was also disclosed that the above mentioned heat cure and PROBAN finish, which had been used only for cotton could be applicable also to viscose with better results compared with those from cotton.

The overall results led us to conclude that flame retardant samples finished under the conditions found by our investigations gave better results in every case compared with those given by samples finished under the conditions used so far. However, LOI values were limited to 28-30% at highest, close the critical value.

Therefore, nondurable flame retardant finishes were investigated since nondurable flame retardant finished samples have such merits that are not possessed by durable ones.

Cotton fabric was treated with many kinds of inorganic compounds containing N, P, S, halogens and B singly as well as 2 or 3 elements together.

As the results of investigations on the flame retardances and physical properties of finished samples, nondurable flame retardant samples showed much better results compared with durable flame retardant samples. Among all nondurable flame retardant samples investigated by the author et al., a mixture of boric acid and borax gave the best results.

Since it is hazardous to contact melting polymers with the skin, most widely used PET was used as a representative synthetic material for the investigation on flame retardant finish from both angles of thermo-fixing aftertreatment and melt spinning.

Br and P were adopted as flame retardant elements for PET and extremely minute investigations were performed by preparing different kinds of solutions extending over a wide range with many variaties of mutual ratios and concentrations, by which remarkable synergistic effect of Br and a slight amount of P on flame retardance of PET was obtained.

Cotton/PET blended fabrics have been dealt in the world-wide market since they possess an improved commodity value by mutual compensation of demerits of both fibers. However the flame retardation of this kind of materials involves much difficulty.

Therefore, the authors attempted a challenge to achieve flame retardant finishes with PET rich cotton 35%/PET 65% blended fabric.

1-5-3 Effects of Flame Retardant Finishes on Discoleration of Dyed Cotton Fabric Caused by Ultraviolet (UV) Irradiation

Since majority of fabrics used for our daily life are dyed and frequently exposed to sunshine, the authors observed effects of the above mentioned durable and nondurable flame retardant finishes followed by UV irradiation on cotton fabrics dyed with various kinds of dyes consisting of different chromogens and functional groups practically used in common for commercial dyed fabrics in the market. The results disclosed that durable flame retardant finishes caused, in combination with UV irradiation, larger discoloration compared with that by nondurable flame retardant finishes, particularly PROBAN finished sample showed the most considerable discoloration. It was concluded from the overall results that every dyed fabric finished with boric acid and borax showed little or entirely no discoloration not only by flame retardant finish but also by UV irradiation.

1-5-4 Effect of Flame Retardant Finishes on Propagation behavior of Smoldering in Fiber Assemblies and Heat of Combustion

The cause of fire which happened at Hotel New Japan in 1982 was a cigarette fire left on a futon, which was attributed to that futon was not made of flame retardant materials against the rule by Fire Defense Agency. It could be happened also at each individual home, particularly possibility will be more serious in the case of aged persons who live alone.

Therefore, the authors investigated to see how the heat of ignited cigarette propagates in fiber assemblies under various possible conditions. In addition, cotton fiber assemblies were treated with Pyrovatex CP for durable flame retardant finish as well as with various inorganic compounds for nondurable flame retardant finishes to use for the above mentioned investigations to confirm the effects of flame retardant finishes on heat propagation of smoldering.

Furthermore, miniature sleeping mattresses (Japanese futon) were made according to JIS L-4403. In this case, unfinished and flame retardant fiber assemblies finished with boric acid and borax were used as cottòn fiber assemblies, and blended fiber assemblies such as cotton (80%)/PET (20%) and cotton (50%)/PET (50%) were prepared with each unfinished and finished cotton fiber assemblies. As tickings, unfinished cotton fabric and finished cotton fabric treated with boric acid and borax were employed.

Thus effect of flame retardant finish was observed by varying the combination of unfinished and finished fiber assemblies and tickings mutually.

Many significant and useful results were obtained by the above investigations, but only a part of them will be shown here, i. e., flame retardant finished fiber assemblies showed remarkable reduction of heat propagation in every direction at every position, which clearly proved effect and necessity of flame retardant finish. Another information to which attention should be paid was that in the case of futon, sufficient flame retardant effect was found only when both fiber assemblies and ticking were flame retardant.

The investigation on cigarette fire was further extended to preparing a simulated cigarette with a device to slide the body of cigarette backward at the burning rate of real cigarette, which enabled us to obtain constant burning conditions as well as to vary heat quantity and heating time of heat source freely depending upon the purpose of investigation. Investigations with such simulated cigarette gave significant informations, e. g., it should be kept in mind that even though cigarette itself is quenched occasionally, the self-sustained smoldering of fiber assemblies proceeds once ignited without any heat source, which involves a possibility of flaming to an outbreak of fire. Remarkable depression of heat propagation was observed with flame retardant fiber assemblies also in this case.

On the other hand, heat of combustion is an important item to which attention should be paid since the majority of subsistence commodities in our living environment consists of flammable organic substances. Owing to direct contact with the skin of the human body, the heat of combustion of clothing materials is recognized as an important element for the safety of human beings. Therefore, we extended our investigation to evaluate the safety from the standpoint of the heat of combustion of textile products as materials for clothes, beddings and buildings by using many kinds of durable and nondurable flame retardant samples in comparison with unfinished samples, which were prepared or purchosed in the market.

The results showed that heats of combustion of nondurable flame retardant samples (excluding commercial samples) were lower than that of unfinished sample, of which those with LOI values higher than 30% showed remarkable reduction, particularly halides containing halogens and much water content exhibited the largest reductions followed by those finished with 20% solutions of boric acid and borax or diammonium hydrogen phosphate, whereas durable flame retardant samples showed similar or higher levels of heat of combustion compared with that of the untreated sample. Consequently durable flame retardant finishes can not be expected to secure any safety from reduction of heat of combustion.

Reviewing nondurable flame retardant finish is highly required also in this sense.

1-5-5 Thermal Analytical Observations of Fibers - Comparison Between Flame Retardant and Flammable Samples

Part 1 : Thermal Degradation Behavior of Fibers Observed by Thermogravimetric Analysis

It was thought to be indispensable to study on the thermal degradation which can be recognized to be the origin of combustion since it is initiated by ignition of flammable gases generated by the thermal degradation of any flammable materials exposed to high temperatures. Therefore, attention was paid to the thermal degradation behavior observed by the thermogravimetric analysis (TGA) as well as to the difference in the thermal degradation behavior observed between with and without flame retardance.

1) In the case of cotton fiber

Cotton fabric was treated with inorganic compounds containing N, P, S, Cl, Br and B each alone or 2 or 3 together to prepare many kinds of nondurable flame retardant samples. These samples were subjected to TGA to obtain TG curves, of which thermal degradation onset point (TDOP) and maximum degradation rate point (MDRP) were obtained and flash point (FP) was obtained by a flash point tester.

TG curves of nondurable flame retardant samples shifted to lower temperature. Flammable samples were ignited immediately or soon after TDOP before MDRP requiring Ea higher than that of unfinished sample, whereas flame retardant samples were ignited considerably for above TDOP after MDRP with Ea lower than that of unfinished sample. Thus, the thermal retardant samples showed characteristic differences in thermal degradation behavior as well as in Ea compared with those of combustible samples.

Such early onset of thermal degradation reflected on the structural modification of the chemical structure of cellulosic fiber observed by IR spectroscopy.

2) In the case of PET fiber

PET fabric was treated with Br compound HBCD and P compounds (TPPA, DPEP and DPMP) each singly and both together and thermo-fixed.

TDOP, MDRP and FP of these samples were all higher than those of cellulosic fibers.

Flame retardant PET showed little characteristic difference in thermal degradation behavior compared with that of flammable PET, which was unlike that observed in the case of nondurable flame retardant cotton samples.

Observations for Ea values suggested that flame retardant samples required higher Ea for decomposition showing opposite tendency to that observed in the case of nondurable flame retardant samples.

Part2 : Pyrolytic Gas Generation Observed with Thermal Degradation and Effect of Flame Retardation - Including Smoke, CO and CO_2 -

The thermal degradation described above is unavoidably followed by simultaneous pyrolytic gas production. Consequently further investigation was carried out to detect pyrolytic gas products.

N, P and halogens were adopted as effective flame retardant elements and cotton fabric was treated with compounds containing those elements each singly or P or halogens in combination with N and used to observe Pyrolytic gas generation behavior at different stages in the peocess of thermal degradation and overall pyrolytic gas production by instantaneous heating.

From the basic standpoint, pyrolytic gas products were traced in the thermal degradation process by trapping pyrolytic gases at TDOP, MDRP, FP and 500°C on TG curve of each sample and subject to gas chromatographic and mass spectrometric analyses.

In practical cases, the combustion seems to occur by ignition through instantaneous exposure to high temperatures. Therefore, the above samples were pyrolyzed also at a fixed temperature 590°C recognized as the best heating condition to observe pyrolytic gas production by an preliminary experiment.

The results of investigations on the above 2 items are summarized that both gas species and amount of each gas product were reduced in the case of flame retardant samples, especially those containing N and P or halogens showed remarkable reduction by the synergistic effects, and it was concluded that Br was more effective than Cl when compared as halogens and the synergistic effect of N and P was better than that of N and Br.

A further investigation was carried out to observe generation of smoke, CO and CO_2 from cotton cellulose and comparison between effect of inorganic flame retardants and that of organic flame retardants.

The results drew an attention to the fact that inorganic flame retardants showed much less gas generation, particularly boric acid and borax gave the most reduction in the generation of these gases down to 1/200-1/500, which proves another merit of nondurable flame retardant finish for the satety.

1-6 Final Overall Conclusion

As the conclusion of the series of studies on the flame retardation of flammable fibers extending over the wide range, above all the author wants to specially emphasize that attention should be paid to merits of nondurable flame retardant finish for cellulosic fibers from various aspects.

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Chapter 2

Chapter 2 Evaluation Methods for Flame Retardance

2-1 General Methods for Evaluation of Flame Retardance

Flame retardant materials have been generally evaluated by the methods regulated by each country as well as by the universally used common methods regulated by, for example, ISO.

In Japan, the burning test methods regulated by JIS L 1091-1992 and limiting oxygen index methods (LOI) regulated by JIS K 7201 have mainly used for textile and plastic materials.

2-1-1 Introduction of JIS L 1091-1992

JIS L 1091-1992 is classified into 4 methods, i.e., A is a method to measure the degree of extension of combustion, char length, char area, afterflaming time and afterglowing time, B is for measuring the degree of extention of combustion on the surface and applied to thick materials, C is a testing method for combustion rate and D is applied to melting textile products.

Method A is further classified into 4 classes, i.e., Method A-1 (for textile products weight of which is less than 450 g/m^2), Method A-2 (for thicker textile products more than 450 g/m^2), Method A-3 and Method A-4 . A sample is set up at an angle of 45° for Methods A-1 and A-2 and ignited with a microburner (A-1) or Meckel burner (A-2). The method of this type is called 45° method and adopted by the Fire Defense Agency. This 45° method was originated by JIS Z 2150 which was established for building materials in 1950s.

This 45° method evaluates the flame retardance by measuring char area after the termination of combustion.

For Method A-3 called horizontal method, a sample is set up horizontally and ignited with a flame of burning ethanol placed in a brass container for which the volumes of ethanol and container are designated. On the contrary, a sample is placed vertically in the case of Method A-4 and ignited with a Bunzen burner, which is called alternatively vertical method. This method corresponds to U.S. DOS FF 3-71, a universal method. We have found that the results obtained by the Method A-4 were identical with those obtained by the DOS FF3-71.

2-1-2 Introduction of JIS K 7201 (Limiting Oxygen Index:LOI)

This method regulates the testing methods which measure the flammability of materials in a wider range not only textile products but also extending over rubber and plastics etc.

The LOI value is a measure of the flammability obtained by determining minimum O_2 volume required for continuous burning of sample fabric piece for 3 min or longer as well as for giving char length of 50 mm or longer after ignition under the certain testing condition in combination with N_2 volume simultaneously obtained at this time, which is calculated by the following formula;

$$\mathrm{LOI}(\%) = \{[O_2]\ \mathrm{l/min} \,/\, ([O_2]\ \mathrm{l/min} + [N_2]\ \mathrm{l/min})\} \times 100$$

2-1-3 Introduction of Mushroom method

This method is regulated by Part 1633[1] for the general clothing materials administered by NBS (National Bureau of Standard). Flame contact time is regulated as 3 sec for samples which ignite at 3 sec, and also as 12 sec for those which require longer time for ignition.

The heat transfer rate (HTR) is obtained from the steepest slope of burning curve shown by combustion of each sample after ignition, and calculated as follows;

$$X = V_L \times T_1 / V_1\ (\mathrm{Jcm^{-2}/V^{-1}})$$

where V_L ($\mathrm{Jcm^{-2}sec^{-1}}$) : HTR of standard lamp (0.439 at this time), T_1 (sec) : time, V_1 (volt) : heat transfer rate after T_1.

HTR is obtained from X by the following equation;

$$\mathrm{HTR} = X \times V_2 / T_2\ (\mathrm{Jcm^{-2}sec^{-1}})$$

where T_2 (sec) : time, V_2 (volt) : heat transfer rate after T_2.

Since T_1 or T_2 and V_1 or V_2 correspond to the base and the height for tangent respectively, any desired HTR value was calculated by selecting a part of the steepest slope of any burning curve as an oblique side from which T_1 or T_2 and also V_1 or V_2 are decided as a base and a height respectively.

2-1-4 Other Tests for Special Specimens

The test methods introduced above are not applicable to any sample which melts or shrink by heat. The following tests are applied to these samples.

1) 45° Coil Test (for specimens which melt by heat)
2) 45° 5% Loose Test (for specimens which shrink by heat)

2-2 Investigations on Mutual Correspondence Between LOI Values and Results Obtained by Other Burning Test Methods

2-2-1 Introduction

The comparison of the above mentioned burning test methods leads us to conclude that the burning tests regulated by JIS L 1091 are practical and useful for screening the flammability of commercial products according to the regulated critical values to decide flammable or flame retardant. However, they can hardly be the measure for any minute and detailed comparison among many samples in the cases of fundamental and systematic investigations. Whereas LOI is expressed numerically and consequently enable us to accurately compare and evaluate the flame retardance or flammability of samples which show little difference in char length or char area with poor reproducibility when obtained by the burning testers. Moreover, the favorable reproducibility and reliability of LOI method have been confirmed by the fact that LOI values observed with the same samples at several laboratories in universities (including our's) and institutes were surprisingly identical[2].

Thus, such clearly expressed numerical evaluation provides a favorable merit for achieving any study which involves detailed comparison among many samples with a little difference in flammability to be taken into consideration.

Therefore, investigations were carried out to correspond the results of the measurement by LOI method with those by the burning test methods mentioned above as well as with HTR obtained by mushroom method.

2-2-2 Experimental

1) Materials

(a) Fabrics

Fabrics used for the investigations were 100% cotton plain woven fabric (100g/m^2) with a yarn count of 20 tex in warp and 16 tex in weft as well as with fabric count of 141/5 cm in ends and 135/5 cm in picks, and 100% viscose woven fabric (75g/m^2) with a yarn count of 13 tex in warp and 13 tex in weft and with a fabric count of 175/5 cm in ends and 109/5 cm in picks.

(b) Treating reagents

(1) Nondurable flame retardants

Treating solutions were prepared by mixing the following reagents in the molar ratios (in parentheses) or in % concentrations as indicated below ; mixtures of boric acid and borax (8:3), boric acid, borax and diammonium hydrogen phosphate (8:3:6), boric acid and diammonium hydrogen phosphate (11:5), sulfamic acid and diammonium hydrogen phosphate (4:1) and orthophosphoric acid and urea (6:23) were prepared in 1.2-26%, 2.3-35%, 1.0-20%, 2.0-40% and 6.0-70% respectively, in addition, single solutions of organic reagents, guanidine phosphate and guanylic urea phosphate were prepared in a range of 3-20%.

(2) Durable flame retardants

A single solution of 40% Pyrovatex CP (Py below), 35% of Py containing 3% of orthophosphoric acid and 6.5% of hexamethylolmelamine and 35% solution of Py containing 1% of urea, 0.4% of ammonium chloride and 6.5% of hexamethylolmelamine were prepared.

2) Methods

(a) Flame retardant finishes

(1) Nondurable flame retardant finishes

The above mentioned cotton and viscose fabrics were impregnated with the mixtures described above and padded to 80% pickup after 2 dip-2 nip process and air dried.

(2) Durable flame retardant finishes

The cotton fabric was immersed in the above mentioned treating solutions and padded to 60-80% pick up, which was cured by heating for 5 min at 160°C after drying at 80-90°C, and followed by soaping with 0.2% of sodium carbonate by impregnating for 30 sec at 90°C and rinsing 3 times with hot water at 50-60°C and air dried after centrifugation.

(b) Evaluation of flame retardance

Flame retardance of each sample was evaluated by 45° method (Method A-1), vertical method (Method A-4) , LOI method and mushroom method described above.

2-2-3 Results and Discussion

Flame retardance of the same sample of each treated sample was evaluated by the different test methods mentioned above and LOI values were corresponded to the results obtained by other methods. Fig.2-1 shows relationship observed between LOI values and afterflaming times and afterglowing times, Fig. 2-2 illustrates relation between LOI values and char lengths and Fig. 2-3 exhibits that between LOI values and char areas. As shown in these figures, afterflaming and afterglowing times, char lengths and char areas all decrease rapidly at LOI value 27-28% reaching the level for flame retardance, which proves that LOI value of 27-28% corresponds to the results obtained by measuring char length, char area afterflaming time and afterglowing time which can be evaluated to be the critical value for flame retardance.

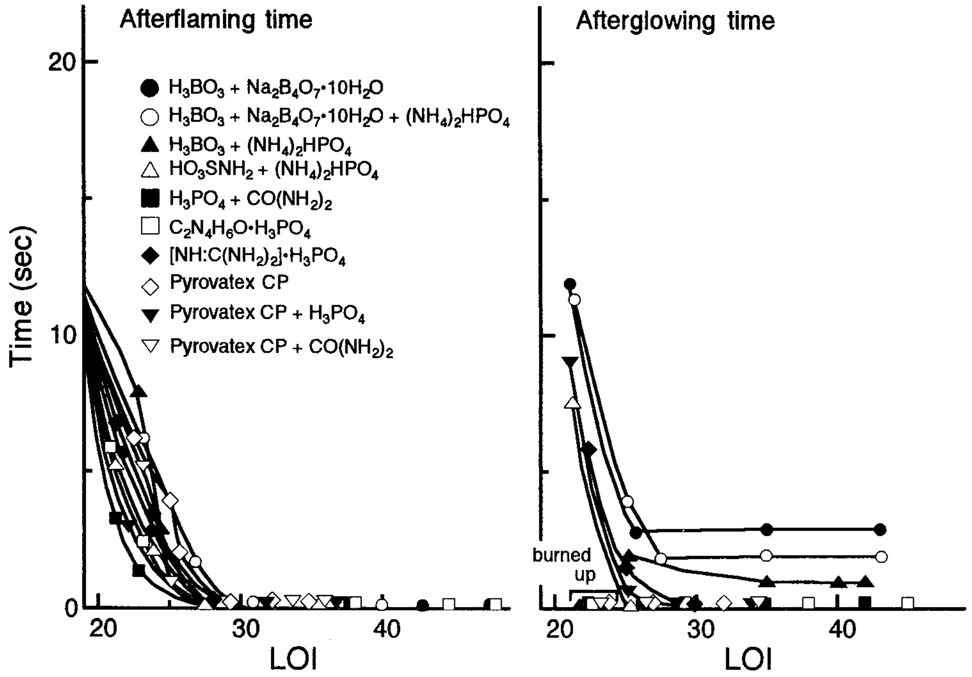


Fig. 2-1 Relation beween LOI and times for afterflaming and afterglowing observed in flame retardant fabrics.

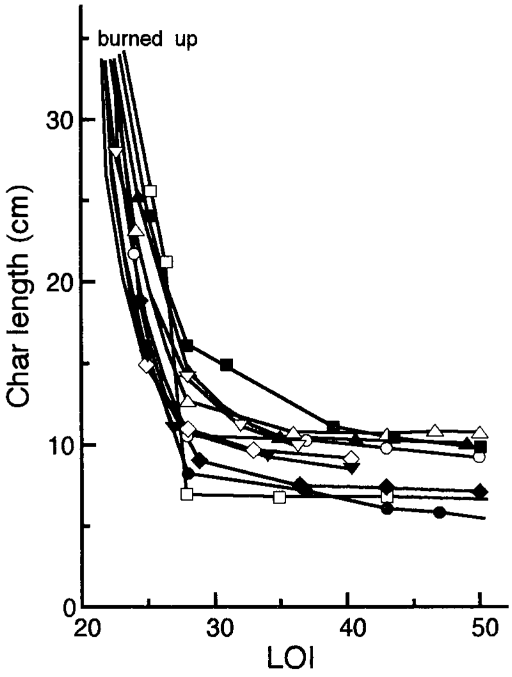


Fig. 2-2 Relation between LOI and char length observed with flame retardant fabrics after burning.

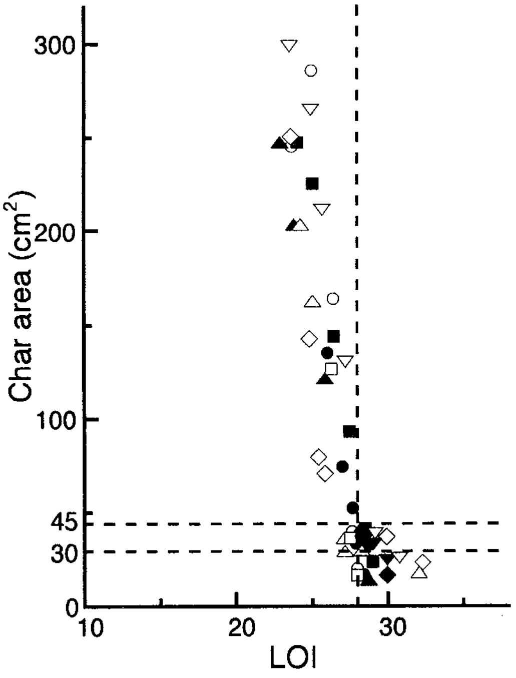


Fig. 2-3 Relation between LOI and Char area observed with flame retardant fabrics after burning.

Furthermore, Fig. 2-4 shows relationship between LOI values and heat transfer rates, which also proves that heat transfer rate was steeply shortened to approximately 0.4 J/cm2sec at LOI value 28%. This level of HTR, 0.4 J/cm2sec was identical with that regulated by NBS as the critical level for flame retardance.

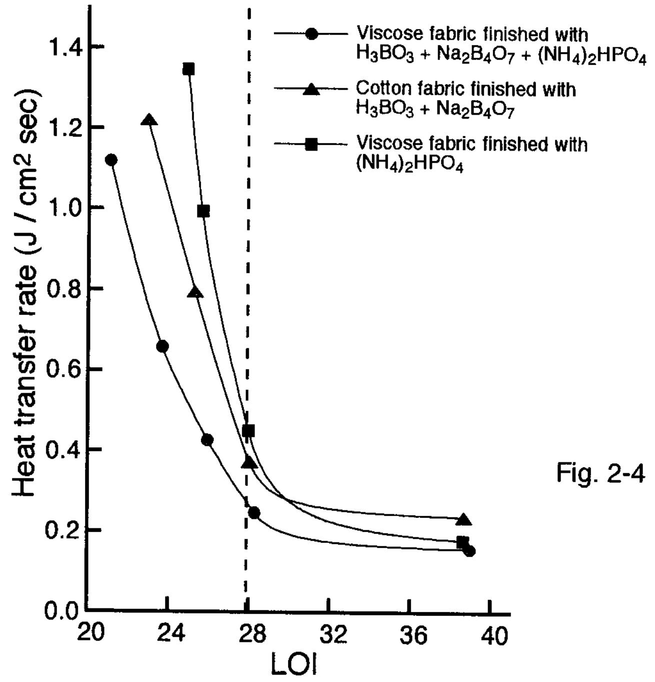


Fig. 2-4 Relationship between LOI values and heat transfer rates observed with cotton and viscose fabrics finished with various concentrations of flame retardants.

2-2-4 Conclusion

The overall results of the investigations covering the test methods mainly used not only in Japan but universally for the evaluation of flammability, and flame retardance have proved that char lengths including afterflaming time and afterglowing time, char areas and HTR show rapid decrease to reach the level of flame retardance at LOI 27-28%.

Therefore, it was decided to use LOI value as a representative measure for the evaluation of flame retardance all through a series of the present studies to be mentioned below.

2-3 Confirmation for Reliability of Evaluation by Comparison Among Results of Different Tests

2-3-1 Introduction

The flame retardation is the most important project in the present society for which the safety of the living environment is universally required, the majority of which is related to the protection from fire since it is unlike the hazard of earthquake which is beyond the human power. The most effective way for prevention of hazard from fire is not to extinguish after the outbreak of fire but rather use materials capable to prevent ignition or propagation of flame for our living environment, which clearly means that the flame retardation of any flammable materials surrounding our living environment is highly required.

However, if it accidentally happens that any misevaluated commercial product in the market is purchased by consumers, e.g., any flammable material happens to be evaluated as flame retardant, terrible problems may be resulted, which means that strict accuracy is highly required for the evaluation of flame retardance.

Therefore, we further extended our investigations to compare the results of several tests mainly used universally as well as in Japan to confirm "to what extent the results from the different methods would be identical?" and to see "how much the result obtained by only one test method could be reliable", for which not only many kinds of commercial products but also a large numbers of cotton and viscose samples treated with various kinds of flame retardants with many different concentrations were collected and flame retardance of each sample was evaluated by LOI, char length, HTR, and ignition time.

2-3-2 Experimental

1) Materials

(a) Fabrics

One hundred % cotton and 100% viscose the same as described in 2-2 were also used for this investigation.

(b) Flame retardants

As shown in Table 2-1, inorganic flame retardants, boric acid, borax and diammonium hydrogen phosphate were used singly or as mixtures of 2 or 3 kinds of these compounds, and Pyrovatex CP was used as a durable flame retardant together with diammonium hydrogen phosphate, melamine and ortho-phosphoric acid as additives.

2) Methods

(a) Flame retardant finishes

The above mentioned cotton and viscose fabrics were treated with nondurable inorganic and durable flame retardants under the conditions described in 2-2-2.

(b) Evaluation of flame retardance

Flame retardances were evaluated by LOI method, Method A-4 for char length and mushroom method for HTR and ignition time as described in 2-1.

The critical level for flame retardance was regarded as > 27-28% for LOI value, < 20 cm for char length, < 0.4 J/cm^2sec for HTR and > 3 sec for ignition time respectively.

2-3-3 Results and Discussion

1) Comparison of results evaluated by different test methods

In order to compare the results of 4 different tests systematically from the fundamental standpoint, concentrations of representative nondurable flame retardants were minutely varied to prepare flame retardant samples containing stepwisely varied add-ons which were expected to provide some information to show how the flame retardance would improve with increase in add-on and how it would be reflected on the results of evaluation tests. The result of each evaluation is listed in Table 2-1. The results better than the critical level is indicated by ○ and those worse by × in the Table. As for char length, as the results of several repetition of burning tests, samples burned down even only once were indicated as ×.

As shown in the table, among samples treated with nondurable flame retardants, those treated with 4% or lower concentrations of flame retardants are all recognized as flammable, and those treated with 10% or higher concentrations were as flame retardant in all cases irrespective of the test method and kind of flame retardant. Samples with LOI values higher than 40% were never ignited, which means that such samples extinguished themselves even after 20 sec flame contact. But, attention should be paid to samples for which evaluations by different tests were not identical, e.g. samples No.4, 46, 51, 53, 54, 56 and 59. LOI values of No.4, 46, 51 and 59 are the critical level or close to the critical value of LOI, No.46 and 59 show the critical value of 3 sec for ignition time, HTR of No.53, 56 and 59 are also close to the critical value of 0.4 J/cm^2sec and are evaluated as flame retardant only by these results respectively. But evaluations by other test methods are not identical. Thus, it should be noted that in the case of any sample with only one critical value by which evaluated as flame retardant by a single test method, evaluations by other methods are not always identical.

Another attention should be paid to the fact observed in the cases of Pyrovatex finished samples (No.53, 54, 56, 57 and 59), i.e., these samples are evaluated as flammable by LOI values considerably lower than 27-28% as well as by infinite char length, but, on the contrary, recognized as flame retardant by HTR a little lower than the critical value 0.4 J/cm^2sec and by ignition time the same as or longer than that of the critical time of 3 sec. Such disagreement is observed with samples treated with Pyrovatex of 20% or higher concentration (32%) with an additive, whereas samples treated with lower concentration (10%) show an identical evaluation as flammable in every case. The reason for such contradiction observed between the results of mushroom method and those of LOI Method and Method A-4 is thought to be the difference in position of flame contact, i.e., the point of contact is the surface of fabrics in the case of mushroom method, and the vertical Method (Method A-4) requires cut edge ignition. Flame contact at cut edge generally allows easier ignition compared with flame contact at the surface of fabrics, and the ignition seems to retard when the surface is covered or coated with, for example, flame retardants. Inorganic solutions of lower concentrations which can not give flame retardance have no effect on the ignition at surface, and samples treated with such solutions are evaluated as flammable by identical results of all tests, whereas since durable flame retardant finish requires much higher concentrations of flame retardants, e.g. 32%, 20% and 10% at least, enough to cover the surface of fabrics, it has been found that the surface ignition is much more retarded showing longer ignition time and smaller HTR compared with the ignition at cut edge[3]. But, any insufficient add-on gives little flame retardance showing LOI values much lower than the critical level and infinite char length in the case of cut edge flame contact (samples No.53, 54, 56, 57, 59).

On the other hand, samples finished under the proper conditions are never ignited by the surface flame contact (samples No.62-65) with higher LOI values and shorter char length, which shows the identical evaluation by all test methods shown in the table.

From the overall results, it has been clearly disclosed that samples with sufficient flame retardance finished under the favorable conditions are evaluated to be flame retardant with coincidence by all test methods, whereas those without flame retardance finished under undesirable conditions are evaluated to be flammable by all test methods without any contradiction. However, when any result obtained by any test method shows the critical level or close to this level, evaluations by the different methods show disagreement, consequently, it is not safe enough to rely on only one test in such case, which, therefore, requires other plural tests to confirm reliable results from different angles.

Table 2-1 Comparison of evaluations obtained by different kinds of burning tests observed with cotton and viscose fabrics treated with flame retardants of step wisely increased concentrations.

Cotton(C) or Viscose(R) Fabrics Unfinished or Finished with	(%)		MUSHROOM				A − 4		OXYGEN INDEX		
			I.T. (sec)	○ or X	H.T.R. J/cm² sec	○ or X	Char length (cm)	○ or X	LOI (%)	○ or X	Max.temp °C
1. Unfinished		C	0.60	X	2.173	X	∞	X	19.2	X	105.0
2. $H_3BO_3+Na_2B_4O_7$	2.5		0.70	X	1.519	X	∞	X	25.2	X	54.5
3. "	3.5		0.85	X	1.378	X	∞	X	26.8	X	40.6
4. "	4.0		1.0	X	1.186	X	19.5	○	27.2	○	33.2
5. "	5.0		3.0	○	0.369	○	11.0	○	29.8	○	27.6
6. "	7.5		5.0	○	0.167	○	9.9	○	30.9	○	26.7
7. "	10.0		10.0	○	0.163	○	9.1	○	32.0	○	26.6
8. "	20.0		N.I.	○	—	○	—	○	40.0	○	—
9. Unfinished		R	0.5	X	2.078	X	∞	X	20.5	X	137.4
10. $H_3BO_3+Na_2B_4O_7$	2.5		0.62	X	1.013	X	∞	X	24.6	X	63.5
11. "	5.0		3.00	○	0.384	○	17.0	○	29.0	○	38.0
12. "	7.5		5.0	○	0.230	○	12.3	○	32.3	○	27.0
13. "	10.0		10.0	○	0.210	○	11.1	○	35.1	○	26.9
14. "	20.0		N.I.	○	—	○	—	○	40.8	○	26.8
15. $(NH_4)_2HPO_4$	2.5	C	0.5	X	1.896	X	∞	X	23.3	X	117.0
16. "	5.0		1.0	X	1.118	X	∞	X	25.1	X	43.1
17. "	5.5		2.0	X	0.623	X	∞	X	26.5	X	40.6
18. "	6.5		3.0	○	0.400	○	13.8	○	28.0	○	31.6
19. "	7.5		5.0	○	0.400	○	9.2	○	30.7	○	28.9
20. "	10.0		10.0	○	0.354	○	8.1	○	35.5	○	27.5
21. "	2.5	R	0.5	X	1.419	X	∞	X	23.3	X	75.1
22. "	5.0		1.0	X	1.219	X	∞	X	25.9	X	40.7
23. "	7.5		5.0	○	0.393	○	10.0	○	28.8	○	28.8
24. "	10.0		10.0	○	0.290	○	9.6	○	33.3	○	27.1
25. $H_3BO_3+Na_2B_4O_7$ $+(NH_4)_2HPO_4$	2.5	C	0.5	X	2.853	X	∞	X	21.2	X	137.8
26. "	5.0		1.0	X	1.838	X	∞	X	23.7	X	43.0
27. "	7.5		1.5	X	1.242	X	∞	X	25.4	X	41.7
28. "	8.5		3.0	○	0.460	○	∞	○	27.6	○	40.8
29. "	10.0		5.0	○	0.290	○	13.6	○	28.3	○	27.3
30. "	20.0		10.0	○	0.167	○	10.0	○	36.3	○	26.3
31. "	2.5	R	0.5	X	1.719	X	∞	X	21.1	X	120.0
32. "	5.0		1.0	X	1.107	X	∞	X	23.2	X	63.3
33. "	7.5		1.5	X	0.773	X	∞	X	26.3	X	40.0
34. "	10.0		3.0	○	0.395	○	19.2	○	27.5	○	39.8
35. "	20.0		10.0	○	0.201	○	9.3	○	36.3	○	26.9

to be continued

Cotton(C) or Viscose(R) Fabrics Unfinished or Finished with : (%)			MUSHROOM				A – 4		OXYGEN INDEX		
			I.T. (sec)	O or X	H.T.R. J/cm² sec	O or X	Char length (cm)	O or X	LOI (%)	O or X	Max. temp. °C
36. H_3BO_3 + $(NH_4)_2HPO_4$	2.5	C	0.5	X	2.088	X	∞	X	21.3	X	131.9
37. "	5.0		1.0	X	1.250	X	∞	X	24.6	X	56.0
38. "	6.0		1.0	X	0.500	X	∞	X	25.0	X	55.5
39. "	6.5		1.0	X	0.450	X	∞	X	25.7	X	52.9
40. "	7.0		1.5	X	0.433	X	∞	X	26.4	X	51.0
41. "	7.5		5.0	O	4.000	O	14.5	O	27.5	O	38.7
42. "	10.0		10.0	O	0.250	O	9.8	O	31.4	O	36.0
43. "	20.0		N.I.	O	–	O	–		46.7	O	–
44. "	2.5	R	0.5	X	1.413	X	∞	X	22.0	X	113.2
45. "	5.0		1.0	X	1.120	X	∞	X	24.9	X	65.0
46. "	7.5		3.0	O	0.565	X	18.8	O	28.0	O	63.0
47. "	10.0		10.0	O	0.165	O	9.6	O	31.0	O	42.5
48. "	20.0		N.I.	O	–	O	–	O	45.7	O	–
49. Pyrovatex	10.0	C	1.0	X	0.679	X	∞	X	20.9	X	112.4
50. "	20.0		1.0	X	0.553	X	∞	X	23.5	X	73.0
51. "	32.0		8.0	O	0.336	O	19.5	O	26.6	X	27.3
52. Pyrovatex $(NH_4)_2HPO_4$	10.0 2.0	C	2.0	X	0.516	X	∞	X	21.1	X	72.2
53. Pyrovatex $(NH_4)_2HPO_4$	20.0 2.0		5.0	O	0.340	O	∞	X	22.0	X	40.2
54. Pyrovatex $(NH_4)_2HPO_4$	32.0 2.0		10.0	O	0.106	O	∞	X	25.4	X	26.2
55. Pyrovatex $(NH_4)_2HPO_4$	10.0 2.0	R	2.0	X	0.804	X	∞	X	20.2	X	58.2
56. Pyrovatex $(NH_4)_2HPO_4$	20.0 2.0		5.0	O	0.300	O	∞	X	21.8	X	32.4
57. Pyrovatex $(NH_4)_2HPO_4$	32.0 2.0		10.0	O	0.123	O	∞	X	24.5	X	26.3
58. Pyrovatex H_3PO_4	10.0 2.0	C	0.5	X	1.416	X	∞	X	21.7	X	134.4
59. Pyrovatex H_3PO_4	20.0 2.0		3.0	O	0.460	O	∞	X	25.5	X	44.4
60. Pyrovatex H_3PO_4	32.0 2.0		10.0	O	0.340	O	15.0	O	27.5	O	34.4
61. Pyrovatex Melamine	32.0 8.0		1.0	X	1.400	X	∞	X	24.9	X	80.0
62. No.61 + H_3PO_4	0.25		N.I.	O	–	O	16.3	O	28.3	O	–
63. No.61 H_3PO_4	0.5		N.I.	O	–	O	13.5	O	28.5	O	–
64. No.61 H_3PO_4	1.0		N.I.	O	–	O	11.0	O	28.6	O	–
65. No.61 H_3PO_4	2.0		N.I.	O	–	O	8.5	O	29.6	O	–

N.I. : Not ignited

2) Relationship between LOI value and char length or with HTR

Fig. 2-5 shows relationships observed among these three values by a three dimensional graph. The longest char length corresponds to the largest HTR and the lowest LOI value, and a tendency that the shorter the char length, the smaller the HTR, also the higher LOI value is observed.

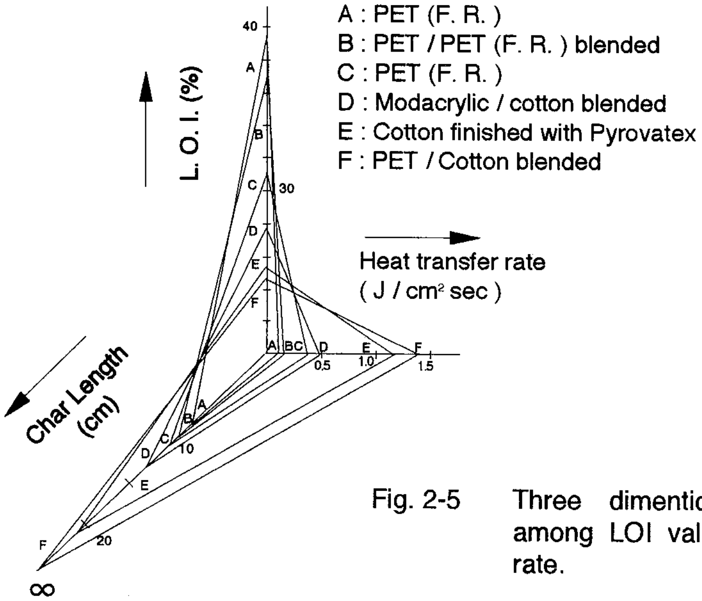


Fig. 2-5 Three dimentional illustration for relationships among LOI value, char length and heat transfer rate.

3) Evaluations of commercial fabrics by different test methods

Various kinds of commercial fabrics were tested by mushroom method, vertical Method A-4 and LOI method as mentioned above and the results of measurements and evaluations are shown in Table 2-2. The first 2 samples are 100% cotton labeled as flame retardant, but evaluated to be flammable by all test methods. Two modacrylic/cotton blended fabric out of 4 are evaluated as flame retardant by all test methods but evaluations show disagreement for the rest 2 samples, i.e., LOI method and Method A-4 evaluate as flammable but mushroom method as flame retardant. Four kinds of modacrylic/acrylic fabrics are all evaluated as flammable at least by LOI values less than 27% though these were in the market as flame retardant goods, probably because 3 of them are evaluated as flame retardant by other methods, particularly 2 of them show char length 3/4 of which are shorter than the critical level (20cm). Such fact suggests that if these samples were evaluated only by Method A-4 measuring char length, they would have happened to be evaluated as flame retardant by such shorter char length. Attention should be paid that since these samples melt by heat, ignition and flame propagation are depressed to show longer ignition time and shorter char length, which results in the misevaluation. Man-made fibers 100% nylon and 100% PET and PET/cotton blended fabrics also show similar tendencies with flame drops.

The above results suggest that mushroom method and Method A-4 are not applicable to the evaluation of samples with melting property for which LOI method is most adequate and recommendable to insure the safety.

Table 2-2 Comparison of evaluation by different kinds of burning tests observed with many kinds of commercial fabrics.

sample	Mushroom					A - 4		Oxygen Index	
	I. T. (sec)	○ or ☒	H. T. R. (J / cm^2•sec)	○ or ☒	M or FD	Char length (cm)	○ or ☒	LOI (%)	○ or ☒
Cotton (F. R.)	0.7	☒	3.03	☒		∞ 2 23.3 1	☒	25.2	☒
//	0.9	☒	3.48	☒		∞	☒	25.6	☒
Modacrylic (F. R.) Cotton	6.5	○	0.14	○	M	13.2	○	30.7	○
//	8.0	○	0.08	○	M	20.6	☒	26.0	☒
//	12.0	○	0.14	○	M	18.5	○	28.3	○
//	4.0	○	3.28	☒		∞ 2 17.6 2	☒	24.6	☒
Modacrylic (F. R.) Acrylic	6.5	○	0.18	○	M	11.0	○	24.7	☒
//	4.0	○	4.36	☒	M	∞ 1 12.6	☒	22.5	☒
//	5.1	○	0.30	○	M	∞ 1 13.8 3	☒	24.2	☒
//	2.0	☒	3.73	☒	M	∞	☒	20.8	☒
Nylon 100%	1.5	☒	0.64	☒	FD	∞	☒	21.2	☒
PET 100%	1.9	☒	0.51	☒	FD	∞ 1 22.2 2	☒	22.9	☒
//	1.5	☒	0.37	○	FD	∞ 2 25.5 1	☒	25.2	☒
//	4.0	○	0.36	○	FD	∞ 1 11.5 3	☒	33.6	○
PET 65% Cotton 35%	4.0	○	1.54	☒		∞	☒	21.5	☒
PET 50% Cotton 50%	1.5	☒	1.85	☒		∞	☒	19.7	☒
PET (F. R.)	2.9	☒	0.50	☒	FD	10.8	○	34.1	○
//	3.5	○	0.12	○	M	8.9	○	39.3	○
//	12.0	○	0.15	○	M	9.8	○	40.4	○
PET 80% Wool 20%	3.2	○	0.72	☒	FD	11.9	○	21.7	☒
PET (F. R.) PET	10.5	○	0.14	○	FD	10.6	○	36.1	○

M : Melting, FD : Flame drop, FR : Flame retardant finished, ○ : recognized as flame retardant,
☒: recognized as flammable, ∞ : entirely burned

4) Relationship between LOI and char length or HTR

Fig. 2-6 illustrates correlations between LOI values and char lengths or HTR observed with all samples used for the present study from the overall standpoints. Each critical value was decided as 27% for LOI value, 20 cm for char length and 0.4 Jcm^{-2}sec^{-1} for HTR and indicated by dashed lines dividing the coordinates into 4 regions, Region A is for samples evaluated as flame retardant by both LOI and Method A-4 or mushroom method, Region B is for those evaluated as flame retardant only by LOI and as flammable by char length or HTR, Region C is for those evaluated as flammable by LOI but as flame retardant by char length or heat transfer and Region D is for those evaluated as flammable by every method. Samples were classified into 2 groups, those without melting property (indicated by ○) and those with melting property (indicated by ●). Samples in Region A show LOI value higher than 27% level with shorter char lengths and smaller heating energy, whereas samples in Region D are flammable and all burned down except 1 molten down and HTR value scatter in a wide range but those with melting property gather in the vicinity of the critical level of 0.4 $Jcm^{-2}sec^{-1}$. In Region B, only 4 samples belong to this region and all samples are burned down, but LOI values are above the critical level 27-28% though extremely close to it. HTR values in this region scatter up to 2.0 $Jcm^{-2}sec^{-1}$ though LOI value are also close to 27-28%. This tendency may suggests difficulty of accurate evaluation to decide flammable or flame retardant for samples the flame retardance of which is at the critical level.

Samples to which most attention should be paid is those belonging to Region C which show shorter char lengths and smaller HTR even though flammable as evaluated from LOI values. They all have melting property which depresses vertical flaming and heat transfer energy resulting in smaller values and evaluated as flame retardant though they are flammable.

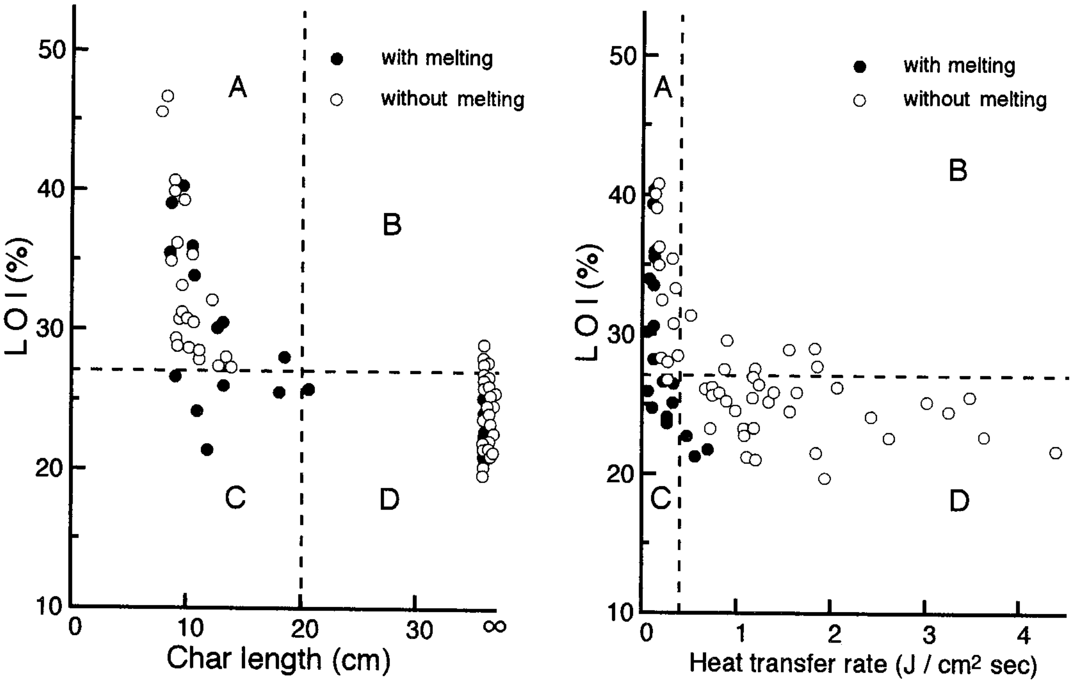


Fig. 2-6 Correlation between LOI value and char length as well as between LOI value and heat transfer rate.

2-3-4 Conclusion

As the results of comparing evaluations of flame retardance by different types of test methods, the conclusion is summarized as follows;

Any test method is applicable to samples without melting property sufficiently flame retardant or entirely flammable, since evaluations for these samples are all identical. But tests by pulpal test methods are required for any sample with insufficient flame retardance showing LOI values close to the critical level for safety.

Any sample with melting property should not be tested only by Method A-4 for char length or by mushroom for HTR since melting property alters the results of tests, reducing char length and HTR with retarding ignition.

Coil method and slackening method should be applied to such melting samples.

LOI method is most widely applicable from the standpoint of safety and reliability, which is very useful for the systematic studies offering delicate difference in flammability between samples, which other test methods can never be substituted.

Reference

1. National Bureau of Standard, Proposed Standard for the Flammability of General Wearing Apparel, J. of Consumer Product Flammability, 288 (1977)
2. Japan Fire Retardant Association, Studies on Flame Retardant Properties of Clothes ed. Flame Retardant Products Organization Committee
3. Ishibashi, H., Bull. Kagoshima Prefectural Junior College, 32, 35 (1981)

Chapter 3

Chapter 3 Establishment of Finishing conditions for the Most Favorable Flame Retardance and Physical Properties for Textile End Uses

- Investigations for Establishment of Finishing Conditions considered to be the Best for Each Flame Retardant Finish -

Introduction

As the objects for the studies on the flame retardant finishes, the three kinds of textile materials, cellulose, polyester and cotton/polyester blend were selected since investigations for improvement of the flame retardant properties have been mostly required for these three for the following reasons: Among textile materials surrounding our living environment, cellulose can be regarded as most flammable, polyester has been the most universally used man-made clothing material and coexistence of two opposite properties, hydrophilic and hydrophobic, involves considerable difficulty in acquiring sufficient flame retardant property in the case of cotton / polyester blends.

Therefore, investigations were carried out to establish any finishing condition evaluated to be the most favorable for each of the above three materials.

Flame retardation of fabrics is generally achieved by durable and non-durable flame retardant finishes.

3-1 Flame Retardant Finishes for Cellulosic Fabrics

As flame retardant finishes for cellulosic fabrics , the following three durable finishes two universally famous finishes and additional one, were adopted first from practical standpoint.

3-1-1 Investigations on Pyrovatex Finish and Effects of Additives

Pyrovatex is one of the representative world famous flame retardants, but it seemed that further improvement would have been required to get better results. Therefore, investigations were carried out with diverse additives containing N, P and S to establish such finishing condition as regarded to be the most favorable from flame retardance as well as from physical property, i.e., tensile strength, from the practical standpoint.

1) Experimental

(a) Materials

(1) Fabric

One hundred % cotton fabric was the same as that described in 2-2-2.

(2) Flame retardant

Pyrovatex CP, product of Ciba Geigy.

(3) Additives

Resins, hexamethylolmelamine (M6) and 4,5-dihydroxy-4,5-dehydro-N,N'-dimethylol-2-imidazolidinane {dimethylol glyoxal monourein (G)} were offered from Mitsuitoatsu Co.

Ortho-phosphoric acid (H_3PO_4), polyphosphocarbamate, diammonium hydrogen phosphate {$(NH_4)_2HPO_4$}, sulfamic acid (HSO_3NH_2), urea and ammonium chloride (NH_4Cl) were all guaranteed quality (Wako Pure Chemical Co.) and used as they were.

(b) Methods

(1) Preparation of treating solutions

Treating solutions were prepared as shown in Table 3-1.

Table 3-1 List of preparation of Treating solutions for Pyrovatex finishes

For selection of Py concentration	1	10, 20, 30, 40% solutions of Py alone	
	2	30% of Py + 5, 8, 10, 12% of M6	
	3	30% of Py + 0.5, 1, 2, 3, 4% of H_3PO_4	
	4	25, 30, 32, 35, 40% of Py + 8% of M6 + 2% of H_3PO_4	
To see effect of N	5	32% of Py + 3% of H_3PO_4 +	5, 8, 10, 12% of M6
	6		8% of M6
	7		8% of G
	8	32% of Py + 3% of H_3PO_4 + 8% of M6 +	1% of urea + 0.5% NH_4Cl
	9		1% of urea + 0.5% NH_4Cl + 2% of H_3PO_4
To see effect of P	10	32% of Py + 8% of M6 +	0.5, 1, 2, 3, 4% of H_3PO_4
	11		5% of polyphosphocarbamate
	12		2% of $(NH_4)_2HPO_4$
To see effect of S	13	32% of Py + 8% of M6 +	0.5, 1, 2, 4, 6% of HSO_3NH_2
	14		0.5% of HSO_3NH_2 + 0.5-2% of H_3PO_4
To investigate the Synergistic effect of N, P, S	15	32% of Py + 8% of M6 + 0.5% of HSO_3NH_2 +	1.5% of H_3PO_4
	16		1% of urea 0.5% of NH_4Cl
	17		1% of urea 0.5% of NH_4Cl 1.5% of H_3PO_4

(2) Preparation of finished fabrics

The aforementioned cotton fabric was impregnated with each solution described above for 40 min, padded, immersed again in the same solution for 10 min, padded again adjusting its pick up to 90% and air dried. This was thermally treated for 4.5 min at 160°C and soaped with 0.2% of sodium carbonate at 90°C to remove formaldehyde (HCHO)

(3) Laundry of finished fabric

The finished fabric was washed for 10 min with 0.2% of a commercial detergent (LAS type) with 30 fold-volume water at 30°C, rinsed twice for 3 min by overflowing and centrifuged for 3 min. This procedure was repeated 25 times.

(4) Evaluation of flame retardance

The flame retardance of each sample was evaluated according to JIS K 7201(1976) described in 2-1-2 in the previous chapter.

(5) Determination of tensile strength

The tensile strength of each sample was measured according to JIS L 1096-1979, labeled strip method, by using TOYO Boldwin Type Tensilon UTM 1.

(6) Determination of HCHO

HCHO was determined by acetyl acetone method modified by Nakanishi. et al.[1] A mixture of sample solution and acetyl acetone reagent (1:1) was heated for 5 min at 60°C, cooled down to room temperature (20-27°C) by dipping in tap water for 1-2 min and optical density was read at 420 nm. The amount of HCHO was determined by using a standard curve from standard solutions, optical densities of which were obtained by the procedure the same as that for each sample solution.

(7) Determination of N

N content of each sample was determined by the micro-Kjeldahl method[2].

(8) determination of P

P was determined by a method based on Allen[3] and modified by Nakanishi[4]. About 10 mg of sample containing 20 μg - 2 mg of P was incinerated in a micro-Kjeldahl flask with 2 ml of 5 M perchloric acid and 1-2 drops of HNO_3 conc. After completion of decomposition of HNO_3, 2 ml of water was added and heated for further several minute to hydrolyze polyphosphoric acid. The same procedure was carried out for blank test with the sample without finishing. The incinerated product was diluted into exact 20 ml, 1-5 ml of which (according to P content of each sample) were transferred into another tube to which 5 M perchloric acid was added so that the total volume of perchloric acid be 0.8 ml taking the volume already contained into consideration, the total volume was adjusted to 10 ml and heated for 15 min at 70°C for complete coloration followed by dipping in water to cool down for the stabilization of coloration. Optical density was measured at 420 nm and P content of each sample was determined by using a calibration curve obtained from the standard solutions.

(9) Determination of S in finished samples

S content in every sample was determined by the flask combustion method, i.e., sulfur dioxide (SO_2) produced by comustion of S containg samples was converted into the from of SO_4 in a flask, which was adsorbed into isopropyl alcohol and titrated with 0.01 N barium acetate-lead acetate mixture in the presence of an indicator changing pink color to blue purple, for which sulfunyl amide was used as a standard.

2) Results and Discussion

(a) Decision of Py concentration

First of all, concentration of Py alone was investigated to determine the most favorable concentration. But, the result showed that Py alone could not give any sufficient flame retardance, i.e., samples treated with 10, 20, 30, 40% or Py alone showed LOI values 19.5, 20.8, 22.2 and 23.4% respectively, which means necessity of some additives.

But, addition of a resin such as hexamethylolmalamine (M6) as a N source or ortho-phosphoric acid (H_3PO_4) as a P source did not give any sufficient effect if each alone was added separately.

Therefore, addition of both N and P to 25, 30, 32, 35, 40% of Py was attempted.

As shown in Fig. 3-1, LOI value increased with concentration of Py before and after laundering and sample treated with higher than 30% of Py maintained flame retardance even after 25 time repetition of laundry, but tensile strength showed a peak at 32% of Py and decreased at higher concentrations of Py. Such results led us to conclude that 32% of Py is most adequate for the finishing condition.

(b) Selection of resin

From the above results, it is clear that resin is indispensable for the flame retardant finish, but it is more desirable to use resin which produces HCHO as little as possible. Therefore, another investigation was attempted with a low formaldehyde type resin glyoxal monourein (G) for the comparison with M6 used above, the result of which showed (Fig. 3-2) that resin G gave very unfavorable flame retardance with lower N and P contents. The determinations of N and P as well as of add-on (M6:19.6%, G:10%) gave the reasonable results since M6 molecule contains N and functional group 3 times (6) compared with those of G (2) resulting in stronger binding capacity with cellulose and Py (see Fig. 3-3). M6 was selected from this result.

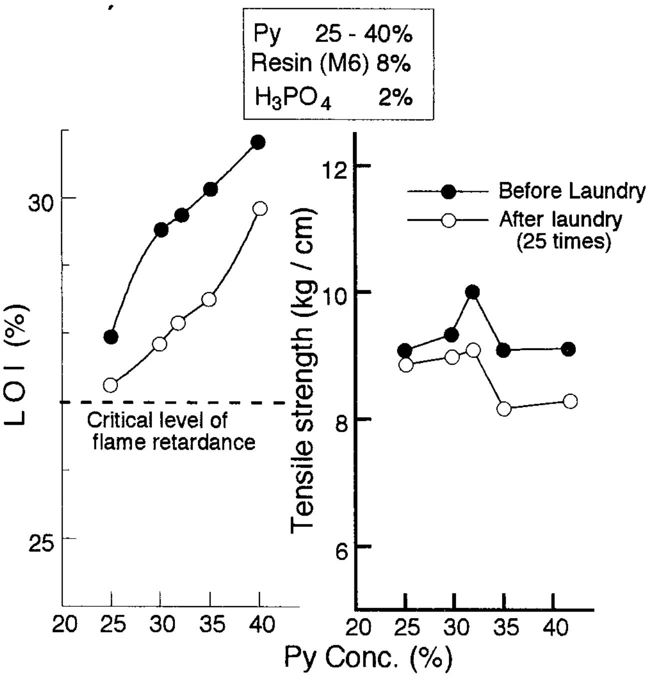


Fig. 3-1 Relationship between Pyrovatex concentrations in treating bath and LOI or tensile strength.

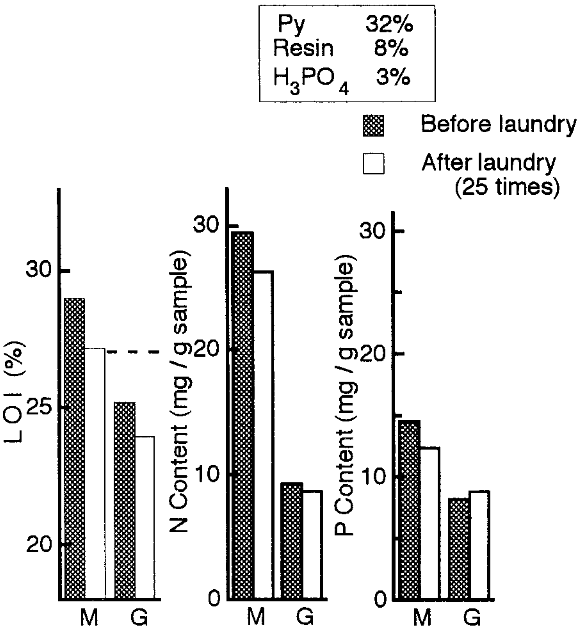


Fig. 3-2 Comparisons of effects of resins observed from LOI, P content or N content.

(c) Decision of concentration of M6

To determine the most favorable concentration of M6, varied concentrations (5, 8, 10,12%) of M6 were added to a mixed solution of 32% of Py and 3% of H_3PO_4 respectively. The result showed that the amount of N increased almost linearly with concentration of resin, whereas P retention did not show any clear proportional relationship though an increase of 5.24 mg/g in P retention was observed with a rise of resin 5-12%. On the other hand, LOI value showed an increase with a rise of resin 5-10% but leveling off with further increase of resin (Fig. 3-4).

Taking HCHO content and stiffness of sample into consideration, samples treated with finishing solutions prepared with 10-12% of resin were recognized as inadequate because of HCHO content higher than the regulated amount and lack of pliability. Therefore, 8% of resin was considered to be the best for finishing.

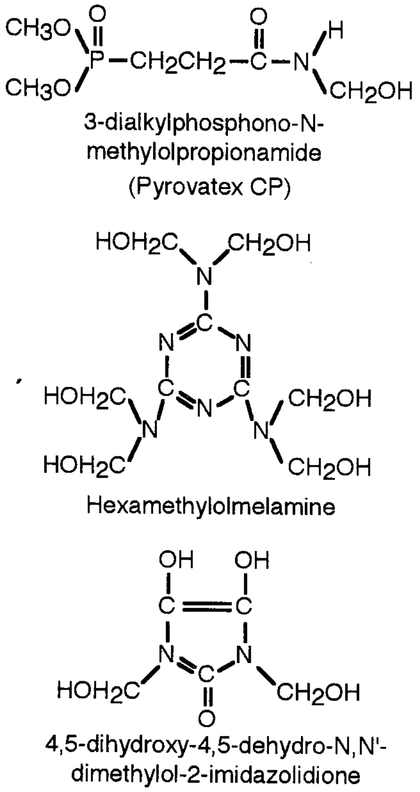


Fig. 3-3 Chemical structures of Pyrovatex CP and resins.

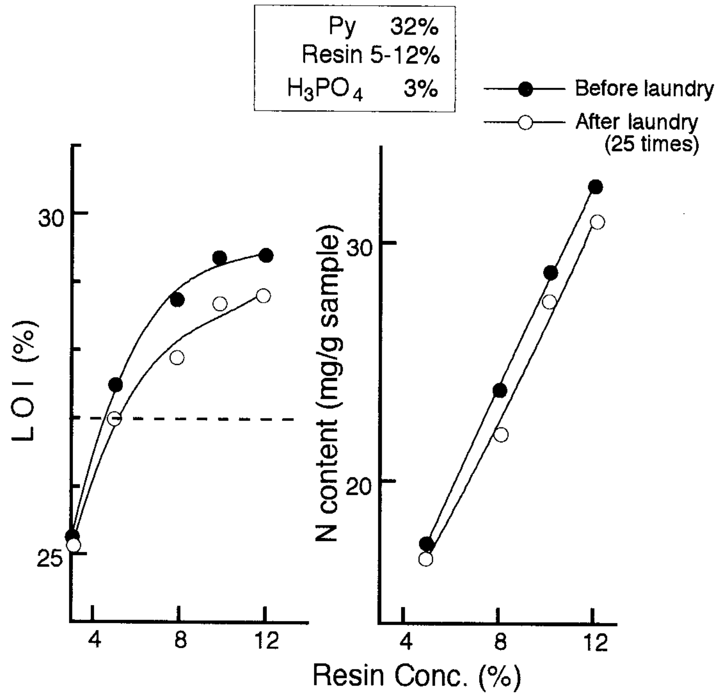


Fig. 3-4 Relationship between resin concentrations in treating bath and LOI or N content.

(d) Addition of N by additives other than resin

Since the above result showed that there should be a limit to use resin as a N supplement, urea and NH_4Cl were selected as representatives of organic and inorganic reagents containing N. The concentrations were determined as 1% for urea and 0.5% (1/2) for NH_4Cl considering the synergistic effect of N and Cl.

Fig. 3-5 shows the obvious effects of further addition of urea and NH_4Cl compared with the control sample consisting of Py, resin and H_3PO_4, i.e., LOI value are higher before and after laundering. The determination of N gave 6 mg (B) and 3mg (C) increase in N amount before and after laundry respectively, which evidences that increase in N by addition of urea and NH_4Cl clearly contributed to the flame retardation.

But, addition of H_3PO_4 gave reduction of tensile strength, which is unfavorable effect on the fabric.

(e) Selection of P

The above investigations used ortho-phosphate as a P source in every case, but it was thought to be better to test also other P sources to compare with ortho type. Fig. 3-6 shows a comparison of effect of P among otho-phosphoric acid type polyphosphocarbamate type and ammonium phosphate type, in which H_3PO_4 exhibited the best result showing the highest P content, whereas N content was in a range of 21-23mg/g.

Not much difference was observed in tensile strength among these three, but much higher level of HCHO (3-2 times) was found in the case of (B) and (C) compared with (A) (54.5μg/g).

Therefore, ortho-phosphoric was regarded as the best.

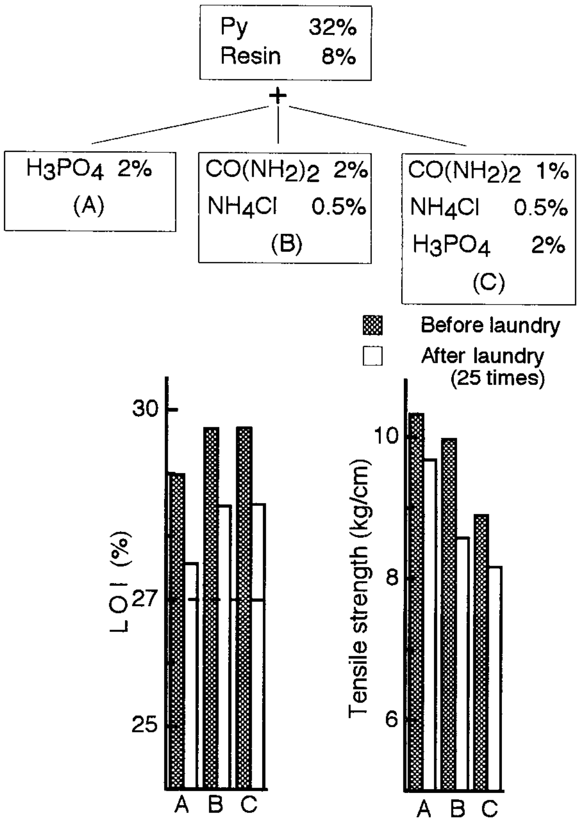


Fig. 3-5 Effects of addition of urea and ammonium chloride.

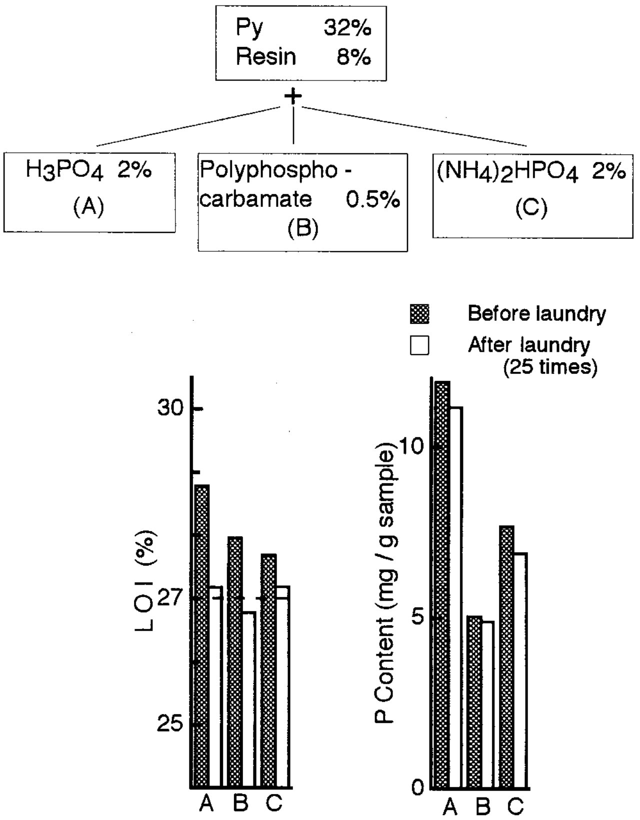


Fig. 3-6 Comparison of effects of phosphorus based additives observed from LOI and P content.

(f) Decision of P concentration

As shown in Fig.3-7, LOI rose up to 2% of H_3PO_4 but leveled off at higher concentrations, whereas tensile strength considerably decreased with increase in concentration of H_3PO_4, which makes to decide that 2% is the most adequate concentration of H_3PO_4 for flame retardant finish.

(g) Decision of concentration of S

Sulfamic acid was used as a donor of S, one of flame retardant elements. Investigations were carried out by adding varied concentrations (0.5-6%) of sulfamic acid to a basic mixture of 32% of Py and 8% of M6, LOI values and contents of N and S are shown in Fig.3-8.

In the cases of 0.5% and 1% of sulfamic acid, LOI values showed almost the same level with that shown in the case of 2% of H_3PO_4, which seemed that effect of S was identical with P. But LOI was lowered with increase in concentration of sulfamic acid. In this case, simultaneous determinations of N and S contents exhibited that only little change was shown in S content, whereas marked reduction of N content was observed with increase in addition of S. This result suggests that any excess amount of S inhibits the fixation of Py or resin monomer to cellulose substrate resulting in the reduction of flame retardance. Accordingly 0.5% is most favorable for sulfamic acid.

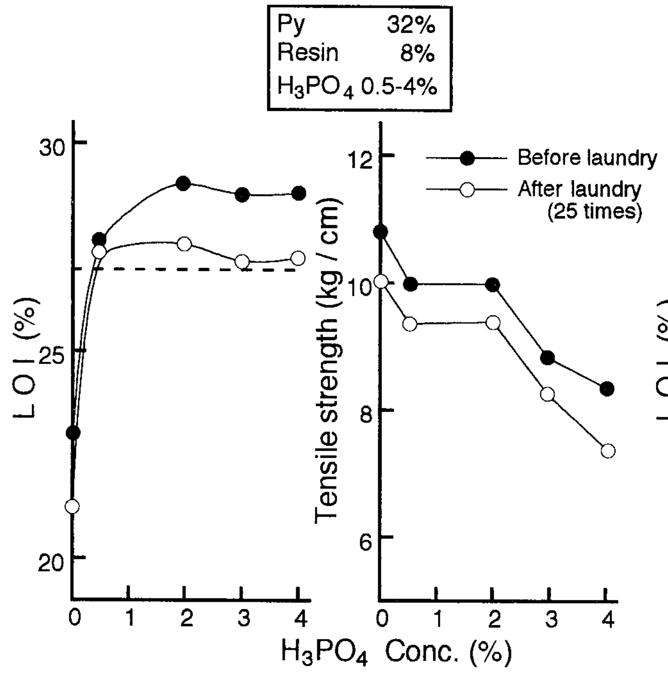


Fig. 3-7 Relationship between phosphoric acid concentrations in treating bath and LOI or tensile strength.

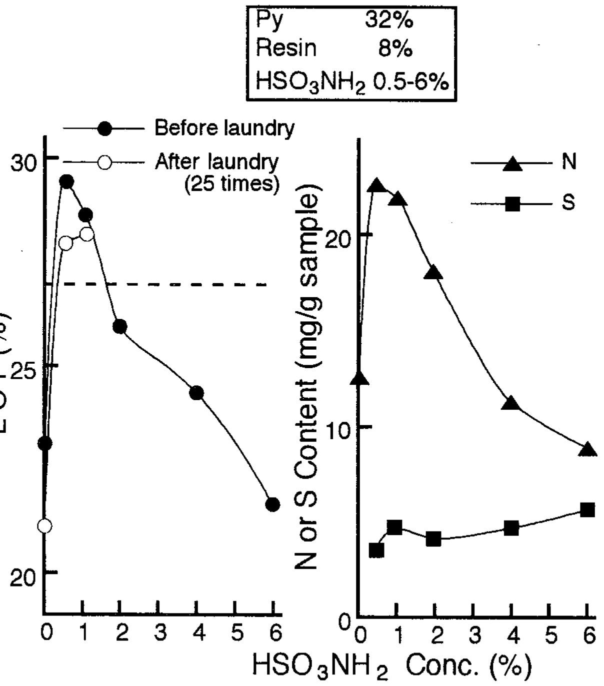


Fig. 3-8 Relationship between sulfamic acid concentrations in treating bath and LOI, and N or S contents.

(h) Synergistic effects of S and P and S, N and P

Addition of both sulfamic acid (0.5%) and H_3PO_4 (0.5-2%) gave LOI level similar to that obtained by addition of each one of these two, therefore it was concluded that the synergistic effect can not be expected from these 2 elements.

Another investigation to see the synergistic effect of S, N and P was carried out and obtained the results as shown in Fig.3-9 which disclosed that further addition of N or N and P to Py mixture in the presence of sulfamic acid brought reduction of LOI value as well as durability. Such result explained that the synergistic effect could not be anticipated also from the combination of N, P and S.

By combination of the all above results, the mutual relationship of N, P and S contents as well as between LOI and these contents were illustrated in Fig.3-10. As seen in the figure, when N content is constant, elevation of LOI is limited even with increase in P and S contents, but LOI values showed certain rise with increase in N content with fixed content of P or S, which means that N is a dominant element for the flame retardation of cellulosic materials.

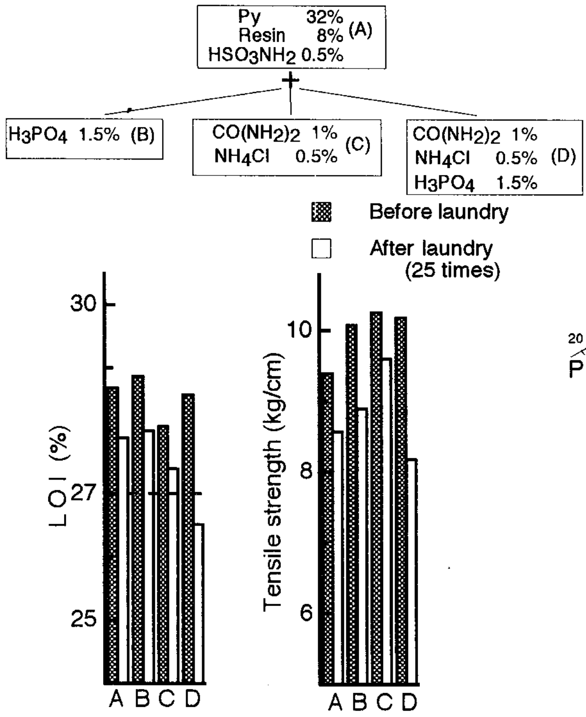


Fig. 3-9 Effects of S, P and N on LOI and tensile strength.

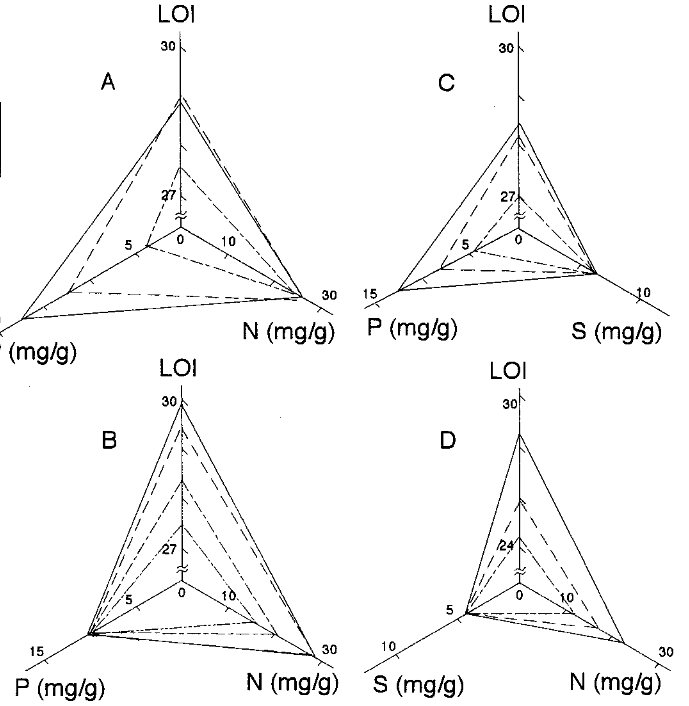


Fig. 3-10 Relationship of LOI to N, P and S contents.

3) Conclusion

The finishing condition which gave the most favorable results not only from flame retardance but also from strength and HCHO content was to prepare a mixture consisting of 32% of Py, 8% of M6, 1% of urea and 0.5% of NH_4Cl. In this case, N and P contents are 20-30 mg/g and 10 mg/g respectively.

3-1-2 Establishment of Finishing Conditions for THPS Ammonia Cure (PROBAN Finish)

PROBAN finish, another world wide durable flame retardant finish, was attempted as a next item to compare with Pyrovatex finish.

PROBAN finish was developed as ammonia cured THPC (chloride), improved in various countries[5-11] and has been applied universally almost to native cellulose cotton, but, so far, very little to regenerated cellulose even though more ignitable and much more flammable than cotton. It is consequently thought that flame retardant finish should be more highly required for regenerated cellulose than for cotton cellulose.

Therefore, the investigation to establish the most favorable finishing condition for PROBAN finish is to be extended also to viscose rayon to see how much the finishing condition we established is effective and to what extent it is practically applicable in comparison with the results obtained from cotton.

1) Expérimental

(a) Materials

(1) Fabric

One hundred % cotton and 100% viscose were the same as described in 2-2-2 above.

(2) Flame retardant

THPS condensed with urea according to the mechanism shown in Fig. 3-11 (THPS-urea precondensate) produced by Albright and Wilson was used.

(3) Additives

Sodium acetate was used to moderate the acidity of sulfate, polyoxyethylene nonylphenyl ether was added as a permeator, 30% of hydrogen peroxide as an oxidant and sodium carbonate to remove HCHO.

Ammonia gas was used for ammonia cure.

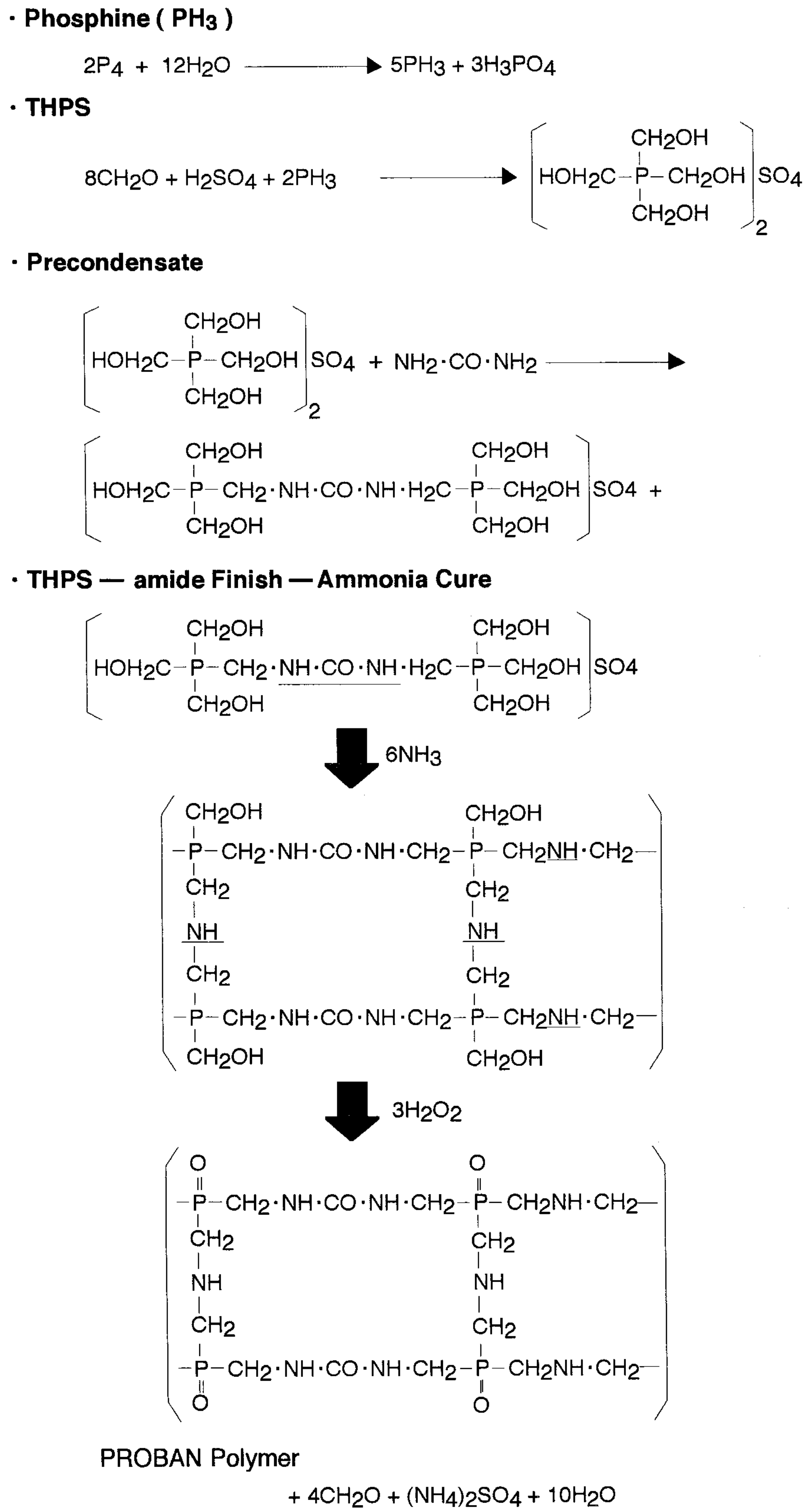


Fig. 3-11 Formation of THPS and its precondensate, and mechanisms for ammonia cure and oxidation of methylol groups with H_2O_2.

(b) Methods

(1) Finishing Procedure (PROBAN finish)

(i) Treating with finishing solutions

To select the adequate concentration, different concentrations (25, 40, 50%) of THPS precondensate were prepared with addition of 2.6% of sodium acetate and 0.2% of the above mentioned nonionic surfactant, in which cotton and viscose fabrics were immersed for 10 min, padded to about 90% pickup and air dried to get about 20% water content since the adjustment of water content of sample fabric at this point is very important for ammonia cure.

(ii) Ammonia cure

Air dried treated samples were placed in a desiccator, to which NH_3 gas was introduced after aspirating to 40 mmHg. Exposure time was varied 30 min - 10 sec decreasing stepwisely. NH_3 gas was released by aspiration after each exposure to exchange with air.

(iii) Oxidation and soaping for removal of HCHO

To find the most favorable condition to oxidize and remove HCHO, concentration of H_2O_2, bath ratio, temperature and time for oxidation and soaping were varied to set up 9 treating conditons combining oxidation and soaping processes as listed in Table 3-2.

(2) Pyrovatex finish

Pyrovatex finished samples were also prepared as mentioned above for comparison with PROBAN finished samples.

(3) Evaluation of flame retardance

Flame retardance of each sample was evaluated as mentioned in 2-1-2.

(4) Determination of nitrogen (N)

(5) Determination of phosphorus (P)

(6) Determination of HCHO

(7) Measurement of tensile strength

(8) Durability test by repetition of laundry

Experiments for the about 5 items were carried out also as described in the case of Pyrovatex finish.

2) Results and Discussion

(a) A new ammonia cure method attempted this time

Ammonia cure was initiated by the fact that methylol group of THPS salts is very highly reactive with NH_3 to convert to water insoluble resinous substance[12,13] and has been applied for flame retardant finish as the ammonia cure method on which numbers of patents have been obtained in England, USA, Switzerland, Germany and Japan etc., e.g., Japanese Patent No.58-18468, US Patent No.2772188, England Patent No.906314 specification, US Patent No.2983623 specification etc.

After studying and investigating about descriptions of the above mentioned patents, it was concluded that all of them had considerable problems such as insufficient interaction between THP salts and ammonia owing to exposure of NH_3 at atmospheric pressure, difficulties in NH_3 control, operation and installment for ammonium cure under pressure, disposal of large amount of NH_3 and waste liquids as well as in minimizing loss of time, labor and energy etc.

Moreover, the results obtained by carrying out according to some of the description were not recommendable because of insufficient flame retardance and durability. Therefore, in our laboratory, samples treated with THPS precondensate were exposed to NH_3 gas under negative pressure to allow NH_3 gas to deeply penetrate into the amorphous region of cellulose molecule without significant hindrance of air for succesful formation of PROBAN polymer by effective reaction between NH_3 and THPS precondensate as shown in Fig. 3-11. The result obtained by this new procedure was remarkably successful as shown below.

Flame retardation mechanism of PROBAN finish is as follows; PROBAN polymer is formed by introducing ammonia to THPS precondensate. Thermal treatment of this polymer bound to cellulose molecule converts it to phosphorus pentoxide which strongly dehydrate cellulose resulting in highly effective char formation with simultaneous conversion of itself into polyphosphoric acid. Such char formation contributes to self-extinguishability of cellulosic materials.

(b) Decision of the most favorable condition for oxidation and soaping

In order to remove HCHO liberated simultaneously with formation of PROBAN polymer as shown in Fig. 3-11, oxidation and soaping were attempted under varied conditions listed in Table

3-2. As shown in Fig. 3-12, only condition No.7 gave a practically favorable result showing the least HCHO less than the regulated limit 75 μ g/g sample.

Table 3-2 Oxidizing and soaping conditions attempted for elimination of HCHO after ammonia cure of THPS-treated samples.

	Oxidizing conditions					Soaping conditions				
	Reagent	Conc. (%)	Volume	Temp. (°C)	Time (min)	Reagent	Conc. (%)	Volume	Temp. (°C)	Time (min)
1	H_2O_2	4	×20	Room Temp. (20 °C)	10	Na_2CO_2	0.2 +0.08	30 : 1	Room Temp. (20 °C)	10
2	〃	〃	〃	〃	30	〃	〃	〃	〃	30
3	〃	〃	〃	〃	10	〃	〃	60 : 1	〃	10
4	〃	〃	〃	〃	〃	〃	〃	〃	60	〃
5	〃	10	〃	〃	〃	〃	〃	30 : 1	Room Temp. (20 °C)	〃
6	〃	〃	〃	〃	〃	〃	〃	〃	60	〃
7	〃	〃	〃	60	〃	〃	〃	〃	〃	〃
8	〃	20	〃	Room Temp. (20 °C)	〃	〃	〃	〃	〃	〃
9	H_2O_2 +Noinon	10	〃	60	〃	〃	〃	〃	〃	〃

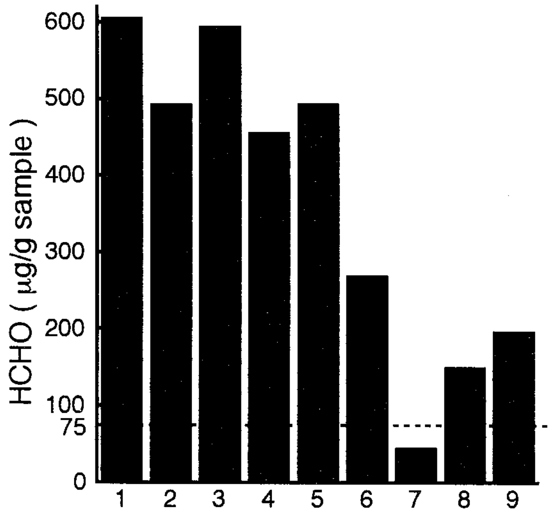


Fig. 3-12 Comparison of HCHO contents observed after oxidizing and soaping under various conditions shown in Table 3-2.

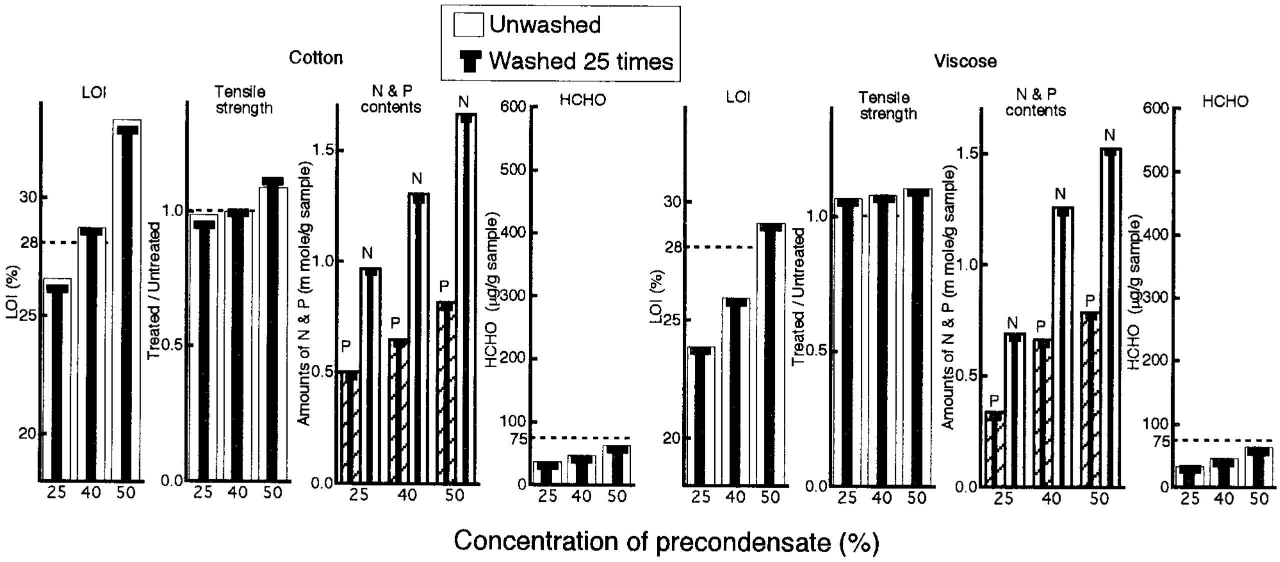


Figure 3-13 Relationship between concentration of precondensate in treating bath and LOI, tensile strength, amounts of N and P and HCHO observed for Proban finished-cotton and viscose.

(c) Decision of concentration of finishing solution

Since it is desirable for any finished sample to contain the minimum amount but meets the requirement for the purpose of finishing, cotton and viscose fabrics were treated with varied concentration of THPS precondensate (25-50%), which gave the results shown in Fig. 3-13. In the figure, black bars show the value obtained after 25 repetition of laundry. To maintain sufficient flame retardance with LOI value higher than 28%, it was found that cotton required 40% and viscose 50%. Cotton showed remarkable increase in LOI with 50% of flame retardant but samples treated with finishing solution higher than 40% were not practically recommendable because of stiffness. Tensile strength was not affected both before and after laundry in every case, even strengthened in the case of 50%. In the case of viscose, sample treated with 50% of treating solution only showed LOI value higher than 28%, which means that 50% was required for viscose. But handing of viscose was not affected by this concentration still maintaining softness, which is unlike cotton. Tensile strength showed some elevation by flame retardant finish in every case even after 25 time laundering, which suggests that the formation of net work PROBAN polymer in the amorphous region occupying the major part of viscose cellulose molecule could strengthen the resistance of molecule against any stretching force. The above results led us to conclude that the most favorable concentrations were 40% for cotton and 50% for viscose. Such difference in the concentrations of flame retardant required for the sufficient flame retardance is probably owing to different surface areas due to different surface structures between them.

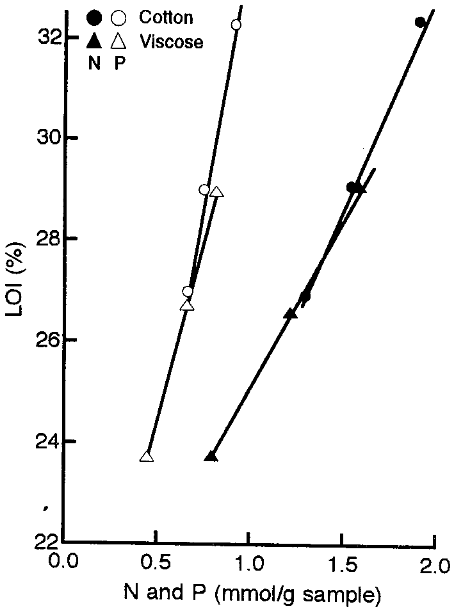
As for the detected amount of N and P, the ratio of N and P was shown as 2:1 in every case, which proves that PROBAN polymer is formed by cross-linking between NH_3 molecule and 2 methylol groups bound to 1 molecule of P contained in THPS as shown in Fig.3-11[14].

(d) Correlation between LOI and N and P contents

As mentioned above, difference was observed between concentration of THPS precondensate required for the flame retardation of cotton and that of viscose. Therefore, correlation between LOI and N and P contents was checked to see how such phenomenon was observed. It was suggested from the result that LOI value would be decided by contents of both N and P irrespective of cotton and viscose showing linear elevation with increase in both N and P contents in some fixed ranges as seen in Fig. 3-14. The same contents of N and P gave the same LOI value in both cases, cotton and viscose. This result also made clear that 1.3-1.4 mmol/g of N and 0.6-0.7 mmol/g of P would be required to obtain flame retardance with LOI value of 27-28%.

(e) Decision of curing time

By shortening the exposure time from 30 min down to 1 min for the 1st step, the result showed that 1 min would be enough as shown in Fig. 3-15. The further investigation to see the result of exposing for 1 min and shorter time showed that even 10 sec would be sufficient to complete ammonia cure in both cases of cotton and viscose from every viewpoint as shown in Fig. 3-16. It was suggested from such result that THPS and NH_3 would react really instantaneously.



ig. 3-14 Relationship between LOI values and N and P contents.

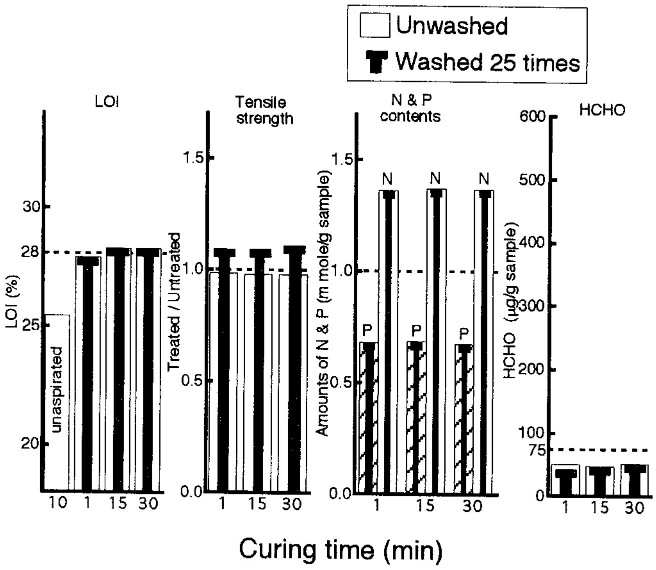


Fig. 3-15 Effects of curing time on LOI values, tensile strength, HCHO liberation and amounts of N and P retaining on THPS-treating cotton fabric.

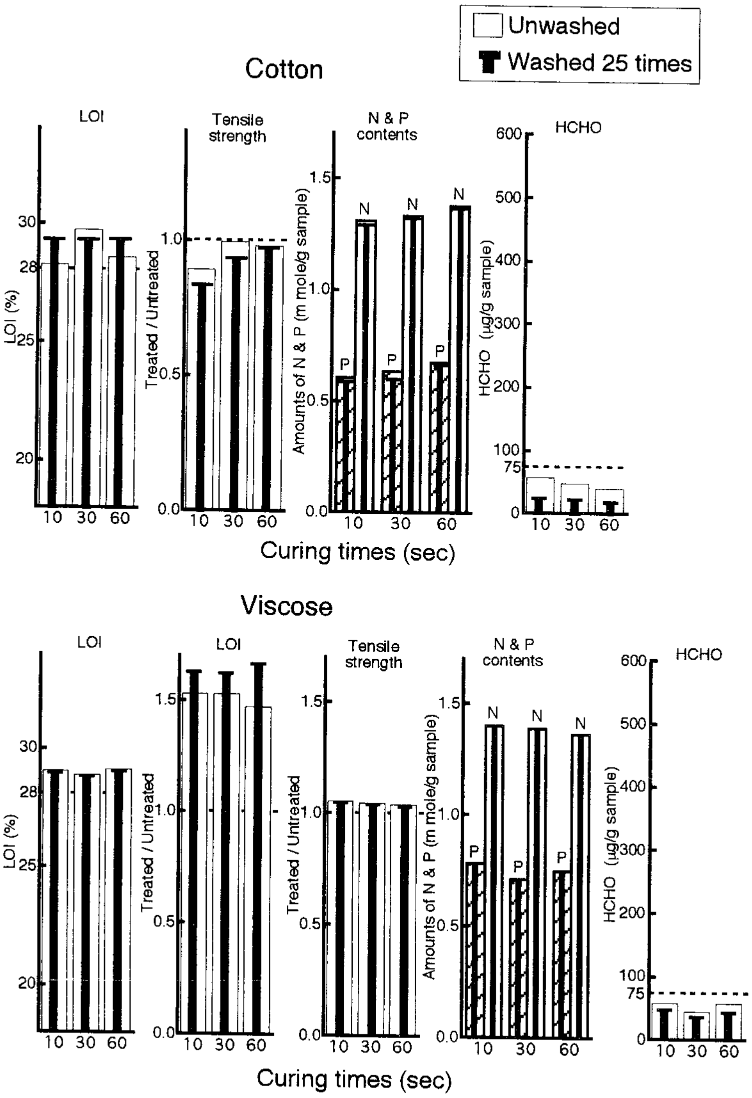


Fig. 3-16 Effects of curing time in the order of sec on LOI values, tensile strength, HCHO liberation and amounts of N and P contents on THPS-treated cotton and viscose fabrics.

(f) Durability for repeated laundry

Attention should be paid to the fact that PROBAN finished fabrics exhibited very favorable durability even after 25 time repetition of laundering as shown by central solid bars compared with outside open bars. Particularly, the ratios of treated / untreated for LOI are higher after laundry in the case of viscose, which is probably because LOI value of unfinished viscose is gradually reduced by laundering owing to increase in air content of damaged and loosened structure of fabric and fiber itself whereas PROBAN polymer offers some reinforcing effect to the viscose structure to contribute to resist against the mechanical farce to inhibit the reduction of flame retardance caused by such physical damage resulted from repeated laundering.

(g) Comparison with samples prepared by Albright & Wilson Co.

In order to compare the samples finished in our laboratory with those prepared by Albright & Wilson Co., the origin of PROBAN finish, to see if sample prepared by the new curing method works favorably, I sent a fabric sample the same as that used for this investigation to Albright & Wilson Co. to request the perfect PROBAN finish, with which the sample prepared in our laboratory was compared. In Fig. 3-17, sample by Albright & Wilson Co. and our sample were indicated by A and B respectively. Both LOI and tensile strength of B are higher than those of A, which means that our sample showed more favorable results. N and P contents are also slightly higher in the case of B, which was thought to reflect on the difference in LOI value observed between these two samples. The result of viscose was similar as that of cotton and omitted in the figure. But in the case of viscose, B showed stable results, whereas a tendency that values were varied sample to samples showing insufficient reproducibility was observed for A. Thus, it was thought that our technique could be applicable to the commercial level.

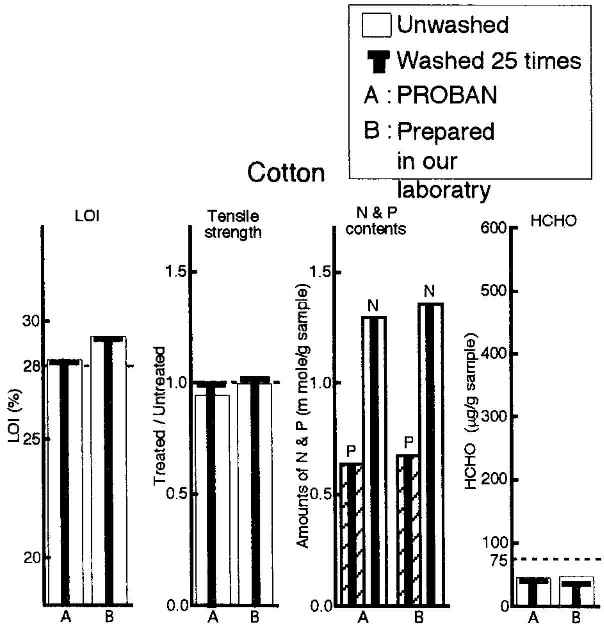


Fig. 3-17 Comparison between THPS-treated cotton fabric finished by Albright & Wilson Co. and that by the authors from the standpoints of flame retardance, tensile strength and contents of N, P and HCHO liberation.

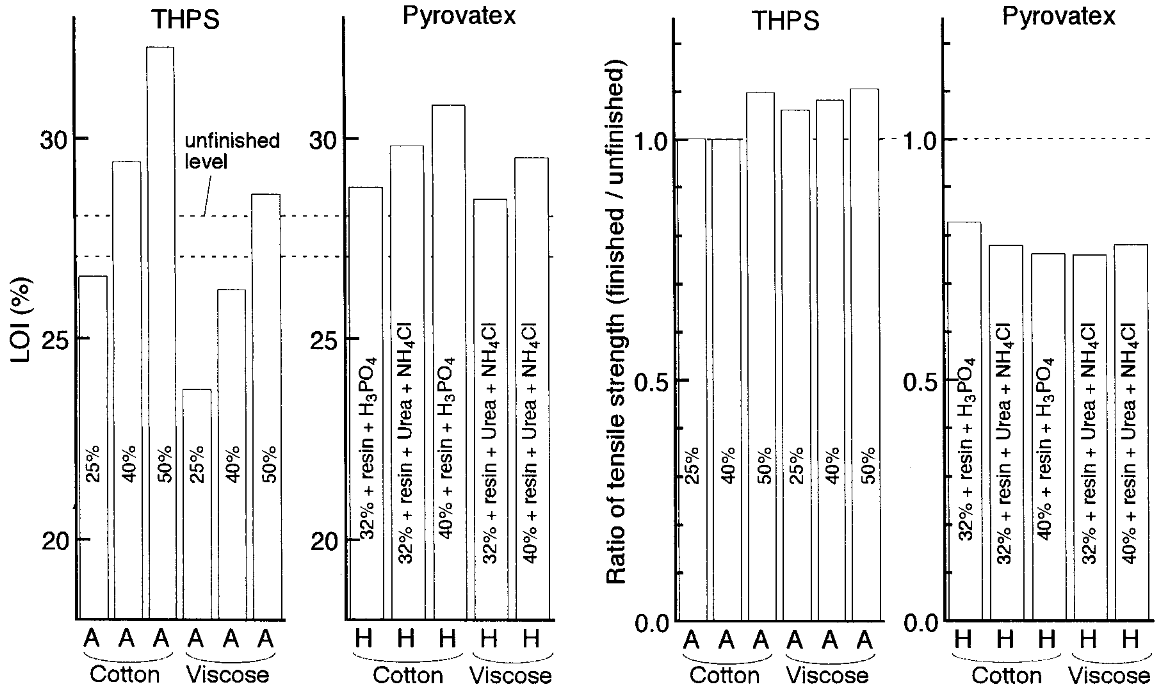


Fig. 3-18 Comparison between cellulosic fabrics treated with THPS precondensate and those treated with Pyrovatex from the standpoints of flame retardance and tensile strength (A : Ammonia cure, H : Heat cure).

(h) Comparison between PROBAN finished sample and Pyrovatex finished sample

Finally, performances by two universally famous durable flame retardant finishes were compared, the results of which are shown in Fig. 3-18. From the practical standpoint, comparing the results obtained from samples treated with 40% of THPS precondensate for cotton and 50% for viscose with those by Pyrovatex finish under various conditions, it was found that little difference was observed in flame retardance, LOI values, but considerable reduction of tensile strength was obvious in the case of Pyrovatex finish because of the thermal treatment, whereas PROBAN finish showed the same or even higher tensile strength in both cases of cotton and viscose.

3) Conclusion

PROBAN finish, widely famous durable flame retardant together with Pyrovatex finish, was investigated from the fundamental standpoint and discussed extending over the practical point of view, which is summarized as follows;

(a) NH_3 cure method was succeeded by exposing NH_3 gas under negative pressure, against the positive pressure used by A & W Co. or other patentees. It was proved that 10 sec was enough for the complete cure.

(b) The finished fabric showed sufficient flame retardance with LOI values higher than 28% and none of reduction of tensile strength and durability was also favorable.

(c) Ratio of N and P was found to be 2:1 which was very reasonable according to the mechanism of formation of PROBAN polymer.

(d) HCHO was sufficiently removed by oxidation and soaping under the condition attempted by this study.

(e) Application of PROBAN finish to regenerated cellulose was also successful by the finishing technique attempted this time. Therefore, it is strongly emphasized that recognition and positive attitude toward the flame retardation of the regenerated cellulose for which the flame retardant finish is more highly required.

3-1-3 THPS Finish by Thermo-fix

PROBAN finish proved that THPS ammonia cure gave comparatively favorable performances from both flame retardance, physical properties such as tensile strength and durability, but ammonia cure involves considerable problem, for example, necessity of special large scale installment and undesirable, stimulating and harmful NH_3 gas. Dyestuffs usable for ammonia cure are considerably limited since ammonia gives large discoloration to many dyestuffs. At these points, advantage of heat cure is undeniable. Moreover, THPS itself can be used in the case of thermal treatment whereas ammonia cure requires THPS-urea precondensate. It can be recognized as a merit that THPS itself can be used without any further process for precondensate.

Therefore, it was thought that it was worth investigating on THPS finish by heat cure to compare results with those shown by ammonia cure.

1) Experimental

(a) Materials

(1) Fabrics

One hundred % cotton and 100% viscose were the same as those used for PROBAN finish

(2) Flame retardant

THPS (Nihon Kayaku Co.)

(b) The finished fabric showed sufficient flame retardance with LOI values higher than 28% and none of reduction of tensile strength and durability was also favorable.

(c) Ratio of N and P was found to be 2:1 which was very reasonable according to the mechanism of formation of PROBAN polymer.

(d) HCHO was sufficiently removed by oxidation and soaping under the condition attempted by this study.

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1) Experimental

(a) Materials

(1) Fabrics

One hundred % cotton and 100% viscose were the same as those used for PROBAN finish

(2) Flame retardant

THPS (Nihon Kayaku Co.)

(3) Bases

Sodium hydroxide (NaOH), triethanolamine and triethylamine were used to adjust pH of treating mixture.

(4) Resins

Trimethylolmelamine (M3) and dimethylol glyoxal monourein (G) were used as resins. As catalysts, aminomethylproparnol (catalyst P®) was used for M3 and magnesium chloride ($MgCl_2$) for G.

(5) Urea and ortho-phosphoric acid (H_3PO_4) were also used as additional supplements.

(b) Methods

(1) Flame retardant finish

(i) Selection of THPS concentration

The both fabrics were impregnated with each of 20, 25, 30, 32 and 35% of THPS solutions containing 5% of a pH adjuster, triethanolamine, 12% of M3 and 1% of catalyst P, padded to about 90% pickup after 2 dip - 2 nip process and air dried, which was heated for 5 min at 150°C and followed by oxidation and soaping according to the method used in the case of ammonia cure.

(ii) Selection of pH adjuster

As pH adjusters for acidic THP sulfate, each of triethanolamine, triethylamine and NaOH was added to the above mentioned mixture so as to be 5% in the treating solution, by which pH was adjusted to 7.0 ± 0.2. The fabrics were finished with the treating solutions containing these three pH adjusters separately, thermally fixed and HCHO was removed by oxidization and soaping as in the case of ammonia cure.

(iii) Selection of resin

To select resins, most favorable for cotton or viscose for cross-linking between cotton or viscose molecules and retardant molecules, 12% of methylol type resin (M6) and glyoxal type (G) were compared by carrying out the same procedure as also described above. In each case, a catalyst was simultaneously added, 1% catalyst P® for M6 and 3% of $MgCl_2$ for G. Cotton and viscose fabrics were finished with those finishing mixture containing different kinds of resins under the conditions mentioned above.

(iv) Curing condition

In the cases of experiments (i) - (iii), the condition for thermal treatment was preliminarily selected to be heating for 5 min at 150°C, but a further investigation was attempted to establish the most favorable heating condition by varying such as 140°C, 20 min; 160°C, 5 min; 180°C, 3 min in addition to 150°C, 5 min. The rest of procedures were the same as described above.

(v) Effect of addition of ortho-phosphate

Ortho-phosphate was added to the mixture the same as that used for the above (iii) or (iv) so that the final concentration be 1% and thermally treated under the conditions, at 140°C for 20 min, at 150°C for 5 min followed by oxidation and soaping as described above.

(vi) Effect of addition or urea

The finishing mixture was prepared as above mentioned (iii) and (iv), to which 10% of urea was added for cotton and 10% and 13% for viscose. Finishing procedure, evaluation of flame retardance and also determination of physical property were carried out as mentioned above.

(2) Durability test

To test the durability, 25 repetition of laundry was performed also in this case as in the cases of Pyrovatex finish and PROBAN finish.

(3) Evaluation of flame retardance, Test for tensile strength and Determination of HCHO were carried out as those described in the cases of above two finishes.

2) Results and Discussion

(a) Decision of THPS concentration

As the results of the investigation, the limit concentration of THPS which gives LOI value higher than 28% is 25% for cotton. LOI value continues rising with increase in THPS concentration, but samples treated with higher concentrations were practically not so favorable because of slight stiffness. Consequently, it was thought that additives would be required for higher LOI value.

On the other hand, viscose fabric treated with 25% of THPS showed LOI values of 27% and char length of 20cm which are both critical values for the flame retardance. Therefore, 32% the same concentration used for Pyrovatex was tried to be applied for viscose, which resulted in remarkable flame retardance as shown in Fig. 3-19. It was concluded that the most favorable concentrations were 25% for cotton and 30-32% for viscose, which were used for all experiments below.

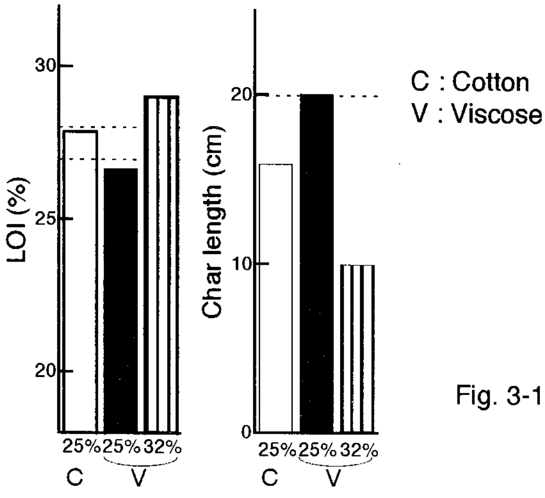


Fig. 3-19 Concentrations of THPS solutions required for cotton and viscose to obtain sufficient flame retardance.

(b) Decision of resin applicable for this finish

Since addition of resin was thought to be indispensable for this finish for cross-linking between cellulose and THPS molecules as well as for supplement of N for better flame retardance as in the case of Pyrovatex, applicability and most adequate condition of resin were investigated by using M3 and G as the representative of different types of resins. The cross-linking mechanism by these resins is that 2 methylol groups of resins react with a OH group of cellulose at one side and with P of THPC or THPS at the other side simultaneous liberation of HCl or H_2SO_4 and H_2O as shown in Fig. 3-20 in comparison with the case of Pyrovatex.

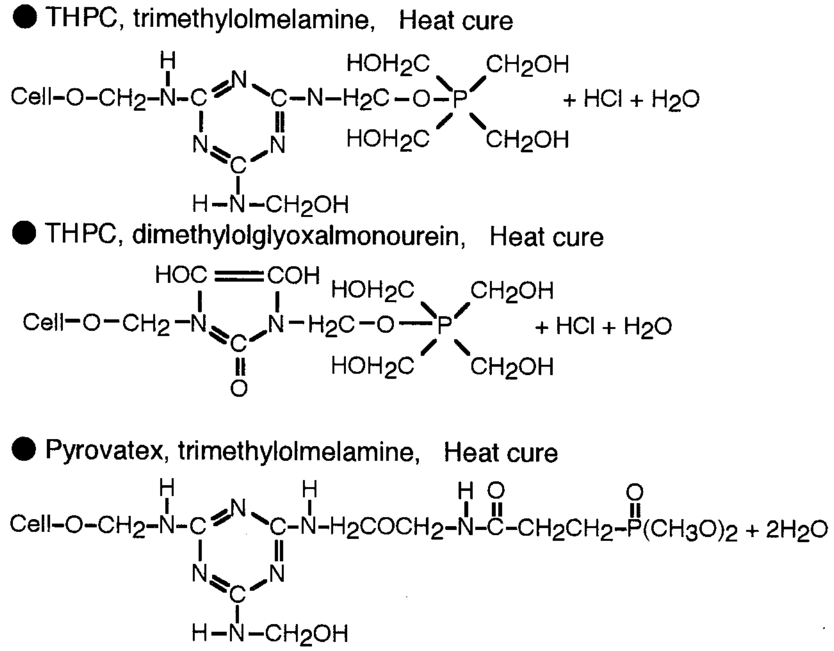


Figure 3-20 Cross linking actions of resins between cellulose and flame retardants.

THPC is shown instead of THPS for simplifying the illustration.

An investigation on the concentration revealed that 12% would be the most favorable for both resins because of insufficient effect with lower concentration and unfavorable stiffness with higher concentration. On the other hand, cotton and viscose required different types of resin respectively, i.e., G gave more favorable results to cotton and M3 was more effective for viscose as shown in Fig. 3-21. In the case of cotton, change in values after oxidation and soaping is indicated by arrows, but values only observed after oxidation and soaping were shown for viscose. In both cases, attention should be paid to the reduction of elongation, particularly in the case of viscose. This is probably because of increase in Young's modulus with decrease in flexibility brought by the cross-linkage formed in the amorphous region as well as by thermo-fixed resin formed in the fabric structure. At any rate such reduction of elongation could participate in the dimention stability of fabrics, which one of merits brought by the flame retardant finish.

(c) Selection of bases for pH adjustment

It is necessary for cellulose to adjust pH to neutral since THPS is strongly acidic. Therefore, triethanol amine and triethyl amine were selected other than NaOH because these organic bases can serve by supplying additional amounts of N. In Fig. 3-22, arrows show change in values after oxidation and soaping for cotton, whereas values observed after oxidation and soaping are shown and the results of HCHO was omitted in the case of viscose because no difference was observed between cotton and viscose. As shown in the figure, triethanol amine gave the higher LOI values both before and after oxidation and soaping in the case of cotton, and little difference was observed among three bases. HCHO was largely reduced down to less than the regulated value after oxidation and soaping.

Little difference was observed with viscose in both cases of LOI value and tensile strength, though triethylamine showed lower values of char length and elongation. From the above results, triethanolamine was selected as a pH adjuster for both cotton and viscose.

(d) Decision of curing condition

Since the most important conditions for heat cure are temperature and time, 120, 150, 160 and 180°C were selected as temperature conditions and time was considered to be longer for lower temperature and shorter for higher temperature as described above to minimize any damage to be caused by thermal effect. Fig. 3-23 shows the results obtained under varied curing conditions by using G for cotton and M3 for viscose. The values shown here are all those observed after oxidation and soaping. As seen in this figure, cotton showed a remarkably high LOI value by heating at lower temperature 140°C for longer time 20 min with shortest char length and best tensile strength, which means that this curing condition is the best for cotton. Whereas in the case of viscose, little difference was observed among curing condition for both LOI value and tensile strength though the shortest char length was observed by heating for 20min at 140°C.

In both cases of cotton and viscose, it was unexpected fact that better curing effect was given by heating at comparatively lower temperature, e.g., 140°C for comparatively longer time, e.g., 20 min rather than at higher temperature, e.g., 150°C or higher for shorter time, e.g., 5 min or less.

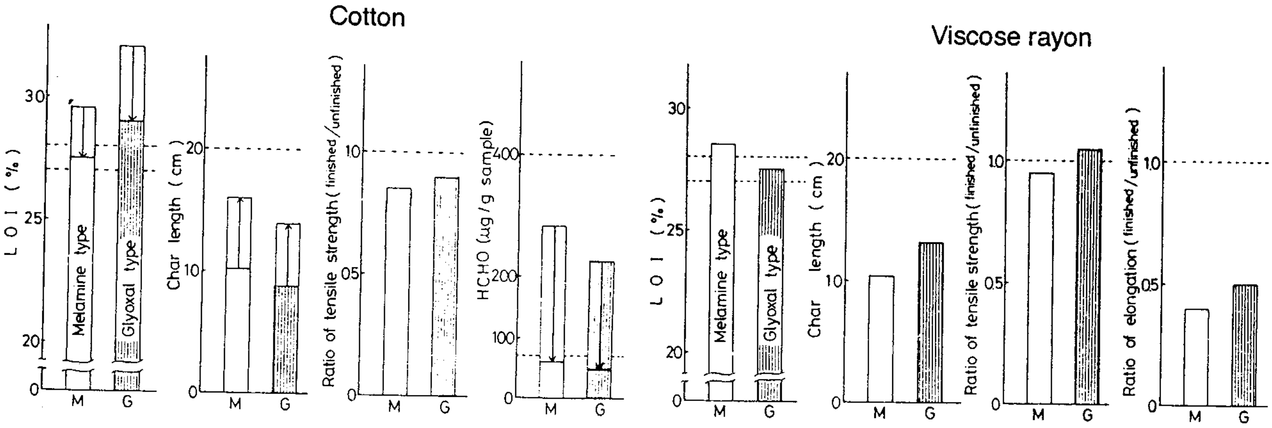


Fig. 3-21 Effects of resins on flame retardance, tensile strength and elongation of cotton and viscose fabrics treated with THPS and additives.

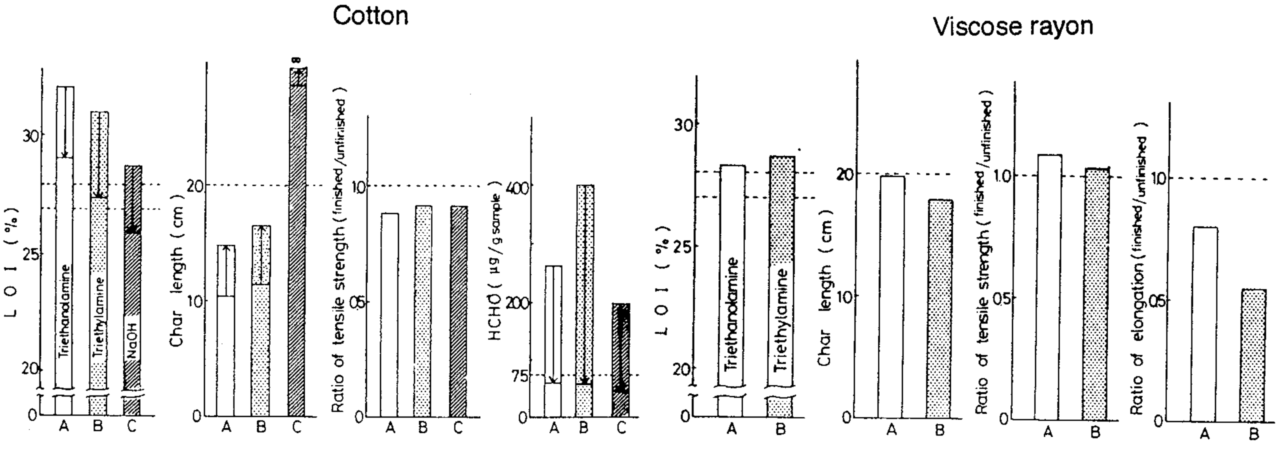


Fig. 3-22 Effects of bases on flame retardance, tensile strength and HCHO contents of cotton and viscose fabrics treated with THPS and additives.

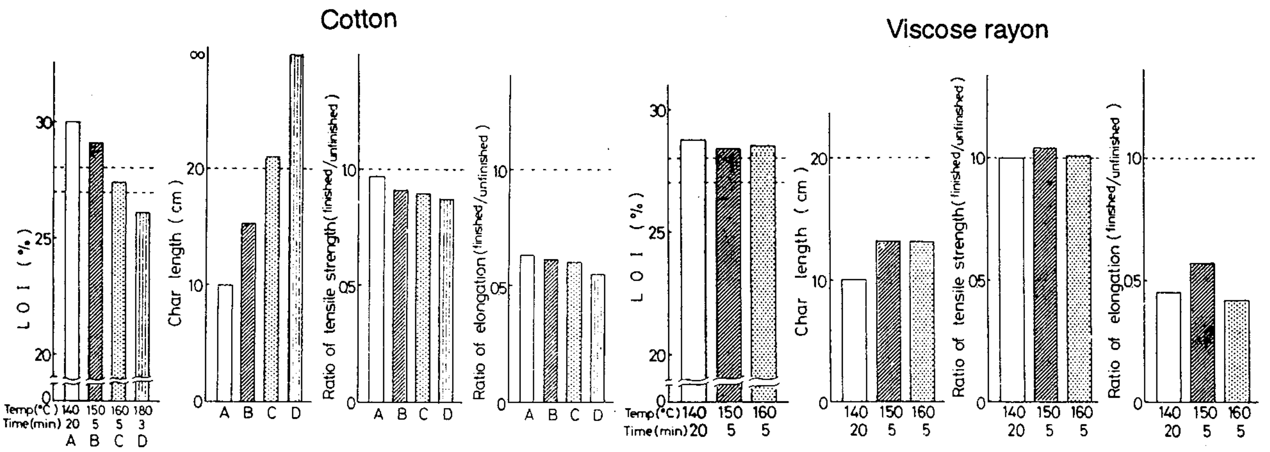


Fig. 3-23 Effects of heating conditions on flame retardance, tensile strength and elongation of cotton and viscose fabrics treated with THPS and additives.

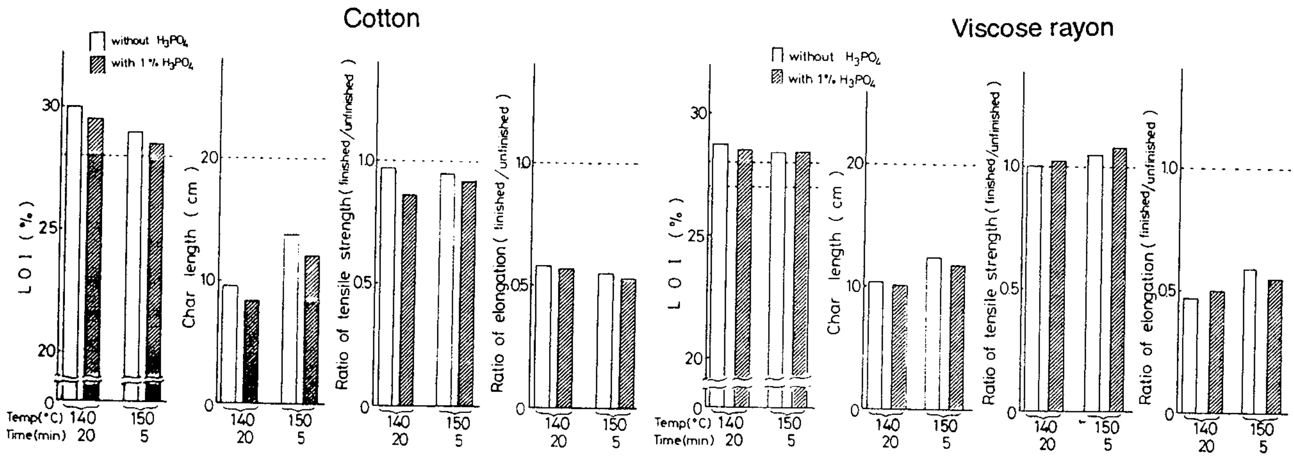


Fig. 3-24 Effects of addition of phosphoric acid to THPS on flame retardance, tensile strength and elongation of cotton and viscose fabrics treated with THPS and additives.

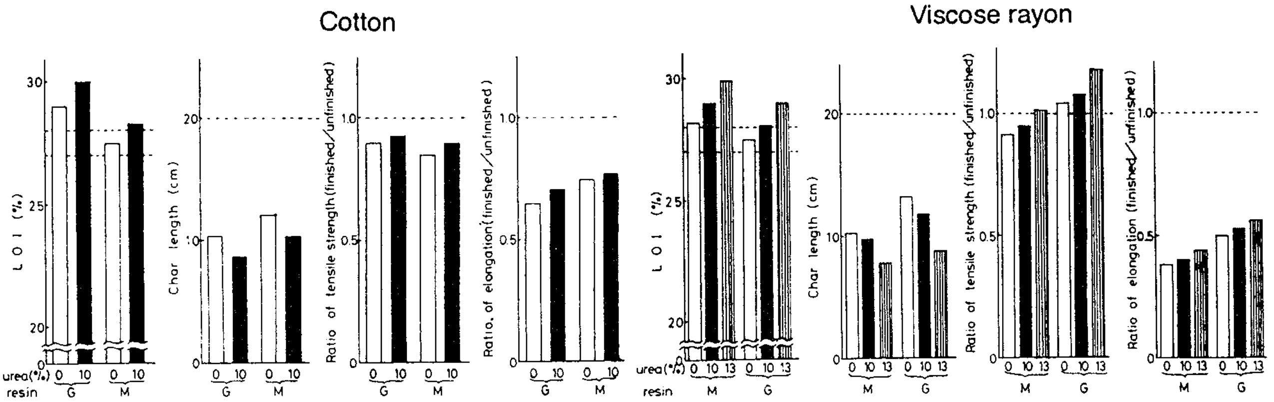


Fig. 3-25 Effects of addition of urea to THPS on flame retardance, tensile strength and elongation of cotton and viscose fabrics treated with THPS and additives.

M : melamine type G : glyoxal type

(e) Correlation between heat condition for flame retardant finish and that for resin finish for crease recovery

Taking the curing condition for resin finish for crease recovery studied by Nakanishi et al. into consideration, relationship between heating condition and flame retardant effect mentioned above showed markedly good agreement with that observed between thermal condition and crease recovery effect, i.e., according to the study on the resin finishing condition by Nakanishi et al.[15-21], the best crease recovery both dry and wet, was given by the finishing condition the same as that shown by the flame retardant finish as found in this study, e.g., at 140°C for 20 min. Nakanishi found good correlations also between increase in crease recovery and that in the rigidity of resin as well as in the amount of HCHO to be liberated simultaneously with the reaction between resin molecules as well as between cellulose and resin molecules. In these all cases, the best result was observed with samples treated under the above condition for 20 min at 140°C. The overall conclusion by taking the above all results obtained so far into consideration suggests that the flame retardance is highly dominated by the reactivity between resin and cellulose molecules and resin and THPS molecules just as in the case of resin finish.

(f) Effect of addition of P

From our experience that addition of P is effective to improve the durability in any case of finish which requires heat cure, addition of 1% of H_3PO_4 was attempted also in this case. But there found no positive effect of P on flame retardance, tensile strength and elongation as shown in Fig. 3-24.

(g) Effect of addition of urea

As addition of urea showed a favorable effect on flame retardance playing a supplemental role of N in the case of Pyrovatex finish, urea was added together with resins also this time.

In the case of cotton, 10% of urea was added to 25% of THPS with both types of resin, M3 and G. Addition of urea gave better results in both flame retardance and physical properties, i.e., flame retardance was elevated, particularly LOI value reached 30% in the presence of G, and such tendency that reduction of tensile strength and elongation to be caused by heat cure otherwise was somewhat moderated by addition of urea as shown in Fig. 3-25.

On the other hand, 13% of urea was also added in the case of viscose since it was found that viscose required 32% of THPS, 1.3 times that required by cotton and compared with the result obtained by addition of 10%. As is seen in Fig. 3-25, LOI showed a linear rise with increase in amount of urea with decrease in char length showing a larger reduction between 10% and 13%. It is surprising that such a little difference, only 3%, gave a larger effect than that observed with a difference of 10% which is more than 3 times. Melamine type resin showed a larger efficiency compared with glyoxal type resin in the case of viscose also in this study. Tensile strength and elongation also showed rise with increase in added amount of urea, which proved a merit of addition of urea. Since urea is highly water soluble, if urea was merely adsorbed on the surface of fiber, it would be readily removed by oxidation and soaping. However, the effect of urea is maintained even at the final step. Moreover, the reactivity of resin to cellulose, i.e., glyoxal type to cotton cellulose and melamine type to regenerated viscose cellulose, is directly reflected on the results shown in Fig. 3-25, which suggests some possibility of participation of, for example, chemical bonding between resin and fiber molecules, resin and THPS molecules as well as among resin, THPS and urea etc.

(h) Durability

Since durability, specially resistance against laundering is an important factor for fiber products for which repeated laundering is highly required, both cotton and viscose samples finished as mentioned above were tested by repetition of laundry. The results are shown in Fig. 3-26, in which results for viscose are omitted because of similarity with those of cotton. LOI value showed gradual decrease with rise in char length with increase in number of repetition of laundry. Yet, LOI level is maintained at nearly 28% and char length at the level of 14-15 cm.

As to the tensile strength, no apparent change was observed up to 10 time repetition, but 10% of reduction was shown after 25 time repetition. However, the ratio of tensile strength of finished sample to that of unfinished sample increased as shown by solid bars in Fig. 3-26 when the ratio values were obtained by using unfinished sample washed 10 or 25 times together with the finished samples.

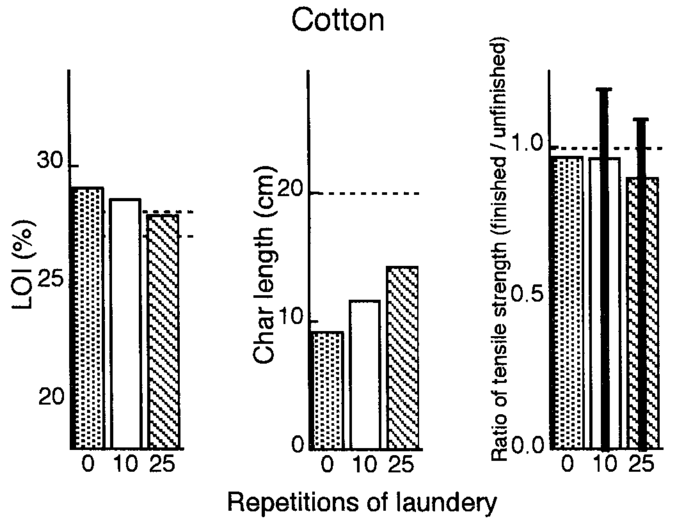


Fig. 3-26 Changes in flame retardance and tensile strength after repetitions of laundery.

This is probably because unfinished fabrics would be damaged to the mechanical degradation of fabric structure by repeated laundering, whereas such mechanical damage is inhibited by the effect of cross-linkage in the case of finished fabrics. Therefore, the merit of flame retardant finish was proved not only from the security but also from the standpoint of consumers end-uses.

(i) Comparison with Pyrovatex finish and PROBAN finish

The results of investigations on a flame retardant finish with THPS by heat cure instead of ammonia cure were compared with those of Pyrovatex finish and PROBAN finish with ammonia cure, which is shown in Fig. 3-27. In the figure, results of THPS heat cure are indicated by shaded bars.

In both cases of cotton and viscose, samples finished by THPS heat cure showed most favorable results among the practically usable samples though a shaded bar for tensile strength of cotton is lower than open bars for PROBAN finish with ammonia cure by 10%, but higher than that of Pyrovatex samples by 10%. In the case of viscose, tensile strength of THPS heat cure showed the highest value.

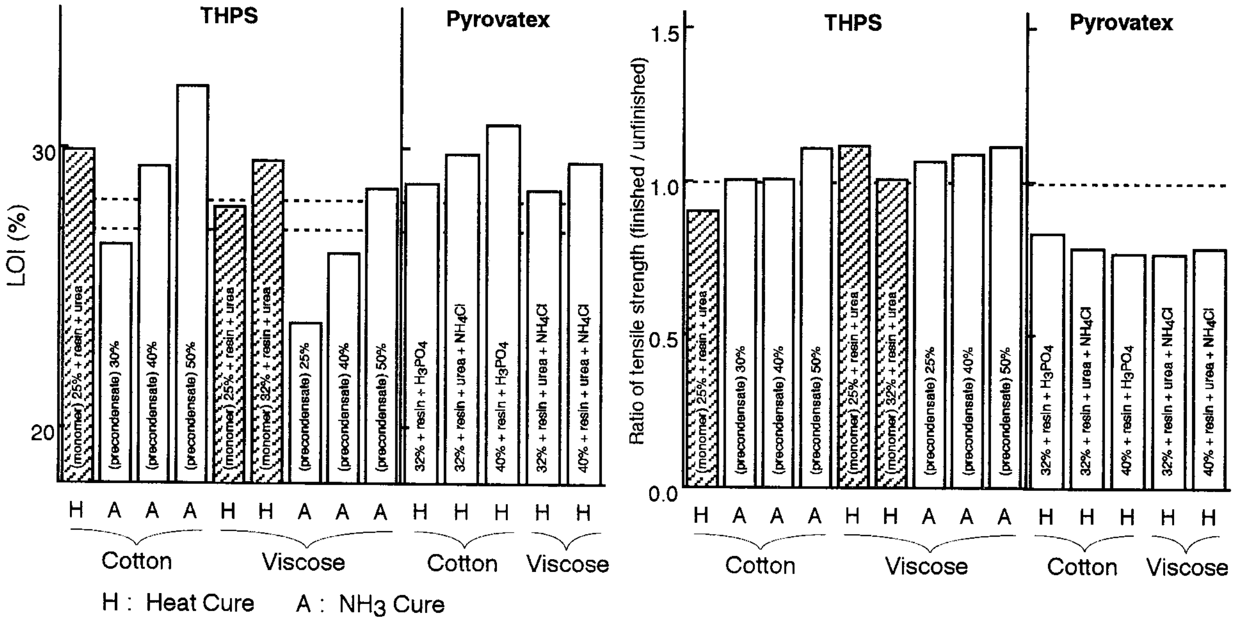


Fig. 3-27 Comparison of LOI values (left) and ratios of tensile strength (right) observed among 3 kinds of finishing conditions : heat cure for THPS monomer, ammonia cure for THPS precondensate and heat cure for Pyrovatex.

3) Conclusion

The above results obviously disclosed that samples finished by THPS heat cure showed flame retardance together with physical properties equal or even better than those shown by Pyrovatex finish and THPS ammonia cure, which means that THPS heat cure is sufficiently applicable rather than Pyrovatex finish or PROBAN finish providing certain advantages for practical applications.

3-1-4 Nondurable Flame Retardant Finishes

We have paid much attention to nondurable flame retardant finishes for many materials which do not require any repetition of washing because of remarkably simpler and handy process, just dip and dry, extremely much lower costs, easier availability for general consumers and possibility for repetition of retreatment after washing as well as considerably higher flame retardance compared with that obtained by any durable flame retardant finishe mentioned before.

Therefore, an investigation was carefully performed for flame retardant finishes with inorganic compounds containing each of P, S or halogens in combination with N as well as containing boric acid and vórax to compare flame retardance and physical properties most important for consumers end-uses such as tensile strength and elongation with those observed with durable flame retardant finished cotton samples shown in the previous sections.

1) Experimental

(a) Materials

Cotton fabric was the same as described in 3-1-1 ~ 3-1-3.

Treating reagents are listed in Table 3-3.

(b) Methods

Treating solutions were prepared according to mixing ratios and concentrations as listed in Table 3-3. These concentrations were decided to afford sufficient add-on in all cases. The cotton fabric was immersed in each solution for a few min., padded to about 90% pickup after 2 dip- 2 nip procedure and air dried.

Flame retardance was evaluated for each sample by LOI method mentioned in Chapter 2.

Tensile strength and elongation were determined as described in 3-1-1.

2) Results and Discussion

Flame retardance evaluated by LOI value, tensile strength and elongation expressed by the ratio, treated/untreated for each sample are shown in Table 3-3, from which it was obviously confirmed that all treated samples gave not only sufficiently high LOI values much exceeding 28% but also favorable stability for the physical properties, showing little change in strength and dimensional stability compared with those of untreated cotton fabric. Such results prove that nondurable flame retardant finished samples can be useful practically for any purpous for which washing or cleansing is seldom or not necessary.

Table 3-3 List of nondurable treating reagents with prescriptions for treatments, flame retardances evaluated by LOI method and physical properties for textile end-use.

Treating reagent	Mixing ratio W/W	Conc. (%)	LOI (%)	Tensile strength	Elongation
				treated / untreated	
$(NH_4)_2HPO_4$		10	38.0	0.95	0.99
		20	43.4	0.97	1.02
$(NH_4)_2SO_4$		20	34.0	0.96	0.99
$NH_4SO_3NH_2$		20	35.8	0.98	0.95
NH_4Br		20	40.0	1.0	1.0
H_3BO_3 + $Na_2B_4O_7$ ($\cdot 10H_2O$)	3 :7	10	39.2	1.16	1.10
		20	44.2	1.20	0.98
		30	48.0	1.20	1.02
H_3BO_3 + $(NH_4)_2HPO_4$	1 :1	10	35.0	1.0	1.0
		20	44.0	0.97	1.05
$(NH_4)_2HPO_4$ + $NH_4SO_3NH_2$	1 : 3	10	38.0	0.96	0.97
		20	46.2	0.98	0.99
H_3BO_3 + $Na_2B_4O_7$ + $(NH_4)_2HPO_4$	3 : 7 : 5	10	38.0	1.01	1.10
		20	42.0	0.96	1.06
		30	48.5	1.02	1.04
H_3BO_3 + $Na_2B_4O_7$ + polyphosphocarbamate	3 : 7 : 5	10	39.5	0.90	1.0
		20	45.0	0.90	0.93
$(NH_4)_2HPO_4$ + NH_4Cl + $(NH_4)_2SO_4$	1 : 1 : 1	10	36.0	0.95	0.98
		20	40.0	0.97	1.08

3) Conclusion

For the reason of various merits of nondurable flame retardant finishes as mentioned above, investigations were tried to prepare many kinds of nondurable flame retardant finished cotton fabric with 10-30% solution of inorganic compounds containing each of P, S or halogens together with N as well as boric acid and borax, the results of which have revealed that all treated samples were highly flame retardant with high LOI values, 35-48%, and maintained favorable physical properties, tensile strength and elongation. Therefore, nondurable flame retardant finished samples are sufficiently useful and hopeful for any material for which frequent washing is unnecessary as well as for paper products. In addition simple retreatment is possible even after repeated washing.

3-1-5 Forms of Flame Retardant Elements to be Effective for Flame Retardation of Cellulose

1) In the case of nondurable flame retardant finish

(a) Element effective with a single component B can exhibit flame retardance in the form of borate.

(b) Elements which show flame retardance only by the synergistic effect

P, S and halogens can not be effective when added each alone but act as flame retardants only in combination with N, and vice vasa also for N itself.

In this case, P acts most effectively when it exists so that it can form phosphoric ester with $-CH_2OH$ of cellulose molecule, S is supposed to be in the forms of SO_4^{2-}, SH_3H^- or $SO_3NH_2^-$ and halogens to be Br^- or Cl^- which requires NH_4^- as a counter ion, N should be ammonium salts with those elements.

2) In the case of durable flame retardant finish

Every durable flame retardant requires N and P to achieve flame retardation by the synergistic effect of both molecule but THPS itself contain only P with which N is combined by the condensation with urea.

3-1-6 Minimum contents of B, N and P Required for the Critical Level of Flame Retardance (LOI value 27-28%)

As shown below, durable flame retardant finishes required 2-2.7 times total amounts of N and P compared with those required by nondurable flame retardant finishes.

		B		N		P	
		%	mmol / g	%	mmol / g	%	mmol / g
Nondurable flame retardardants		0.7	0.65	0.5	0.36	1.0	0.32
durable flame retardardants	PROBAN THPS			1.8	1.29	2.0	0.64
	Pyrovatex CP			2.0-3.0	1.43	1.0	0.32

3-2 Flame Retardant Finishes for Poly (ethylene terephthalate) (PET)

3-2-1 Synergistic Effects of Bromine (Br) and Phosphorus (P) on Flame Retardance of PET Fiber

PET fiber has captured very high percentage of the total wearing apparel fiber market because of ease of its care and low cost as well as of its outstanding physical properties. A majority of this fiber is used in outerwear where flammability of the garment must be considered as an important factor in the overall fabric performance.

Recently, owing to increased public awareness and concern and the adoption of more severe fabric flammablity standards, the need for the development of flame-retarding PET fiber or fabric has become critical.

In the past, the flame retardation of cellulosic fibers centering around thermal degradation has been studied extensively[22-29], whereas that of synthetic fibers such as PET has not received as much attention, and consequently the exact mechanism of the thermal degradation as well as of the flame retardation of PET fiber has not been made clear.

Although the mechanism for P-halogen synergism has been explained by Jacques and Lyons[30,31], and the practical importance of flame retardants containing both halogen and P has been well known, but there is no satisfactory evidence to strongly support proposed P-halogen synergisms, and any detailed information concerning the synergistic effect of halogens and P on PET fiber by systematic studies has not so far been available.

Therefore, the research project this time has been focused on an extensive and detailed investigation into the relationship between the flame retardant tendency of PET fabric and a halogen (bromine this time) and P contents.

In particular, this investigation has been concentrated on the Br and P ratio in the PET fabric with a view to establishing the conditions for a synergistic effect, and also extended over observing how such synergistic effect will be reflected in the flammability of PET fabric at high environmental temperatures from the practical standpoint.

This was approached by the following two methods.

1. The flame retardants were applied to the PET woven fabric from solvent and cured by a thermo-fix process.

2. The products were incorporated into PET polymer by premixing followed by melt spinning.

1) Experimental

(a) Chemical Treatment (Preparation of flame retardant finished woven fabrics)

(1)Materials

(i) Fabric (Woven fabric)

100% PET

Analysis of fabric

Fabric structure: twill

Weight: 98.0 g/m^2

Count	Warp:93/in	
	Weft:66/in	
Picks and Ends	Warp:45/Yarn	
	Weft:63/Yarn	
Decitex	Warp:13.61	(0.302 DPf)
	Weft:17.31	(0.275 DPf)

(ii) Reagents

★ Hexabromocyclododecane (HBCD)	from ALDRICH Chem. CO.
★ Triphenylphosphate (TPPA)	
★ Acetone	
★ Oligomeric cyclic phosphonate (AMGRAD CU)	from Albright & Wilson CO.
★ Na_2HPO_4	from ALDRICH Chem. CO.

(2) Method

(i) Flame retardant finish with HBCD and TPPA

★ Preparation of acetone solutions of HBCD and TPPA:

0.2-10% of HBCD acetone solutions and 2.5-40% of TPPA acetone solutions were prepared respectively, and both compounds were also combined according to the following concentrations and ratios shown in Table 3-4.

★ Impregnation: The fabric was immersed in the aforementioned solutions.

★ Drying and thermo-fix: All samples were dried for 2 min at 100°C followed by a thermal treatment for 2 min at 190°C.

★ Removal of extra additives: In order to remove any extra additives on the surface of the fabric, treated samples were rinsed with acetone.

Table 3-4 Preparation of acetone solutions of HBCD and TPPA for flame retardant finish of woven PET fabric.

Weight Ratio	Molar Ratio		Concentration	
HBCD : TPPA	HBCD : TPPA	Br : P	HBCD	TPPA
9 : 1	1 : 0.22	1 : 0.03	10 ~ 0.2 +	1.1 ~ 0.022%
8 : 2	1 : 0.50	1 : 0.07	10 ~ 0.2 +	2.5 ~ 0.05%
7 : 3	1 : 0.85	1 : 0.11	10 ~ 0.2 +	4.28 ~ 0.086%
6 : 4	1 : 1.30	1 : 0.18	10 ~ 0.2 +	6.67 ~ 0.134%
5 : 5	1 : 2.0	1 : 0.27	10 ~ 0.2 +	10 ~ 0.2%
2.5 : 7.5	1 : 6.0	1 : 0.8	10 ~ 0.2 +	30 ~ 0.6%
2 : 8	1 : 8.0	1 : 1.0	10 ~ 0.2 +	40 ~ 0.8%

(ii) In the case of flame retardant finish with oligomeric cyclic phosphonate (AMGARD CU®)

★ Bath preparation: A pad bath was prepared by mixing the following components:

AMGARD CU® 50.0 g
Na_2HPO_4 1.6 g (to adjust pH to 6.4-6.5)
SANDOZ IN 0.4 g (as a wetting agent)
Water 948 ml

★ Impregnation: The fabric samples (untreated and treated with 5% HBCD solution, cured and rinsed as mentioned above) were immersed in the above pad bath for 30 min at room temperature (≒20°C) and padded by a pad-mangle using a double dip/double nip process.

★ Drying and Thermo-fix: The immigrated samples were dried by heating for 2 min at 120°C and thermally fixed by heating for 2 min at 195°C.

(iii) Determination of Add-on

Add-on of above mentioned each sample was obtained by the conventional gravimetric method.

(b) Melt spinning (preparation of build-in flame retardant knitted fabrics)

(1) Materials

(i) Polymer

D217 PET from ICI

(ii) Additives

★ Decabromophenoxybenzene (DBPB)	from ALDRICH Chem. CO.
★ Red phosphorus compound (AMGARD CRP®)	from ALBRIGHT & WILSON CO.
★ AMGARD CU®	
★ Na_2HPO_4	from ALDRICH Chem. CO.
★ Wetting agent	from SANDOZ CO.

(2) Method

(i) Application of additives

★ Application of DBPB: 2, 3 or 6 g of DBPB were dispersed in 40-50 ml (enough to wet the polymer) of acetone to which 100 g of PET polymer were added with a vigorous agitation to get an even distribution of the additive through out the polymer.

★ Drying: Prior to spinning, PET polymer untreated standard and that coated with DBPB as mentioned above were dried at 125°C in vacuo overnight.

★ Blending with AMGARD CRP: The PET polymer both standard and that coated with DBPB were blended with AMGARD CRP granules in an inert atmosphere of nitrogen.

★ Application of AMGARD CU: Knitted fabrics (prepared as mentioned below) the filaments of which were spun from the untreated standard PET as well as from the samples treated with DBPB were finished with AMGARD CU in the manner described above.

(3) Conditions for melt spinning

(i) Spinning (by Rod Spinner)

Wind up speed: 140 m/min for 10 hole spinner, 180 m/min for 1 hole spinner.

(ii) Drawing (by Deines Draw Frame) only for filaments spun by 10 hole spinner

Feed roll temperature 90°C

Hot plate temperature 150°C
Traveler size No.24
Spindles 5300 RPM
Draw ratio 6.1
Draw roll 150 m/min

(c) Knitting

Filaments spun as mentioned above were knitted by KRENZLER (with circular gauge No.24)

(d) Evaluation of flammability

(1) LOI at room temperature

(i) Stanson Redcraft FTA Flammability Tester was used with Ronson Hi-Heat Butane gas.

(ii) Each sample was cut into pieces, 14-15 cm long, 5 cm in wide and stitched with glass fiber thread to make PET fabric sustain flame (3 lines per piece for woven fabric, 5 lines for Knitted fabric).

(iii) Prior to test, the testing samples were conditioned in a conditioning room at R.H. 63% at 20°C.

(iv) The calibration was carried out before testing.

(v) Conditioned samples were mounted vertically on a frame and placed in the center of the combustion chamber.

(vi) The mixed gas was allowed to flow in the combustion chamber for 30 s before ignition.

(vii) The sample was ignited at the top edge by an above mentioned ignition torch with approximately 1 inch flame length.

(viii) The flame application time adopted was minimum but sufficient to establish burning less than 5 cm across the edge of the fabric specimen.

(ix) The above (v), (vi) and (vii) were repeated altering O_2 concentration until the sample was burned for a length of around 5 cm. The O_2 concentration was determined by direct reading from a digital voltmeter.

In all cases the LOI values were determined by confirming the reproducible values.

(2) LOI at high temperature (HLOI)

(i) For this experiment, Stanson Redcraft HFTA Flammability Tester equipped with another type of burning chamber was used.

The burning chamber consists of two concentric glass cylinders, the inner one conforms to ASTM 2863-76, 75 mm i.d. and 450 mm length, and has the column heater wound on its outer surface.

There are two heaters for heating the flowing gas in the inner chimney (column heater) and a preheater at the base of the column.

A thermocouple is inserted in the chimney for temperature control.

(ii) The gas flow rate was maintained at 10.6 l/min in this case, and calibration was done before testing.

(iii) The temperature was set at a desired temperature and the temperature gradient was checked over the sample length, and two dials for column heater and preheater were adjusted to get the desired temperature and minimize the temperature gradient.

(iv) The samples were conditioned and mounted on a samples holder as mentioned above, which was placed into position on the spigot by using a transfer handle.

(e) Quantitative determination of Br and P

(1) Br determination

(i) The samples were burned in Schöninger flask filled with oxygen and containing 10 ml H_2O_2.

(ii) The solution was then made alcoholic and titrated with 0.1-0.01 N mercuric nitrate solution using bromophenol and diphenylcarbazone as indicators. Color changed from yellow to purple.

(iii) Mercuric nitrate was standardized with exact solution of NaCl.

The amount of Br present in the sample was found from

1 ml 0.1-0.01 N $AgNO_3$ = 0.007992-0.0007992 g Br

(2) P determination

(i) The samples were digested in Kjeldhal flasks using H_2SO_4. and HNO_3.

(ii) The solution was then transferred to a beaker to which 3 ml $HCl_{conc.}$. and 4 ml sodium molybdate (15%) solution were added and made up to 50 ml with H_2O. Then quinoline phosphomolybdate precipitate was obtained by adding dropwise 6 ml quinoline HCl solution (2%).

(iii) The precipitate was allowed to stand for 2-3 hours (not overnight), and filtered into a dry Gooch crucible, dried and reweighed.

(iv) Calculation is as followes:

Precipitate is $(C_9H_7N)_3H_3(PO_412MoO_3)$

Molecular weight: 2213

$$\frac{\text{M.W. of P}}{\text{M.W. of ppt}} = \frac{31}{2213} = 0.014$$

P is determined by multiplying the weight of precipitate by this value.

2) Result and Discussion

(a) Effects of Br, P and combination of both elements on the flame retardance of PET fabric.

HBCD and TPPA acetone solutions of almost saturated solutions and combined solutions containing both compounds in various mutual ratios extending over HBCD:TPPA = 1:4 - 9:1 were prepared for the treatment of PET fabric, by which effects of Br and P alone and combination of both elements on the flame retardance of PET fabric were observed. Fig. 3-28 illustrates the relationship of LOI values to add-ons of HBCD and TPPA separately as well as of HBCD + TPPA observed for the samples treated as mentioned above. The percentages stand for the concentrations of flame retardants used for the treatment of PET fabric for this experiment.

It has been found in the figure that 10% solution of TPPA gave an increase in LOI value to some extent but leveling off was shown between 10% and 30%, and only a little increase was observed even at 40%.

While the samples treated with HBCD showed considerably higher LOI level increasing linearly with add-ons in a range from around 5% to 20%.

On the other hand, when both compounds are combined, LOI values are much more enhanced showing a peak at the mutual ratio HBCD 8% : TPPA 2% and converging to the LOI values of samples treated with HBCD 10% : TPPA 0% as well as with HBCD 0% : TPPA 10%.

Since the result obtained here clearly illustrates a synergistic effect of Br and P at this stage, it was considered best to carry out experiments in more details on this point.

Therefore, an attempt was made to prepare samples treated with various concentrations at each mutual ratio as shown in Table 3-5. The ratios were set up extending from HBCD 9 : TPPA 1 to HBCD 2.5 : TPPA 7.5 (1:3).

At each ratio, the highest concentration of HBCD was kept at 10% almost saturated concentration to which TPPA was added on the bases of the concentrations of HBCD according to the mutual ratios shown in the table. It is because the dominant component for the flame retardance of PET fabric was considered to be Br rather than P deducing from the result shown in Fig. 3-28.

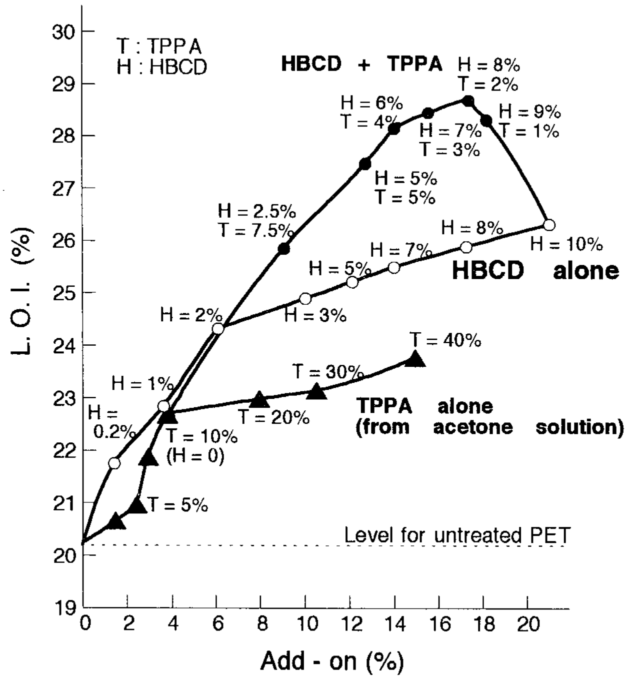


Fig. 3-28 LOI values vs add-ons of PET fabric treated with acetone solutions of HBCD and TPPA each alone as well as of combination of both elements.

Table 3-5 Mutual ratios of HBCD and TPPA for preparation of treating baths.

Mutual Ratio (%)	HBCD : TPPA 9 : 1	H : T 8 : 2	H : T 7 : 3	H : T 6 : 4	H : T 5 : 5	H : T 2.5 : 7.5
Concentration (%)	10.0 : 1.11	10.0 : 2.50	10.0 : 4.30	10.0 : 6.67	10.0 : 10.0	10.0 : 30.0
	8.0 : 0.89	8.0 : 2.00	8.0 : 3.43	8.0 : 5.33	8.0 : 8.0	8.0 : 24.0
	6.0 : 0.67	6.0 : 1.50	6.0 : 2.57	6.0 : 4.00	6.0 : 6.0	6.0 : 18.0
	5.0 : 0.55	5.0 : 1.25	5.0 : 2.14	5.0 : 3.33	5.0 : 5.0	5.0 : 15.0
	3.0 : 0.33	3.0 : 0.75	3.0 : 1.29	3.0 : 2.00	3.0 : 3.0	3.0 : 9.0
	2.0 : 0.22	2.0 : 0.50	2.0 : 0.86	2.0 : 1.33	2.0 : 2.0	2.0 : 6.0
	1.0 : 0.11	1.0 : 0.25	1.0 : 0.43	1.0 : 0.67	1.0 : 1.0	1.0 : 3.0

(b) Retention of Br and P in PET fabric

It is essential to acquire some information about the affinity of Br and P with PET fabric prior to further investigations on effects of Br and P on PET fabric.

Therefore, instead of using add-on, the samples were analyzed for the determination of Br and P retained in PET fabric after the thermal fixation.

The result is shown in Table 3-6.

Table 3-6 Comparison between concentrations of Br and P in treating solutions and contents of Br and P in PET fabric.

Br

Conc. in Soln		Content in Fabric	
HBCD	Br (75%)	Br	
● 10%	7.50%	12.45%	1.56 mmol/g
8%	6.00%	10.24%	1.28 mmol/g
6%	4.50%	7.41%	0.93 mmol/g
5%	3.75%	6.09%	0.76 mmol/g
1.5%	1.13%	1.85%	0.23 mmol/g

P

	Conc. in Soln		Content in Fabric	
	TPPA	P (9.5%)	P	
From Aceton Soln	● 40%	3.80 %	1.35 %	0.44 mmol/g
	30%	2.85 %	0.91 %	0.29 mmol/g
	25%	2.38 %	0.80 %	0.26 mmol/g
	10%	0.95 %	0.33 %	0.11 mmol/g
	7.5%	0.71 %	0.27 %	0.09 mmol/g
	5.0%	0.48 %	0.23 %	0.07 mmol/g
From Emulsion	10%	0.95 %	0.10 %	0.03 mmol/g

Br + P

HBCD : TPPA	Conc. in Soln		Content in Fabric		Conc. in Soln		Content in Fabric	
	HBCD	Br	Br		TPPA	P	P	
25 : 75	10 %	7.5 %	4.05 %	0.51 mmol/g	30.0 %	2.85 %	1.00 %	0.30 mmol/g
50 : 50	10 %	7.5 %	7.25 %	0.91 mmol/g	10.0 %	0.95 %	0.35 %	0.11 mmol/g
60 : 40	10 %	7.5 %	8.60 %	1.08 mmol/g	6.7 %	0.64 %	0.30 %	0.10 mmol/g
70 : 30	10 %	7.5 %	10.90 %	1.36 mmol/g	4.3 %	0.41 %	0.25 %	0.08 mmol/g
80 : 20	10 %	7.5 %	11.50 %	1.44 mmol/g	2.5 %	0.24 %	0.10 %	0.03 mmol/g
90 : 10	10 %	7.5 %						

When HBCD was used alone starting from 10% which is almost saturated solution as mentioned above, concentrations of Br in solutions are 75% of added HBCD from the formula of HBCD, but observed Br contents retained in the fabric are much higher compared with the concentrations in solutions, which can be attributed to the strong affinity of HBCD molecules to PET fibers.

On the contrary, in the case of TPPA, even though TPPA is highly soluble in acetone and high concentrations are available, the ratio of P in TPPA molecule is only 9.5%, and furthermore, as shown in the table, the retained amounts of P on PET fabric is very low compared with the concentration in solution (about 1/3) in every case tested in the present study. Especially from emulsions, retained amounts of P are about 1/10 of concentrations in emulsions.

On the other hand, combinations of both HBCD and TPPA prepared by keeping the concentration of HBCD at 10% (saturated) and changing the ratio of TPPA from 30% (x3) to 2.5% (x1/4), Br showed a different behavior, i.e., Br retention was considerably reduced at higher ratios of P concentrations in the mixture, probably because of a competitive effect, and increased with decrease in the ratio of P showing values close to those shown in the case of Br alone. Whereas P showed a tendency similar to that observed in the case of P alone, e.g., the ratio of retention is in a range of 1/2-1/3 that in the solutions.

(c) Comparison between flame retardance given by Br and that by P in a lower content range.

Before carrying out a further investigation on the synergism of both Br and P, the first thing to be taken into consideration is to compare the effect and contribution of Br and P separately, especially in a range of lower content since the retention of P in PET fabric is very low.

It seems more comprehensive and better validity to use increase in LOI values rather than LOI value itself, and it is more reasonable to use the actual amounts of Br and P contents than using add-on. Therefore, ΔLOI values (LOI finished - LOI unfinished) were used to express the improvement of flame retardance and the relationship of these ΔLOI values to Br and P contents in the treated PET fabric was observed.

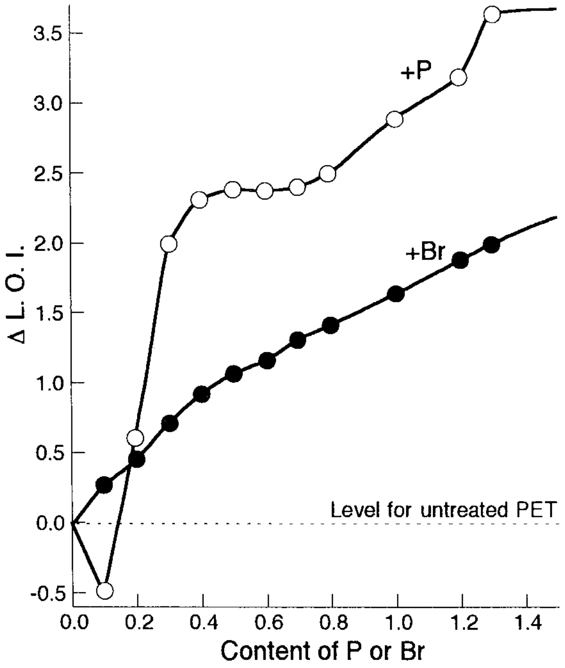


Fig. 3-29 Comparison of ΔLOI values observed between Br-containing PET fabric and P-containing PET fabric at the same content in a range of lower contents.

As shown in Fig. 3-29, P alone gives more contribution than Br alone to the improvement of LOI value in a lower content range, although a very low content range around 0.1% shows rather negative effect as also reported in the literatures[32-34].

It is expected to be of much interest to see how such phenomenon will reflect in the synergism of both components.

(d) Effects of P, Br and combination of P and Br on the flame retardance of PET fabric.

On the basis of the information obtained from Fig. 3-29 concerning the effect of each P and Br alone on PET fabric, Fig. 3-30 illustrates a further findings obtained by combining both elements, i.e., LOI increases with Br contents at every mutual ratio with a tendency similar to that shown in Fig. 3-28 showing a synergistic effect especially above 5% of Br content. Attention should be paid to the fact that the curves converge in higher Br content range, whereas in a range lower than 5-6% of Br content, the higher the ratio of P, the higher the ΔLOI value is observed at the same Br content.

Such phenomena prove that flame retardance of treated fabrics becomes almost irrespective of P contents when sufficient amounts of Br, 9-10% or more are present, while P contents contribute to the flame retardance of PET fabric at lower contents of Br and become dominant when the ratio of TPPA to HBCD is 3 and higher.

On the other hand, when ΔLOI value were plotted against P contents, a very different pattern was obtained (Fig. 3-31). In this case, the scale of X axis is multiplied by 10 compared with that for Br since retained P contents are too low to plot in the same scale as that for Br contents. As is seen in Fig. 3-31, ΔLOI rises very steeply in a very low and narrow range of P content without converging when the ratio of Br content is higher, which is unlike what is shown in Fig. 3-30. It is also shown that, the higher the ratio of Br, the higher the ΔLOI values at the same P content. Moreover, attention may be focused on the fact that when Br content is approximately 10%, an extremely low ratios of P to Br, e.g., 1/100, corresponding to a slight amount, i.e., 0.1% or less, clearly gave a contribution to the synergistic effect in the presence of a certain amount of Br as seen here, and ΔLOI as high as nearly 9% is obtainable.

Whereas, when Br content was less than 5%, even 10 times of P content i.e., 1% gave less Δ LOI values, though a synergistic effect is shown also in this case.

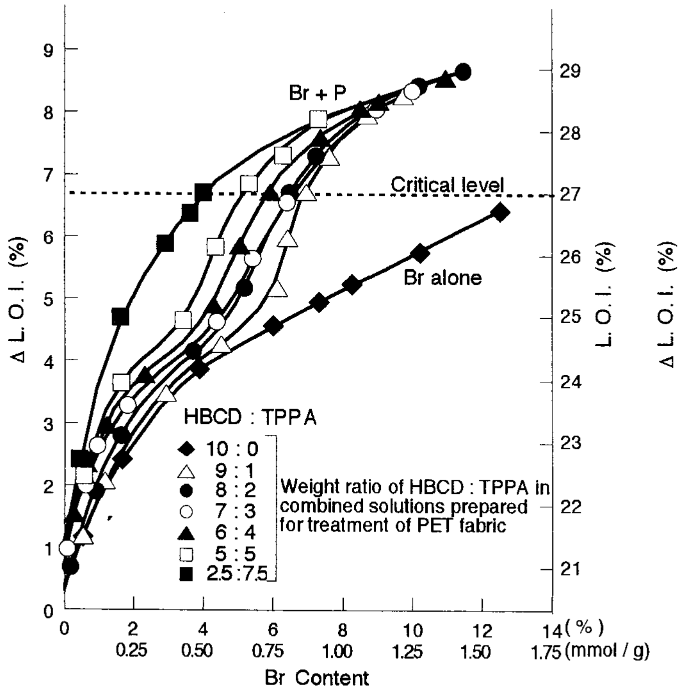


Fig. 3-30 Relationship of LOI and ΔLOI values to Br contents in PET fabric.

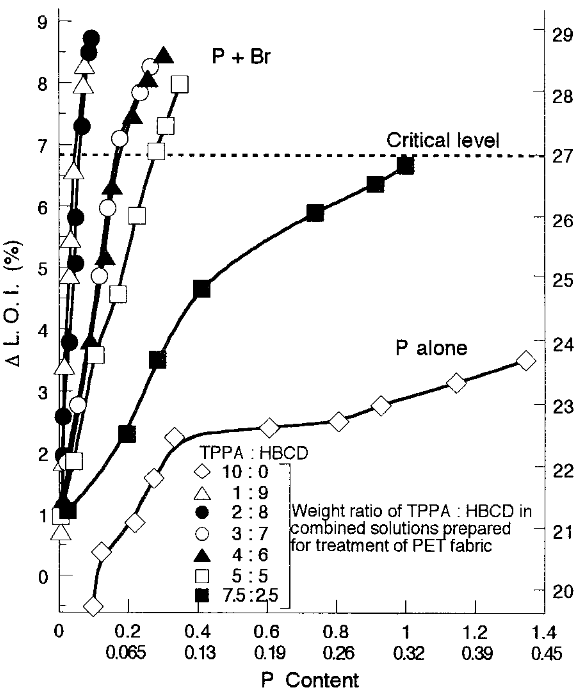


Fig. 3-31 Relationship of LOI and ΔLOI values to P contents in PET fabric.

(e) Evaluation for sufficient or insufficient flame retardance from the practical standpoint (on the basis of the critical level for the flame retardance)

Now, it is worth considering from another point of view. When the flame retardance of fabrics is evaluated to see whether they have sufficient flame retardance or not from the practical standpoint, LOI 27% is regarded as the critical level comparing with char length as well as with char area obtained from alternative test methods. Taking this fact and the results shown in Fig. 3-30 and 3-31 into consideration, it can be concluded that neither Br nor P alone can give sufficient flame retardance at practically available contents, but in combination of Br and P, participation of only 0.05% of P gives sufficient flame retardance with LOI values beyond the critical level 27% if Br content is above 7%, whereas a decrease in Br content to 6-5-4.5%, the minimum amount of P necessary to maintain LOI values above 27% must increase up to 0.17-0.4-0.7%, and Br content as low as 4% requires 1.0% of P content to acquire the sufficient flame retardance for clearing the level of 27%.

Fig. 3-32 gives a curve of Br contents vs P contents showing approximate amounts of Br and P for combinations of both by which sufficient flame retardances are given.

It can be concluded from the above findings that although the effect of P is higher than that of Br in a low content range, the flame retardance of PET fabric is mainly dominated by Br because of small ratio of P retention, but even P/Br = 1/100 can contribute to the synergistic effect to sustain the sufficient flame retardance when Br content is 6% or more.

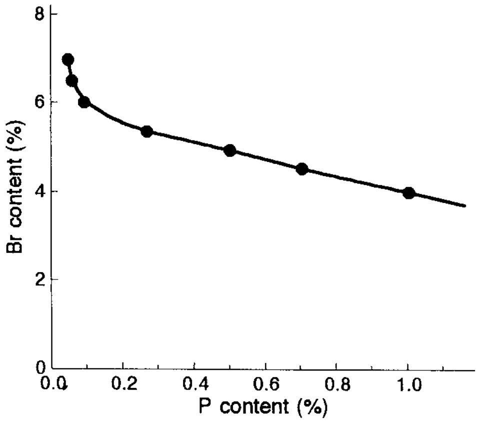


Fig. 3-32 Mutual amounts of Br and P contained in PET fabric which give the critical LOI value, 27%.

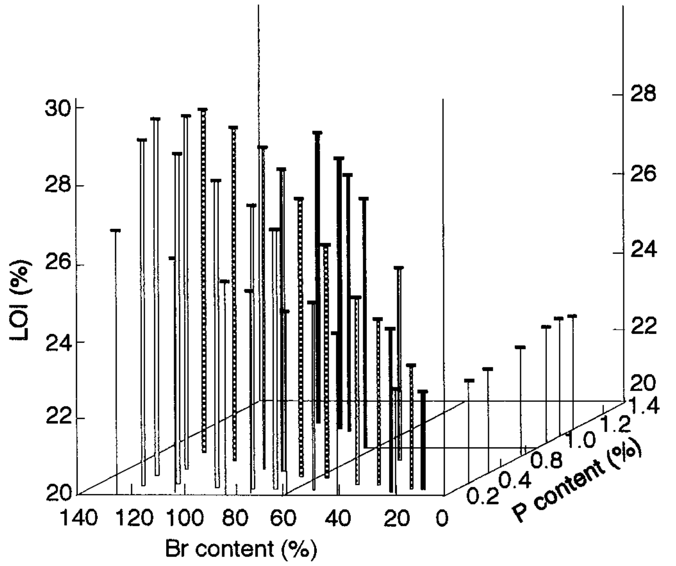


Fig. 3-33 Synergistic effect of Br and P illustrated by a three dimensional diagram.

(f) Mutual relationship of LOI to Br and P contents by three dimensional graphs

A further attempt was made to see a mutual relationship among ΔLOI, Br and P contents with an aid of three dimensional graph as shown in Fig. 3-33.

X axis shows Br content, Y axis is P content the scale of which is multiplied by 10 for the same reason as explained for Fig. 3-31. When treated with Br alone, ΔLOI values enhance with increase in Br content on the zero level of P content, and they further increase by participation of little amounts, for instance, 0.1-0.2% of P showing the synergistic effect.

Moreover, we can see a tendency that ΔLOI values become higher as both Br and P contents increase. But, when Br content is less than 5%, ΔLOI values are lower especially in the absence of Br that is on Y axis, even with much higher P content. However there is also a tendency that ΔLOI value rises with increase in P content.

Thus, this graph clearly illustrates a contribution of Br and P to the improvement of flame retardance simultaneously, clearly showing a synergistic effect, which enables us to comprehend from an overall standpoint.

(g) Effects of Br, P and Br + P on flammability of PET fabric observed with build-in by melt spinning

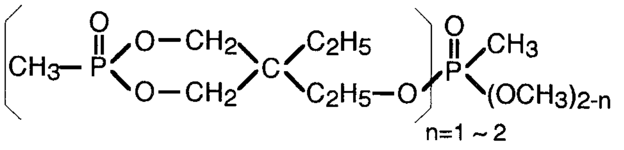
The study was further extended to investigate how Br and P influence the flammability of PET when built into PET polymer at melt spinning in comparison with the result obtained from the PET fabric chemically treated with Br and P compounds.

DBPB was used in this case because other Br compounds decompose at high temperatures for melt spinning, and a red phosphorus compound was selected as a P source since red phosphorus is relatively nontoxic and not spontaneously flammable unlike white phosphorous and therefore has been used for man-made fibers[35].

Fig. 3-34 shows relationships of ΔLOI values to Br and P contents. The samples spun with DBPB which contain only Br show a gradual rise of ΔLOI values with increase in Br contents, showing a leveling off at around 4%.

When P was introduced by spinning with a red phosphorus compound, AMGARD CRP®, the result showed little effect of P on Br-containing spun PET as shown in the figure, which will probably be attributed to that red phosphorus turns to phosphorus oxides when heated and burns up before they become effective.

On the other hand, when the same Br-containing spun PET samples were chemically treated with another P compound, oligomeric cyclic phosphonate (AMGARD CU®) the formula of which is shown below, a remarkable increase in LOI values was observed as shown in Fig. 3-34.



n=1 50%
(more volatile)
n=2 50%

Oligomeric Cyclic Phosphonate

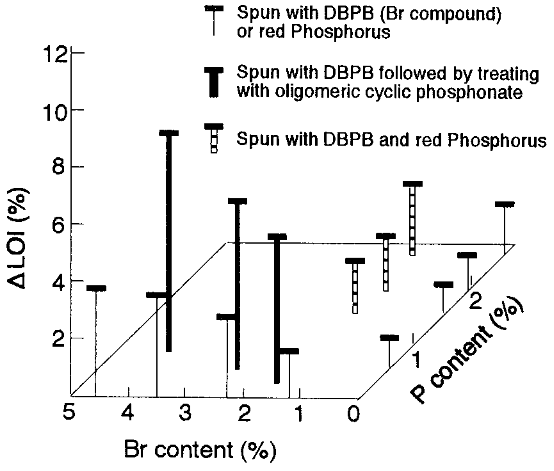


Fig. 3-34 Three dimensional illustration to show difference beween effects of organic P and inorganic red P on the flame retardance of PET fabric finished by melt spinning.

A similar result was also found for P content on Y axis, i.e., when Br and P were both incorporated by melt spinning, ΔLOI values did not show much difference from the values for P alone, but when the chemical treatment was applied with AMGARD CU® after the melt spinning with DBPB, much larger enhancement of ΔLOI was observed.

Such results led us to deduce that the synergistic effect of Br and P on PET fabric to be exhibited by melt spinning requires any Br or P-containing compounds stable enough even at high temperatures for melt spinning, but none of such kind of P-containing compound suitable for melt spinning was available for the present study.

(h) Effects of Br, P and combination of both on flame retardances (LOI values) at high temperature

LOI values define the minimum level at which gas phase oxidation must occur in order that combustible products be continuously produced by substrate decomposition.

Therefore, LOI values are generally affected by the external heat source. As the environmental temperature rises, the transfer of heat from the gaseous phase to the fabric substrate becomes more efficient, accordingly the heat which must be produced in the gaseous phase to reach the decomposition temperature of the substrate is reduced, and consequently a lower oxygen demand is required for combustion, which is reflects by decreased LOI values.

Therefore, it was considered to be indispensable to observe how the effects of Br, P and the synergistic effect between them influence the reduction of LOI values at high temperatures.

Two kinds of PET fabrics treated under the different conditions were used for this experiment to make sure of the reproducibility.

Fig. 3-35-A shows LOI values at room temperature (≒20°C), 100°C and 200°C. As shown in the figure, the LOI values of the untreated samples were lowered at 100°C and even further at 200°C. But, every treated samples showed no reduction of LOI values at 100°C, which is different from the results reported in references. But, such result obtained this time may allow us to consider that the fabrics treated under the conditions used for the present study possess more resistance against the combustion at elevated temperatures, since the result has been confirmed by the fact that the two different kinds of samples showed the identical behavior.

To further confirm the effect of Br and P on the flame retardance of PET fabric at high temperature, an attempt has been made to consider the result from alternative angles by using ΔLOI values. Fig. 3-35-B shows ΔLOI between each LOI values observed at room temperature and that obtained at 100°C and 200°C, which indicates the effect of temperature more clearly and in more details. It is obviously seen that the treated samples all show no difference at 100°C, and -ΔLOI values of the treated samples of the both fabrics No.1 and 2 are all less than those of the untreated fabrics at 200°C. Especially, it should be noted that -ΔLOI values are largest in the case of the untreated fabrics followed by those of the samples treated with P compound TPPA alone. The samples treated with both Br and P compounds which have the synergistic effect show the least reduction in both cases, and samples treated with Br compound HBCD alone (■) fall in between -ΔLOI values for P alone (▲) and those for Br and P mixture (◆). Both fabrics No.1 and No.2 show the same tendency also in this case.

Fig. 3-35-C illustrates ΔLOI values from another points of view, i.e., difference between LOI values of the untreated samples and those of the treated samples at room temperature, 100°C and 200°C respectively. Here, we can see that ΔLOI values increase at elevated temperature in each case especially at 100°C, but it is most important to pay attention to the fact that the samples treated with a mixture of Br and P compounds show the largest enhancement in both cases, the lowest ΔLOI values are shown by the samples treated with P compound alone and the fabrics treated with Br compound alone show intermediate values.

Thus, it has been clarified that the synergistic effect is obviously reflected also in the flame retardance also at high environmental temperature.

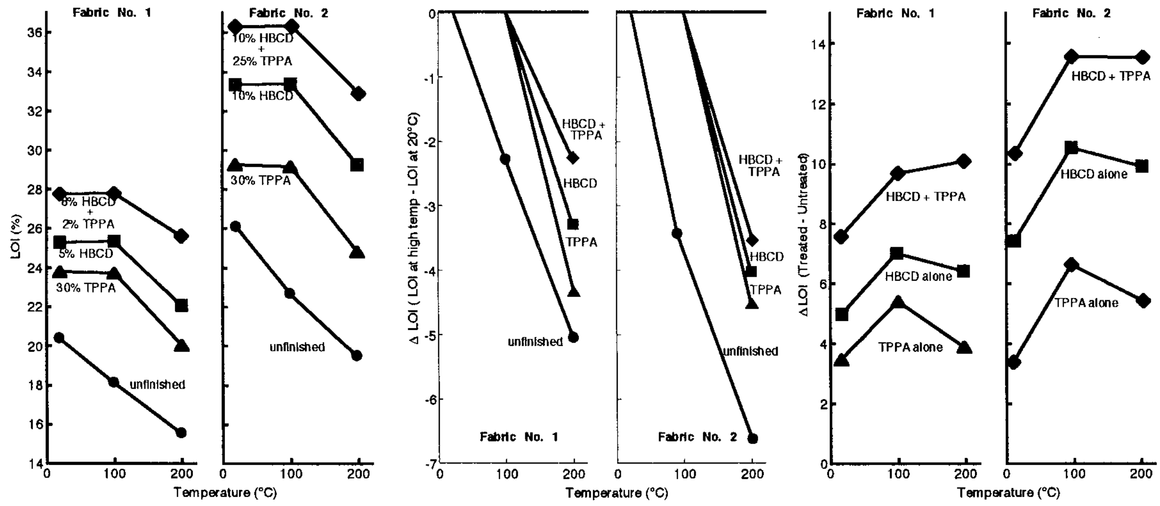


Fig. 3-35 Effects of Br and P alone and synergism of both elements on flame retardancy of PET fabric at high environmental temperatures.

3) Conclusion

Neither Br nor P alone gave any sufficient flame retardance, but combination of a slight amount of P, even less than 0.1%, with Br showed sufficient flame retardance when Br content was

6.5% or higher. Lower Br contents required higher P contents, but considerable improvement of flame retardance was observed with only a slight amount of P if Br content was kept at a certain level. Such phenomena clearly evidenced the synergistic effect of Br and P.

The synergistic effect of Br and P was also reflected in the flame retardance at higher environmental temperatures such as a simulated fire spot.

Such possibility that addition of a slight amount of P enables us to remarkably reduce the amount of Br required for the flame retardation of PET fabric can be an useful information for manufacturing of flame retardant synthetic polymers for which only Br has been used so far.

3-2-2 , Properties of Flame Retardant PET Fabric Finished with Bromime and Phosphorus Compounds Observed from Viewpoint of Textile End-Uses

Another project to deal with properties and performances for the textile end-uses was still left over though they are extremely important from the practical standpoint. Moreover, only triphenyl phosphate (TPPA) was used as a phosphorus source in the previous studies, but this time , diphenyl methyl phosphate (DPMP) and diphenyl ethyl phosphate (DPEP) were synthesized in this study to observe the effects of substituents comparing methyl and ethyl groups with phenyl group.

The investigations in this study covered the flame retardance in connection with the contents of bromine and phosphorus, tensile strength and durabilities against laundry and dry cleaning as well as against the ultraviolet irradiation which are indispensable from the practical standpoint.

1) Experimental

(a) Materials

(1) Fabric

One hudred % PET (commercial product purchased from Teijin) was used (Fabric density: warp 150/in, weft 95/in, Thickness: 150 denir each, Weight: 175 g/m^2).

(2) Reagents for synthesis of phenyl phosphates : Phenol, trichlorophosphates, methanol and ethanol were used for the preparation of diphenyl methyl phosphate (DPMP) and diphenyl ethyl phosphate (DPEP).

(3) Finishing agents : DPMP and DPEP mentioned above and TPPA were used as P sources and HBCD as a Br source.

(4) Reagents for analyses : Sodium chloride, potassium chromate silver nitrate, nitric acid, ammonium thiocyanate and iron alum were used for the analysis of Br, and perchloric acid, nitric acid, ammonium molybdate were used for P analysis.

(b) Methods

(1) Synthesis of DPMP and DPEP : Diphenylchlorophosphate was first prepared by a reaction of one mole of trichlorophosphate and two moles of phenol followed by substituting by addition of methanol or ethanol as shown in Fig.3-36. Thus, diphenyl methyl phosphate was obtained from methanol and diphenyl ethyl phosphate from ethanol.

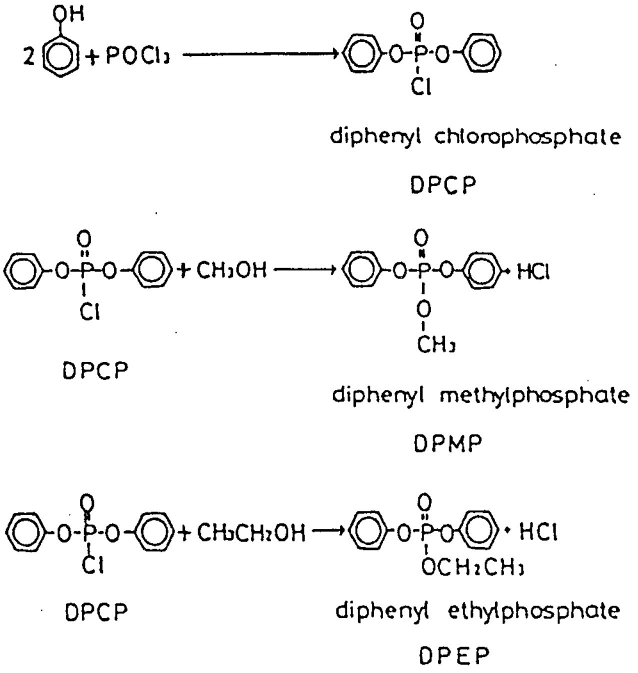


Fig. 3-36 Illustration for synthesis of diphenyl methyl phosphate and diphenyl ethyl phosphate.

(2) The flame retardant finish was carried out in the manner the same as that described in the previous study except that DPMP and DPEP were used as the additional phosphorus sources and the concentrations of these phosphates were adjusted so that the amount of P in the treating baths was the same as that of TPPA.

(3) The flame retardance was evaluated by LOI values obtained by the oxygen index burning test regulated by JIS K 7201-1976 using a burning tester Type ON 1, Suga Shikenki Co. Ltd.

(4) Tensile strength was measured according to JIS L 1096-1979.

(5) The washing durability was evaluated from LOI values and tensile strength determined before and after 25 cycle laundry and dry cleaning.

The laundry test was carried out according to the standard laundering method for washing durability test regulated by Fire Defense Agency Notification No.11. The process of dry cleaning was based on JIS L 0806-1974 using perchloroethylene charged with 0.5% sodium diethyl hexyl sulfosuccinate, 0.5% polyoxyethylene nonyl phenyl ether and 0.1% water.

(6) The light resistance was evaluated by observing LOI value and tensile strength of each sample before and after 24 and 48 hour exposure to carbon arc ultraviolet ray using Ultraviolet Regular Life Fade Meter, Type FA 3 (Suga Shikenki Co. Ltd.)

(7) Br content in the fabric was determined by the combustion of the sample at high pressure of oxygen using Parr 1108 Oxygen Combustion Bomb followed by Vorhard's reverse titration method after collecting Br^- component by rinsing the container with distilled water. In this case the known amounts of HBCD was also analyzed in the same manner to obtain a calibration curve for the determination of the yield of Br^- ion from HBCD since a portion of Br^- to be formed after combustion may be oxidized and converted to Br molecule which is not detectable by Vorhard's method.

(8) P content in each sample was analyzed by the phosphorus-molybdate method modified by Nakanishi et al[4].

2) Results and discussion

(a) Comparison of effects of TPPA, DPMP and DPEP on the flame retardance (LOI values) and relationship between flame retardance and Br and P contents

LOI values of the treated samples are all higher than that of the untreated sample as shown in Fig.3-37-1. Comparing LOI values of the samples treated with HBCD and three phenyl phosphates all alone, HBCD showed slightly higher level, and little difference is observed among those treated with the phosphorus compounds each alone though DPEP showed a slightly lower value. On the other hand, every sample containing both Br and P showed a remarkable rise, especially, the sample treated with a mixture of 10% of HBCD and 2.5% of TPPA (Mixed ratio = 4:1) exhibited the most marked improvement of the flame retardance showing the synergistic effect of Br and P as described in the previous sections. But, the combination of HBCD and DPEP did not give any effect showing the same level as that of TPPA or DPMP alone, while DPMP showed an intermediate effect. Comparing the performances of the above three phenyl phosphates, TPPA exhibited the highest synergistic effect in combination with HBCD.

The differences in LOI values observed between the unfinished sample and each finished sample as well as between each finished sample are confirmed to be significant with 1% level as the result of the analysis of variance.

On the other hand, the contents of Br and P in the fabric are shown in Fig.3-37-2 in comparison with LOI vales. The sample treated with 10% of HBCD alone gave 75 mg/g (7.5%) of Br. whereas those treated with phosphorus compounds are about 10-12.5 mg though the concentration of phosphorus compounds are much higher than that of HBCD. This is probably due to the difference in the affinity of Br and P components of PET molecule as well as due to the difference in the ratio of Br in HBCD and that of P in the three phenyl phosphates.

In the samples treated with mixtures of Br and P compounds, contents of Br did not show much difference from the level of the sample treated with 10% of HBCD alone while P showed much decrease in content around 0.2% because of the much lower concentrations of P in the treating baths in this case.

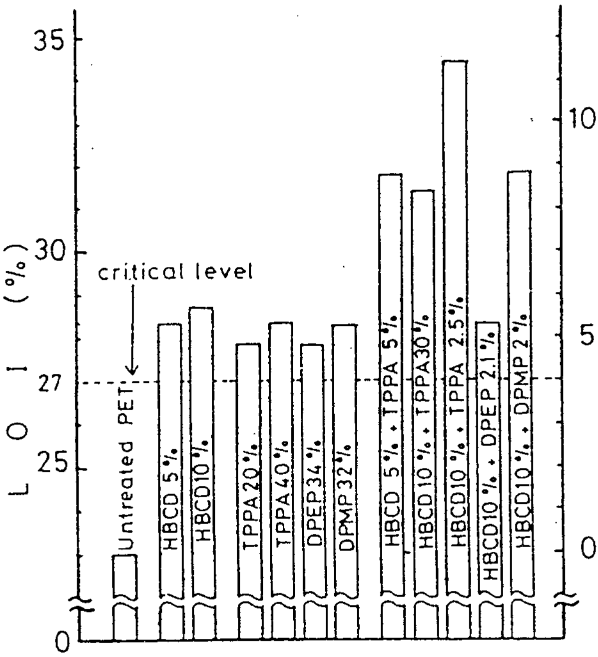


Fig. 3-37-1 LOI values and ΔLOI values of polyester fabric treated with Br and P compounds.

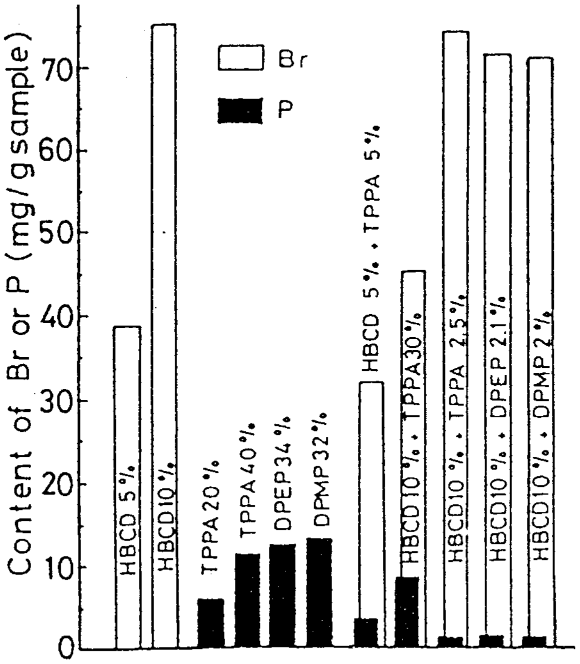


Fig. 3-37-2 Contents of Br and P in polyester fabric treated with Br and P compounds.

Comparing LOI values and contents of Br and P detected in the fabric, the samples containing Br and P each alone showed little difference in LOI values though the content of P is about 1/6 that of Br. Moreover, LOI values of the samples treated with mixtures of HBCD and each of the phosphorus compounds are markedly different, although the contents of Br and P in these three samples are very similar as shown in the figure. Such phenomenon suggests that the performances of these three phosphorus compounds for the flame retardation are different owing to the difference in the substituents in the phenyl phosphate molecules.

(b) Tensile strength of flame retardant PET fabric

The effect of the flame retardant finish on the tensile strength of PET fabric was observed since it is an important factor for the textile end-uses. The results is that the tensile strength of every treated sample exhibited some improvement compared with that of the untreated PET fabric, especially the samples containing both Br and P which have the high flame retardance by the synergistic effect of Br and P showed higher tensile strength. A possible reason for such phenomenon was considered to be due to an increase in density of the fabric, which was denied by its determination since any significant difference was not observed between the densities of unfinished and finished samples. TPPA showed highest tensile strength in combination with HBCD among three phenyl phosphates (see Fig.3-38)

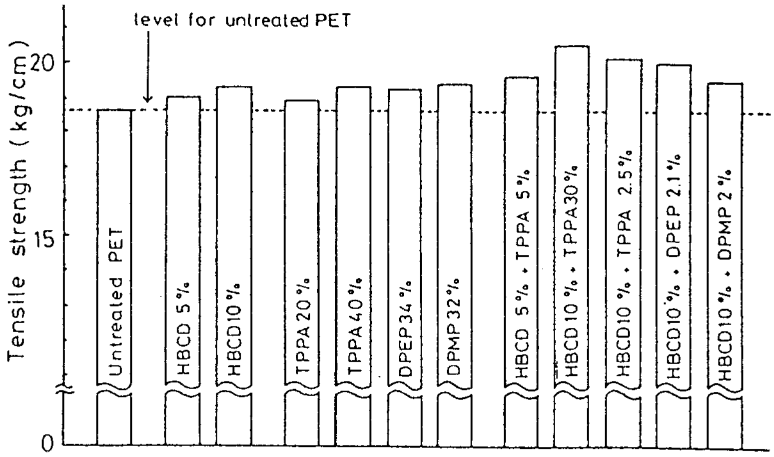


Fig. 3-38 Tensile strength of polyester fabric untreated and treated with Br and P compounds.

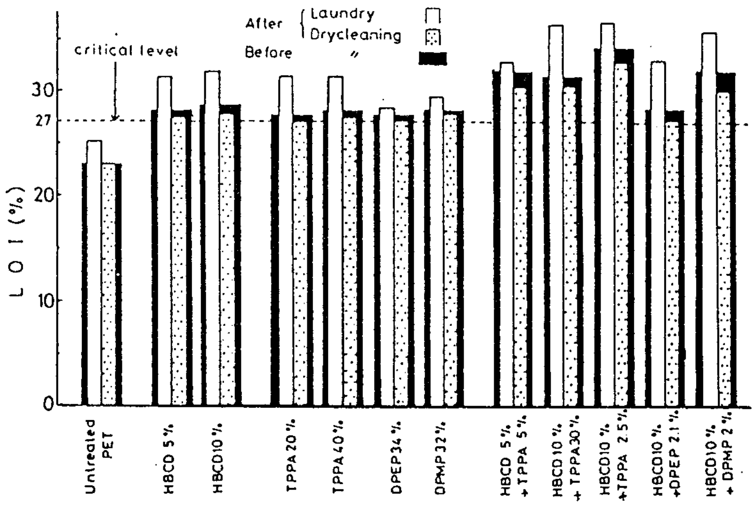


Fig. 3-39 Change in LOI values after laundry and drycleaning observed for evaluation of durability.

(c) Durability against laundry and dry cleaning

It is indispensable to clarify how much the flame retardance and tensile strength will be resistant to washing as one of the evaluations of flame retardant finished fabrics from the practical standpoint.

As shown in Fig.3-39, there found a tendency that LOI values showed some increase after 25 cycle laundry. It is supposed that such phenomenon is probably attributed to increase in water content of the fabric after repeated laundry. Therefore water contents of the selected samples were determined. Fig.3-40-1 illustrates water contents of the representative samples in connection with LOI values. Before washing, the samples treated with TPPA alone showed much higher water content (1.2%) than that of the untreated sample (0.15%) while the water contents of those treated with HBCD alone were very close to that of the untreated sample. This probably means that phosphorus compounds give high water content as observed with inorganic phosphorus compounds. It was obviously shown in Fig.3-40-1 that water contents increased after 25 cycle laundry with improvement of the flame retardance shown by rise of LOI values. In order to confirm this phenomenon, the investigation of water content was extended in more details measuring water contents also after 5, 10 and 15 cycle intervals. The result showed a gradual increase in water content with repetition of laundry, which will evidence the above mentioned results (Fig.3-40-2). From such results, it is probable that even slight increase in water content may contribute to the improvement of the flame retardance when the fabric itself is hydrophobic.

Contrary to the results observed after laundry, some lowering was shown after dry cleaning supposedly because of solvent soluble property of the organic flame retardants used for this study. However, every sample kept a level of LOI value higher than the critical level, 27% showing the sufficient flame retardance even after dry cleaning.

The analysis of variance confirmed also in this case that the significant differences were observed for LOI values between before and after the laundry.

On the other hand, the tensile strength of the all samples showed same decrease after laundry and dry cleaning, but every sample kept a level higher than that of the untreated sample, which means that neither laundry nor dry cleaning will affect the tensile strength of the flame retardant PET fabric as far as the practical use is concerned (Fig.3-41).

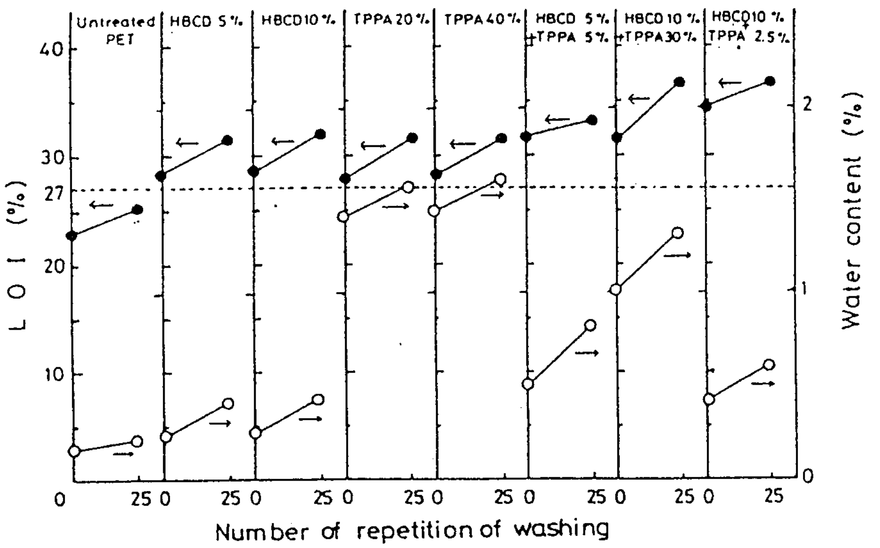


Fig. 3-40-1 Comparison of change in LOI values and water contents observed after 25 cycle laundry.

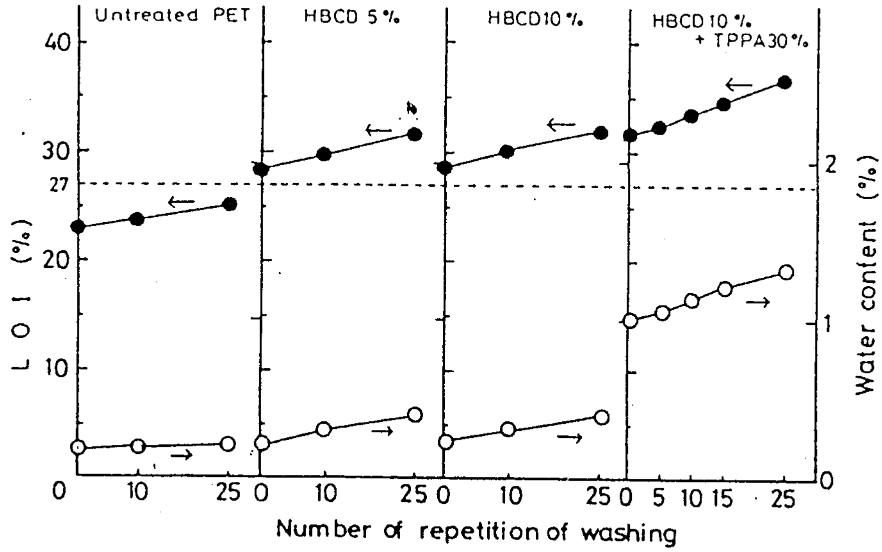


Fig. 3-40-2 Comparison of change in LOI values and water contents observed after 5, 10, and 25 cycle laundry.

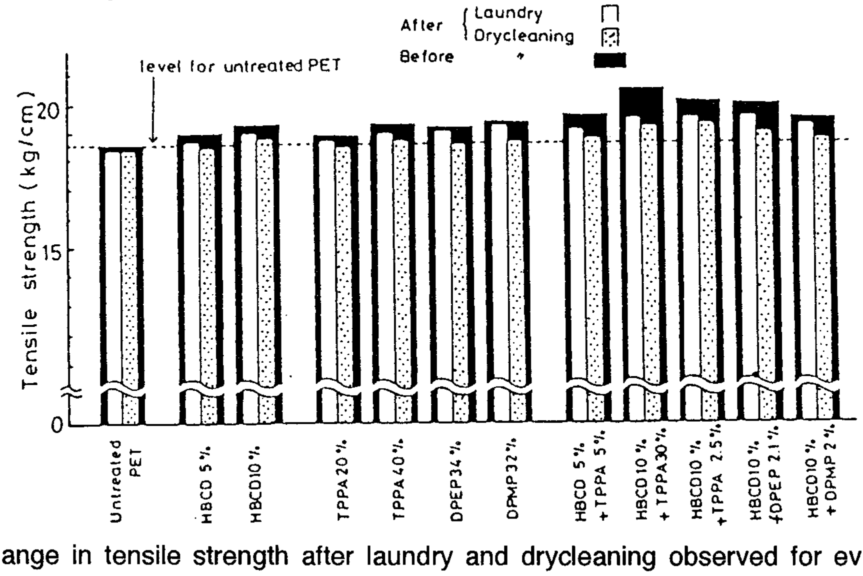


Fig. 3-41 Change in tensile strength after laundry and drycleaning observed for evaluation of durability.

(d) Effects of Br or P and both on reduction of flame retardance and tensile strength of PET

As another evaluation for the durability, the light resistance was evaluated from change in LOI value as well as in tensile strength to know how much resistance they will show against the ultraviolet irradiation. Fig. 3-42 shows LOI values and tensile strength of each sample before and after 24 and 48 hour irradiation. The samples treated with HBCD alone showed no change in LOI value even after 48 hour irradiation, whereas those treated with phosphorus compound alone showed some or considerable decrease. Addition of HBCD to TPPA compensates the decrease given by TPPA showing that the effect of HBCD is stronger than that of TPPA alone.

On the other hand, a contrary effect of irradiation was observed for the tensile strength. HBCD gave considerable reduction whereas TPPA showed much less decrease approximately the same as that given by untreated sample.

The combined effect of HBCD and TPPA was that addition of TPPA to HBCD largely decreased the reduction of tensile strength of fabric treated with HBCD alone observed after ultraviolet irradiation as shown in Fig. 3-42. This suggests another merit of addition of P to Br, in addition to acceleration of flame retardation, for inhibition of the photodegradation shown by Br treated-synthetic polymer products which would be caused by ultraviolet irradiation.

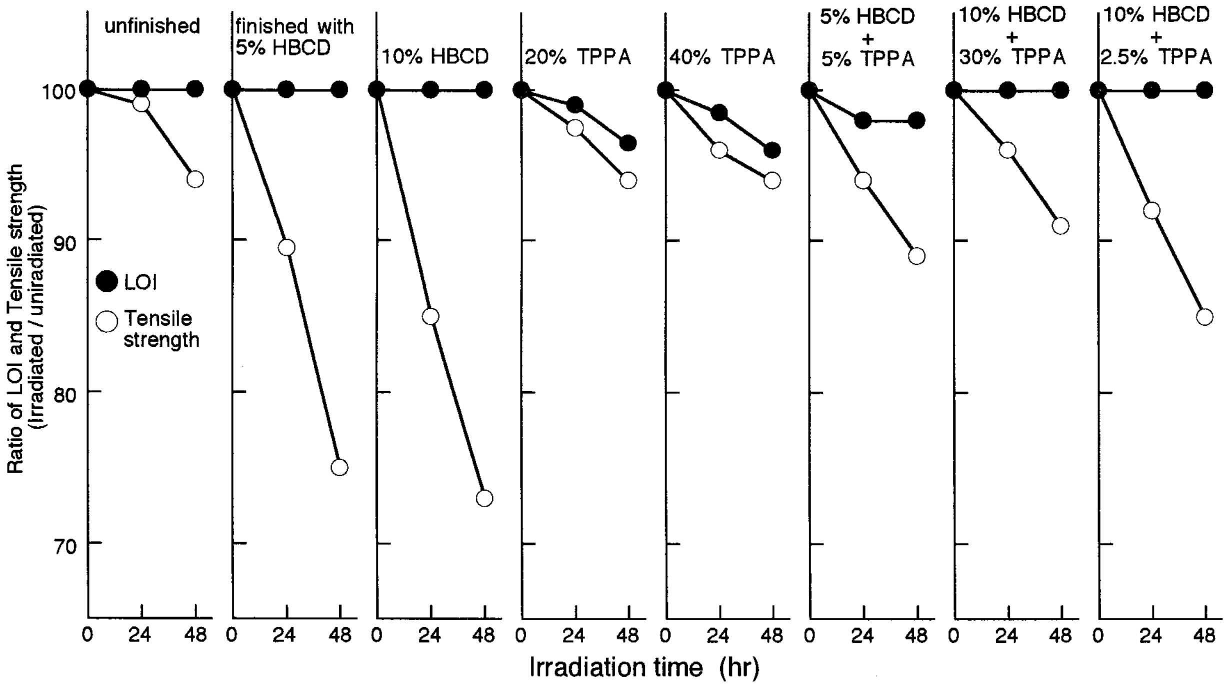


Fig. 3-42 Reduction ratio of LOI and tensile strength observed after ultraviolet irradiation.

3) Conclusion

(a) The tensile strength of every flame retardant finished sample showed higher tensile strength. Such result revealed an additional advantage given by the flame retardant finish attempted by this study.

(b) Durabilities against laundry, dry cleaning and ultraviolet irradiation were as follows:

Every sample showed an improvement of LOI value after 25 cycle laundry. This was supposed to be attributed to increase in water content, which was confirmed by the determination of water content before and after the repetition of laundry. On the other hand, dry cleaning gave some decrease in LOI value in every case, but every value was higher than the critical value.

Tensile strength showed some lowering after laundry as well as after dry cleaning, but kept the level higher than the untreated level.

The ultraviolet irradiation gave no effect on LOI vales of the samples treated with HBCD alone, but some decrease in LOI values was shown by those treated with the phosphorus compounds. On the contrary, HBCD gave considerable reduction of tensile strength much larger than that observed with the phenyl phosphates after ultraviolet irradiation. However, addition of TPPA to HBCD significantly compensate the reduction of tensile strength observed with HBCD treatment caused by the ultraviolet irradiation, which suggests a merit of addition of P compounds to Br compounds for flame retardation.

(c) Comparing effects of TPPA, DPEP and DPMP on the properties of PET fabric, TPPA gave the most favorable results in every case.

3-3 Flame Retardant Finishes for Cotton/Polyester Blended Fabrics

3-3-1 Systematic Investigation on Finishing Conditions and Evaluation of Finished Fabrics

Studies on flame retardant finish of cotton/PET blended fabrics have been retarded and the application of flame retardant finish to this kind of blended fabrics has not been successfully achieved so far, particularly more difficulty has been found in PET rich fabrics although such fabrics have been universally used, which is attributed to the combination of two different kinds of fibers having entirely opposite properties, hydrophilic and hydrophobic. P. Bajaj[36] et al. have attempted considerable investigations on flame retardant finishes for C/P blended fabrics by using diammonium hydrogen phosphate and various kinds of methlylol resins and obtained useful findings, but have not reached to get sufficient flame retardance from the practical standpoint.

Attention was paid to this point in this study and investigations were performed PET rich cotton 35%/PET 65% blended fabric mainly from the fundamental standpoint taking the finishing conditions applied to cellulose as well as to PET studied by Nakanishi et al. into consideration described in 3-2 and 3-3 above.

1) Experimental

(a) Materials

(1) Fabric material

Cotton 35%/PET 65% blended fabric of 117 g/m^2 , 0.2 mm in thickness with fabric sett 145/inch in ends and 73/inch in picks was used.

(2) Flame retardants and additives are shown in Fig.3-43, in which net concentrations of Nonnen A-60EM, Nonnen C-617 and Antimony pentoxide are 40%, 80% and 50% respectively and phosphorus contents of trimethylol phosphate (TMP), trioctyl phosphate (TOP) and AR-200 were 21%, 7.1% and 12.5% respectively.

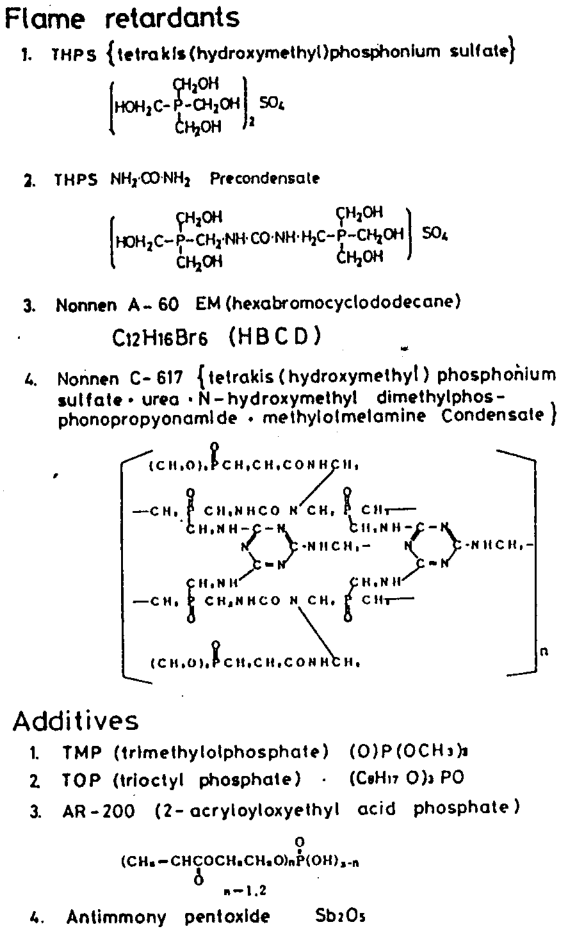


Fig. 3-43 Flame retardants and additives used for the present study.

Table 3-7 List of formulations of treating baths consisting of flame retardants and aditives.

FLAME RETARDANT	Conc	NO.			CURING CONDITION
A:THPS	32%	A-1	+ M_3 TEA	12.0% 5.0%	3 min at 160°C
	32%	A-2	(A-1)+Urea	13.0%	
	32%	A-3	(A-2)+H_3PO_4	2.0%	
	32%	A-4	(A-3)+Non.Surf.	0.05%	
	40%	A-5	The same as (A-2)		
	32%	A-6	"		5 min at 160°C
B:A-60EM	6%	B-1			2 min at 150°C
	6%	B-2	+ PROBAN finish		
	20%	B-3	"		
	30%	B-4	"		
	20%	B-5	(B-3)+M_3	8.0%	
	6%	B-6	(B-2)+TMP	10.0%	
	20%	B-7	(B-3)+TMP	10.0%	
	6%	B-8	(B-2)+Sb_2O_5	6.0%	
	6%	B-9	(B-2)+Sb_2O_5	12.0%	
	20%	B-10	(B-3)+Sb_2O_5	20.0%	
	20%	B-11	(B-10)+TMP	4.0%	
	20%	B-12	(B-10)+M_3	8.0%	
C:C-617	40%	C - 1			3 min at 140°C
	60%	C - 2			
	80%	C - 3			
	40%	C - 4	(C-1)+Sb_2O_5	6.5%	
	40%	C - 5	(C-1)+Sb_2O_5	13.0%	
	40%	C - 6	(C-1)+TMP	10.0%	
	40%	C - 7	(C-1)+TMP	20.0%	
	60%	C - 8	(C-2)+TMP	10.0%	
	60%	C - 9	(C-2)+AR-200	10.0%	
	40%	C-10	(C-1)+Ethanol	25.0%	
	40%	C-11	(C-10)+TOP	10.0%	
	40%	G-12	(C-1)+M_3	12.0%	
	60%	C-13	(C-2)+M_3	12.0%	

M_3 : trimethylolmelamine, TEA : triethanolamine, TMP : trimethylphosphate, Non. Surf. : Nonionic surfactant

(b) methods

(1) THPS heat cure

THPS monomer was used with additives to prepare 6 kinds of finishing solutions according to the condition A listed in Table 3-7. The above mentioned fabric was impregnated with each of these solutions for 10 min, padded, immersed again for 5 min and padded again to 90% pickup, which was cured for 3 min or 5 min at 160°C after drying for 8-10 min at 100-105°C. Each sample was oxidized with 10% of H_2O_2 at 60°C followed by soaping for 10 min at the same temperature with 0.2% of Na_2CO_3 (bath ratio:30).

(2) PROBAN finish

The same fabric was finished by the method as described in 3-1-2 by using THPS-urea precondensate with ammonia cure.

(3) Finish with Nonnen A-60EM

A basic finishing condition B-1 in Table 3-7 was prepared according to the concentration specified by the maker of this flame retardant (Marubishi Oil Chemical Ind. Co.). On the basis of this condition, 11 kinds of finishing solutions (B-2 ~ B-12) were prepared as shown in the table, in which PROBAN finished fabric was immersed for 10 min, padded to 80% pickup after 2 dip - 2 nip process and heated for 3 min at 150°C after preliminarily drying for 3 min at 105°C.

(4) Finish with Nonnen C-617

The fabric was impregnated with each of 13 kinds of treating solutions (C-1 ~ C-13) listed in the same table for 10 min followed by 5 min, padded to 80% final pick up through 2 dip - 2 nip system and cured at 140°C for 3 min after preliminary drying at 120°C for 2 min.

All samples finished as above were treated with 0.5% sodium carbonate for 3 min at 60-70°C (bath racio:30) for soaping.

The concentrations shown in the table are not V/V but actual concentrations prepared by each maker. Bath ratio of each treating bath was 30.

(5) Evaluation of durability (laundering)

(6) Evaluation of flame retardance

(7) Determination of tensile strength and elongation

(8) Determination of P

(9) Determination of N

were all carried out as described above in 3-1.

The measurement was repeated 5-6 times in every case, but tensile strength and elongation were tested with more than 10 stripes of samples, and averaged values are shown in all cases. Deviation are ±0.2-0.7% for LOI, ±0.2-0.5 kg/cm for tensile strength, ±0.5-1.5% for elongation, ±0.5-1.0 mg/g for P and ±0-0.5 mg/g for N.

2) Results and Discussion

(a) Effect of THPS on flame retardance of Cotton/PET blended fabric

THPS heat cure which gave a fairly favorable effective flame retardance to cotton fabric as mentioned previously was applied also to cotton/PET blended fabric this time. The results are shown in Fig.3-44.

(1) Effects of concentration and additives

As concentration of THPS, 32% regarded as most favorable for cotton fabric as the results of the previous investigation (3-1-3) was compared with the result of an increased concentration 40%, but little improvement was observed. So, 32% was thought to be better from less stiffness.

Addition of urea and H_3PO_4 gave marked effect on flame retardance showing LOI values of about 28%, but additional supplement of nonionic surfactant gave little effect though it was added as a penetrant.

(2) Effect of curing time

As shown in Fig.3-44, sample treated by heating for 5 min gave higher LOI value than that heated for 3 min, but coloration and thermal degradation were observed with increase in heating time and 3 min was regarded as a limit.

As conclusion, A-2 was selected as the heat condition since H_3PO_4 was thought to bring about reduction of tensile strength of cotton.

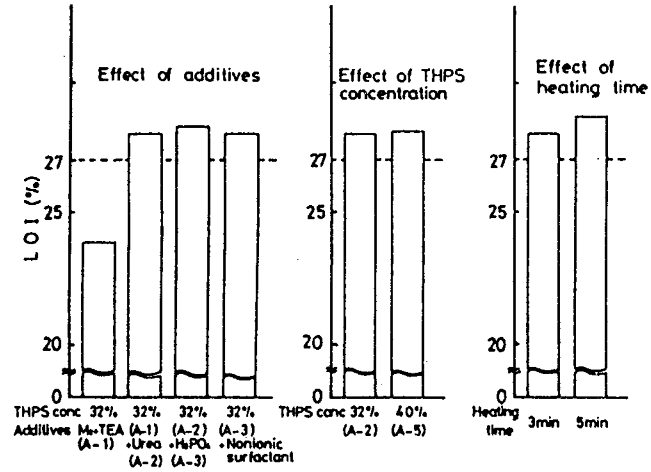


Fig. 3-44 Comparison of flame retardance of a cotton / polyester blended fabric treated with THPS under different conditions.

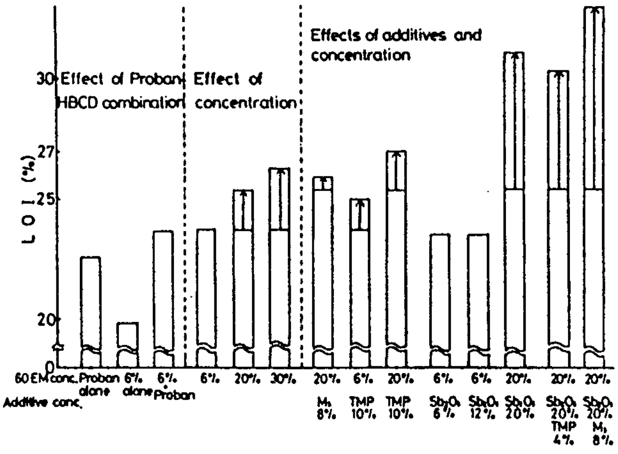


Fig. 3-45 Comparison of flame retardance of a cotton / polyester blended fabric treated with Nonnen A-60EM (HBCD) in combination with Proban finish.

(b) Effects of combination of PROBAN finish and Nonnen A-60RM (HBCD)

Before investigating on the effect of combination of both components, single effect of PROBAN finish effective for cotton and that of Nonnen A-60EM (HBCD) effective for PET were observed separately.

As shown in Fig.3-45, LOI value of sample finished by PROBAN alone was 22.8% showing still flammable. Observation of burning behavior explained that portion of cotton extinguished by itself through converting to char resulting in termination of flaming at initial stage. However, continuous combustion of candle phenomenon was observed with molten PET as a role of wax together with char as a wick. Nonnen A-60EM showed no effect by itself.

On the other hand, combination of both finishes gave higher LOI value compared with the result of each single finish, but yet could not reach the level for flame retardance. Further investigation was carried out by using higher concentrations, 20% and 30%, which considerably increased LOI value but still under the level for sufficient flame retardance.

As to concentration of Nonnen A-60EM, 30% is not practically usable and 20% was thought to be most appropriate concentration from the practical standpoint. Therefore, it was concluded that some additives would be required to acquire sufficient flame retardance also with favorable physical properties for textile end-uses.

(1) Effect of addition of resin

In spite of addition of melamine resin to 20% of flame retardant aiming at the rise of LOI value since addition of resin contributes not only to increase in N but also to a role of cross-linking between cellulose and flame retardant molecules, increase in LOI value was unexpectedly only 0.5%.

(2) Effect of addition of TMP

Since addition of N source was insufficient, addition of TMP was further attempted as a P source. When 10% of TMP was added to 20% of the flame retardant, LOI value reached 27% showing flame retardance, which suggests the synergistic effect of P and Br in the case of TMP. But effect of TMP was thought to be limited by itself.

(3) Effect of addition of Sb_2O_5

It has been known that combination of a halide and Sb_2O_5 gives flame retardance by the synergistic effect of Br and Sb, which has been attributed to that the reaction between a halide and Sb_2O_5 at high temperature produces a volatile antimony halide which acts as an effective active radical scavenger by remaining at the reaction system as a heavy fume. Therefore, addition of Sb_2O_5 was attempted to HBCD, but little effect was observed when Br content was low, e.g., concentration of HBCD was 6%. On the other hand, remarkable increase in LOI value was observed when 20% of Sb_2O_5 was added to 20% of HBCD to make the ratio to be 1:1, which suggested that more than certain amount of add-on would be required to exhibit the synergistic effect of Br and Sb.

(4) Combined effect of Sb_2O_5 and TMP or resin

As a marked effect was given by combination of Sb and Br under the condition of B-10 shown in Table 3-7, further addition of TMP to this combination was attempted, but LOI value showed reduction to some extent, which was thought to be due to the result of inhibition of fixation of Sb by competition between Sb_2O_5 and TMP. On the other hand, combination of Sb_2O_5 (Sb) and resin (N) instead of Sb_2O_5 and TMP (P) brought about a rise of LOI up to 33%, which suggested that N is more effective than P for the combination with Sb. It was concluded from the above results that condition B-12 was regarded as the best for the combination of PROBAN finish for cotton and HBCD for PET.

(c) Effect of finishing with Nonnen C-617

Nonnen C-617 is a condensate produced with 3 components, 2 effective durable flame retardants, THPS and Pyrovatex and 1 resin, e.g. melamine, and has a complicated chemical structure (see Fig.3-43). Cotton fabric was treated with 13 kinds of finishing solutions prepared on the basis of this flame retardant with some additives under the varied conditions.

(1) Effect of concentration

As shown in Fig.3-46, there found no effect with 40% of flame retardant itself and LOI value exceeded 27% with 60% or higher concentration, but only little difference was shown above 60%, which means that effect of single use of this flame retardant is limited and addition of some supplements is required.

(2) Effect if additives

(i) Effect of Sb_2O_5: Since Sb_2O_5 was fairly effective when used with 60EM, effect of addition to C-617 was also attempted, i.e., 6.5% and 13% of C-617 were added to 40% of C-617, but no effect was found by addition of Sb_2O_5 to C-617.

(ii) Effect of TMP and AR-200: Addition of 20% of TMP was effective to some extent though 10% was not so effective. AR-200, another P source showed a similar level of effect. Both of these P sources showed insufficient increase in LOI value with 10% solution which is desirable from touch of fabric.

(iii) Effects of ethanol and TOP: Addition of a polar organic solvent ethanol was also attempted to aid any finishing solutions to have affinity evenly with both hydrophilic cotton and hydrophobic PET, the result of which showed rise LOI value to some extent but further addition of TOP (P source) did not give any effect.

(iv) Effect of melamine resin.

As a N source, 12%, the same as used for THPS heat cure, of melamine resin and 3% of catalyst were added to 40% and 60% of this flame retardant. As seen in the figure, considerable increase in LOI was observed when added to 40% of Nonnen C-617, but not when added to 60% of this flame retardant. In the case of 60% of the flame retardant, LOI value reached 28% by itself without any additional supplement, which required nothing to acquire the flame retardance. This result suggests that since C-617 contains 18 N and 6 P in a molecule, addition of P, only 1/3 N content, is more highly required rather than N when the concentration of flame retardant itself is high enough to obtain sufficient flame retardance.

(d) Effect of alkali treatment

As one of the reasons for the difficulty in successful finishing for C/P blended fabric, difficulty in physical fixation of finishing reagents on the very smooth surface of PET was thought to be not ignored. Therefore, it was expected that it might be possible to improve the fixation of flame retardants on the surface of PET by alkali treatment to make the surface rough.

Sample fabric was immersed in 30% of NaOH at 20°C for varied hours 3,4 and 6 h rinsed with tap water and air dried. The pretreated sample fabric was finished with 40% and 60% of C-617 as mentioned above. As the result of evaluating the flame retardance, sample treated for 3-4 h showed only 0.8% increase, whereas 6 h treatment gave nearly 3% increase showing LOI value exceeding 30% when finished with 60% of C-617. Another effect of alkali treatment requires comparatively long time, e.g. 6 h. This treatment proved an effect of changing the surface of PET for better fixation of finishing reagents as well as of increase in C/P ratio due to decrease in PET component by alkali treatment.

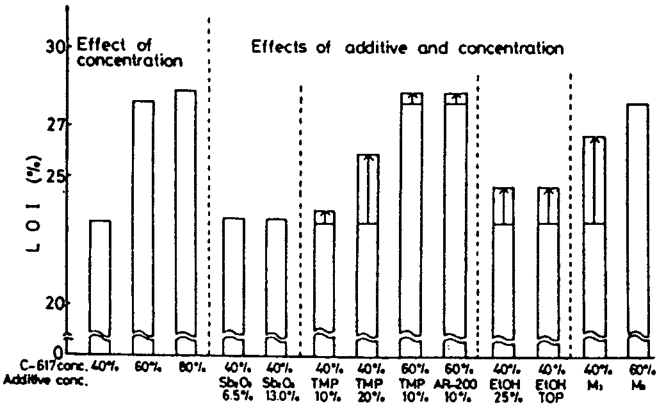
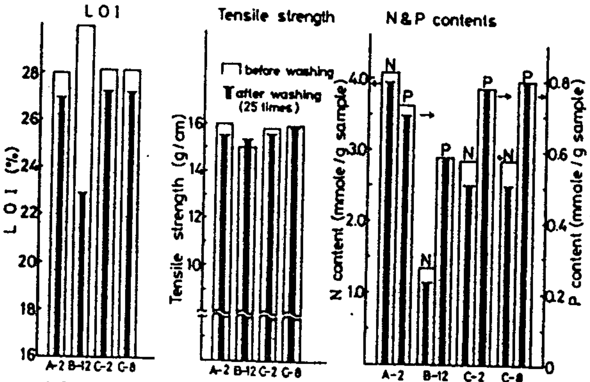


Fig. 3-46 Comparison of flame retardance of a cotton / polyester blended fabric treated with Nonnen C-617 and additivbes.



A-2 : THPS(32%) + Urea + M₃(12%) + TEA(5%), B-12 : A-60EM(20%) + Sb_2O_5(20%) + M₆(8%)
C-2 : C-617(60%) , C-8 : C-617(60%) + TMP(10%)

Fig. 3-47 Durabilities of representative flame retardant finished cotton / polyester blended fabrics observed after 25 repetitions of washing.

(e) Evaluation of durability

The durability was evaluated for representative samples selected from the above mentioned finished samples by determining LOI value, tensile strength and N and P contents before and after 25 repetition of laundering.

As shown in Fig.3-47, LOI value of B-12, the highest before laundry extremely decreased after laundry but others showed only a little reduction maintaining the level of 27% even after 25 time-laundry, which proved that samples finished with THPS and C-617 under the given conditions have durability. Comparison between THPS and C-617 concluded that C-617 would be the best flame retardant because this showed slightly better evaluation numerically from overall standpoint though not clear in the figure. Paying attention to change in N and P contents after laundry, B-12 which showed a large reduction of LOI values after laundry exhibited little change in N and P content. This result clearly supports the fact that the dominant component for the flame retardance of this sample is inorganic Sb_2O_5 mechanically fixed on the surface of the fibers and removed by any mechanical farce such as washing. The reduction of LOI value was not caused by decrease in N or P content which was too low to exhibit the flame retardance from the beginning and the flame retardance was supported by Sb_2O_5.

(f) Relationship between N and P contents in the chemical structures of flame retardants and detected amounts of N and P in finished samples.

In the case of THPS finished samples, a P molecule of THPS containing P alone without N is found with a methylol group of trimethylolmelamine containing 6 N atoms, which means that the atomic ratio of P:N is 1:6. The detected amounts of P and N were 0.7 mmol and 4.1 mmol respectively, which proves that the observed results and theoretical values are highly coincident. On the other hand, C-617 possesses 6 atoms of P and 18 atoms of N in its chemical structure as shown in Fig.3-8, and the determinations of P and N gave 0.8 mmol and 2.5 mmol respectively showing a good agreement with the theoretical molar ratio P:N = 1:3 also in this case. Such results also suggests that at least 2.5 mmol of N and 0.8 mmol of P are required to maintained the flame retardance.

3) Conclusion

Conclusion of PROBAN finish and Nonnen A-60EM gave extremely high LOI value, but the flame retardance entirely disappeared after repeated laundry with removal of Sb_2O_5, which clearly revealed that this is not practically usable because durability can not be expected. On the other hand, THPS and C-617 were recognized to be recommendable also practically showing comparatively favorable durability, i.e., LOI value was maintained at the level of 27% even after 25 repetition of laundering.

It was concluded that C-617 would be most recommendable among the finishing conditions investigated this time since this showed better results, however its LOI value was merely 27% which is the critical level for the flame retardance. Therefore further investigations are highly required for better finishing condition for C/P blended fabrics.

3-3-2 Applicability of Electron Beam Irradiation to Flame Retardant Finish for Cotton/PET Blended Fabrics

Because of the unsatisfactory results of the above investigation, we paid attention to the electron beam irradiation, which has been developed and applied to the surface finish performed by covering the surface with film formed by polymerization and cross-linking reactions of coated substances instantaneously activated by the irradiation. This method is evaluated not only to largely save energy compared with heat cure resulting in cost down but also to enable drastic curtailment of floor area for curing process.

Such irradiation including γ-ray irradiation has been studied on application to 100% cotton[37-41] as well as to 100% PET[42,43], of which that to 100% cotton is expected for the practical use except for a problem of decrease in strength of fabric.

But, studies on application to cotton/PET blended fabrics are still few. Liepin et al.[44] applied the electron beam irradiation to C50/P50 blended fabric and obtained a result that LOI value was kept at 27% level after 25 time laundry, but no investigation was attempted on reduction of strength of fabric which should be an important factor when the applicability of electron beam irradiation is evaluated. Moreover, presuming from the result reported by Bajaj[36] that LOI value showed such reduction as 30.1, 24.6 and 21.9 with increase in the ratio of PET, i.e., C75%/P25%, C52%/P48% and C33%/P67%, LOI value of C35%/P65% estimated from the result obtained by Liepin et al.[44] would be lower than the critical level 27%.

Taking the above facts into consideration, the present study deals with the systematic investigations on establishment of most favorable finishing condition for the application of electron beam irradiation to PET rich C/P blended fabric for which the flame retardation would be most difficult, minimization of reduction of strength and comparison of the results with those observed with the samples finished by other methods described in the previous studies. The present study aims at the applicability of electron beam irradiation to the practical use on the basis of investigations from the fundamental standpoint.

1) Experimental

(a) Materials

(1) Fabric materials

C35%/P65% blended fabric is the same as mentioned in 3-3-1. 100% cotton and 100% PET are the same as those described in 3-1-1 and 3-2-3 respectively.

(2) Flame retardants

The following 4 kinds the chemical structures of which are illustrated in Fig.3-42 were used.

(i) MTS-3GD® Daihachi Chem. Ind. Co.: An organic silicic type neutral liquid compound with specific gravity of 1.180 (20°C). Actual concentration is 84.4%.

(ii) AR-200® (Daihachi Chem. Ind. Co.): A functional P containing monomer, acidic liquid with specific gravity of 1.35-1.37 (20°C).

(iii) THPS® (Nihon Chem. Ind. Co.): Tetrakis (hydroxymethyl) phosphonium sulfate, acidic liquid containing 80% of available concentration.

(iv) Phoscon 76 (Stauffer Co.): A vinyl phosphonate oligomer, acidic liquid with specific gravity of 1.31-1.33. Actual concentration is 100%.

(3) Additives

The following additives were supplied to moderate reduction of strength. Their chemical structures are shown also in Fig.3-48.

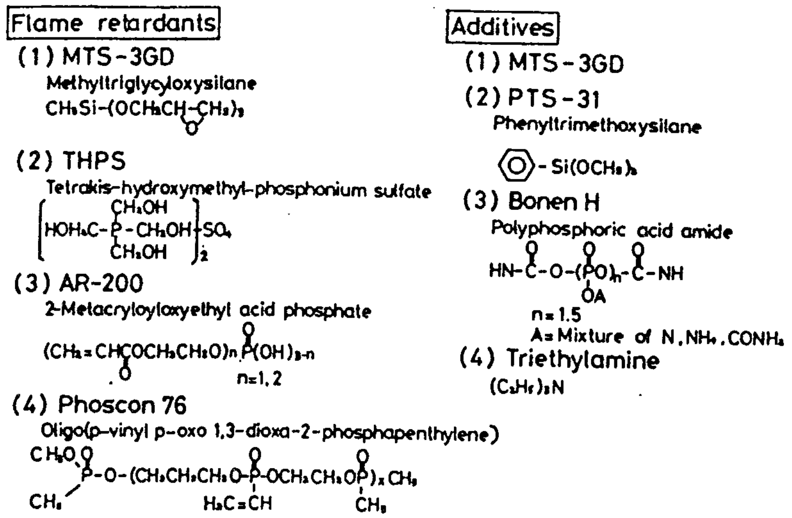


Fig. 3-48 Flame retardants and additives used for this study.

(i) MTS-3GD®: The same substance as mentioned above.

(ii) PTS 31® (Daihachi Chem. Ind. Co.): An organic silicic type compound of alkoxysilane group, neutral liquid with specific gravity of 1.066 (20°C). Actual concentration is 98% of higher.

(iii) Triethylamine (Wako Pure Chem. Co.): An organic base with specific gravity of 0.720-0.730 (20°C) as well as with 99.0% purity.

(iv) Bonnen H® (Ipposha Oil and Fat Ind. Co.): A phosphoric acid-urea condensate, polyphosphate amide, acidic liquid with 47% actual concentration.

(c) Methods

(1) Finish by heat cure

The above mentioned fabrics were immersed in each finishing solution of each concentration shown in Fig.3-49 for 10 min first followed by 5 min - impregnation, padded to 90% pickup through 2 dip - 2 nip process and cured at 150°C for 3 min after drying at 70-75°C.

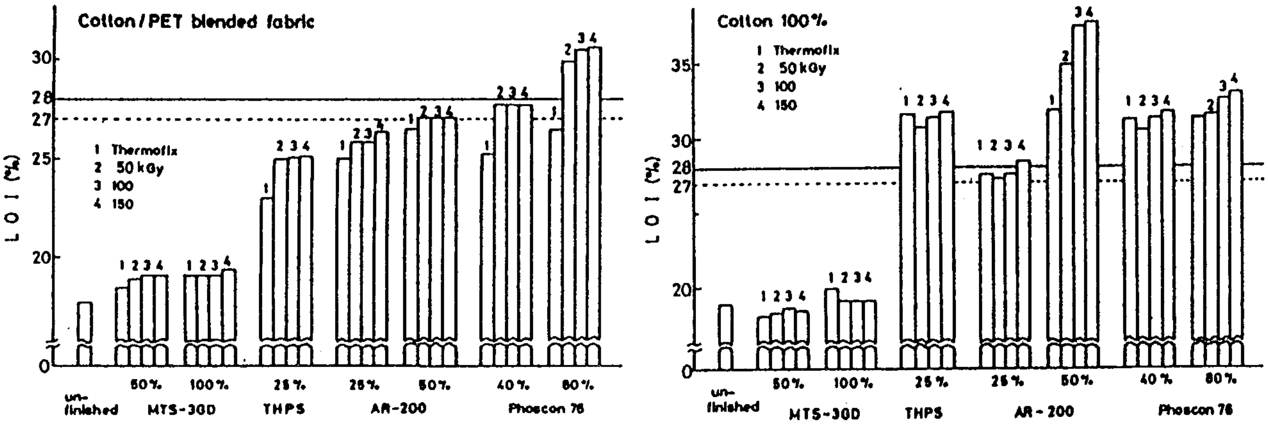


Fig. 3-49 Evaluation of flame retardance of C/P blend and cotton 100% fabrics treated with different kinds of flame retardants and cured by heat and various doses of electron beam irradiation.

(2) Finish by electron beam irradiation

Preparation of finishing solution, impregnation and drying were performed as described in the case of heat cure. Predried samples were irradiated with electron beam under the conditiones listed in Table 3-8 by using a low energy electron irradiation system, Curetron (Nisshin Highvoltage Co.). In this case, both side-irradiation with 10-60 kGy exposure was also attempted to compare with the result of one side-irradiation with 10-300 kGy exposure.

Table 3-8 Irradiating conditions for electron beam curing.

Acceleration voltage (kV)	200	200	200	200	200	200	200	200	200	200	200
Electron current(mV)	5.0	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4
Conveyor speed (m / min)	30.5	50.5	40.5	33.3	28.6	25.0	20.0	16.7	10.0	6.7	3.3
Exposure dose (kGy)	10	20	25	30	35	40	50	60	100	150	300

(3) Soaping method

Samples finished by the above mentioned methods were treated with 0.2% of sodium carbonate containing 1-2 drops of a nonionic surfactant (bath ratio 30:1) for 10 min at 60°C or 90°C followed by 5 times rinsing at 50-60°C.

(4) Add-on and water content were determined by the conventional method.

(5) Determination of LOI, tensile strength, elongation and HCHO were carried out as described above for other finishing methods.

(6) Durability was tested by repetition of laundering as described for other finishing methods.

Numbers of repetition of experiments were 5-6 times other than 10 times for tensile strength and elongation. Deviations were ±0.2-0.7% for LOI value, ±0.2-0.5 kg/cm for tensile strength, ±0.3-0.8% for elongation, ±0.3-0.6% for add-on and 0.5-0.7% for water content, and values were averaged in every case.

2) Results and Discussion

(a) Evaluation of applicability of each flame retardant

Fig.3-49 exhibits comparison between the result of heat cure and that of electron beam irradiation as well as between C/P blended fabric and 100% cotton finished by heat cure and beam irradiation.

Evaluating the flame retardance by LOI level at 27-28%, 100% cotton samples finished by electron beam irradiation are flame retardant showing LOI value higher than 30% except for those treated with 25% of MTS-3GD and AR-200, particularly those treated with 50% of AR-200 showed high LOI value. On the other hand, in the case of C/P blended samples, heat cure was not effective in all cases and only electron beam irradiation worked with 50% of AR-200 and Phoscon 76. Even with Phoscon 76, concentration of 40% was not capable enough to reach the level of LOI 28%. It was found, from the above results, that Phoscon 76 would give the highest flame retardance to C/P blended fabrics.

(2) Selection of soaping temperature

Fig.3-50 shows the results obtained before and after soaping for the purpose of screening. Effects of soaping at 60°C and 90°C were compared by using samples finished with Phoscon 76 to select better condition since soaping process is indispensable and temperature condition dominates removal of flame retardant and effect of flame retardant finish.

As shown in Fig.3-50, decrease was observed in both LOI value and tensile strength after soaping when Phoscon 76 finished samples were used. Reduction of LOI value increased with rise of temperature, whereas change in physical properties, decrease in tensile strength and rise of elongation was not temperature dependent.

According to the results shown in the figure, 60°C was selected as soaping temperature, as C/P blended sample soaped at 90°C showed larger LOI reduction.

(3) Effect of soaping on flame retardant finish

By using the soaping temperature selected as mentioned above, samples treated with AR-200 was compared with those finished with Phoscon 76 to see which is better for application to C/P blended fabrics, which showed that sample finished with AR-200 could not be practically used because of large decrease in LOI value after soaping as shown in Fig.3-51. Therefore, it was proved that only Phoscon 76 would be effective for the flame retardation of C/P blended fabrics.

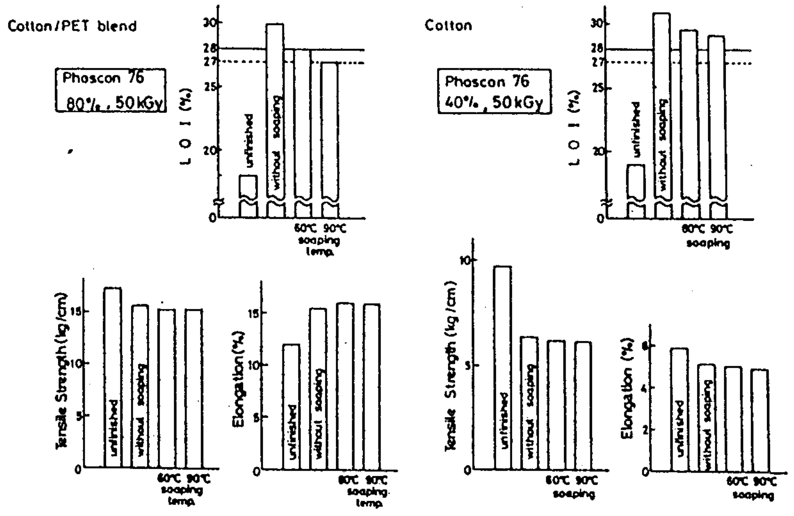


Fig. 3-50 Effect of soaping on LOI value, tensile strength and elongation of C/P blend and cotton fabric finished with Phoscon 76.

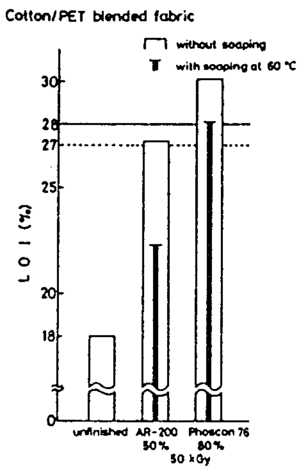


Fig. 3-51 Effect of soaping on LOI value of C/P blend treated with AR-200 in comparison with that treated with Phoscon 76.

(4) Flame retardant finish with Phoscon 76, vinyl phosphonate oligomer

(i) Comparison between effect of heat cure and that of electron beam irradiation on Phoscon 76

As shown in Fig.3-52, thermo-fixed samples entirely lost the flame retardance with extremely large reduction of LOI values after soaping in both cases of C/P blended and 100% cotton fabrics. On the other hand, samples cured by electron beam irradiation maintained 28% or higher LOI level even after soaping not only in the case of 100% cotton but also in the case of C/P blended fabrics. Such difference is probably due to the fact that heat cure can not supply enough energy for sufficient vinyl polymerization of vinyl groups bound to P molecule at the center of each vinyl phosphonate oligomer with simultaneous formation of cross-linking with OH groups of cellulose molecule to acquire the flame retardation, which results in easy release from the surface of fibers by soaping, whereas electron beam energy is strong enough for sufficient vinyl polymerization together with strong cross-linkage with cellulose to achieve the flame retardation so successfully that the flame retardance of fabrics is retained after soaping. Thus, obvious difference in effect observed between heat cure and electron beam irradiation was clearly proved.

On the other hand, tensile strength of C/P blended sample showed little change after soaping in both cases of heat cure and electron beam irradiation, but termo-fixed 100% cotton showed a little rise of tensile strength and elongation after soaping. This is because of removal of acid which may otherwise bring about more degradation of cotton rather than that by heat. It was also found that reduction of tensile strength and elongation observed with 100% cotton cured by electron beam irradiation increased after soaping, which is probably attributed to the fact that electron beam irradiation itself brings about degradation to 100% cotton and further damage is caused by the following mechanical force of soaping.

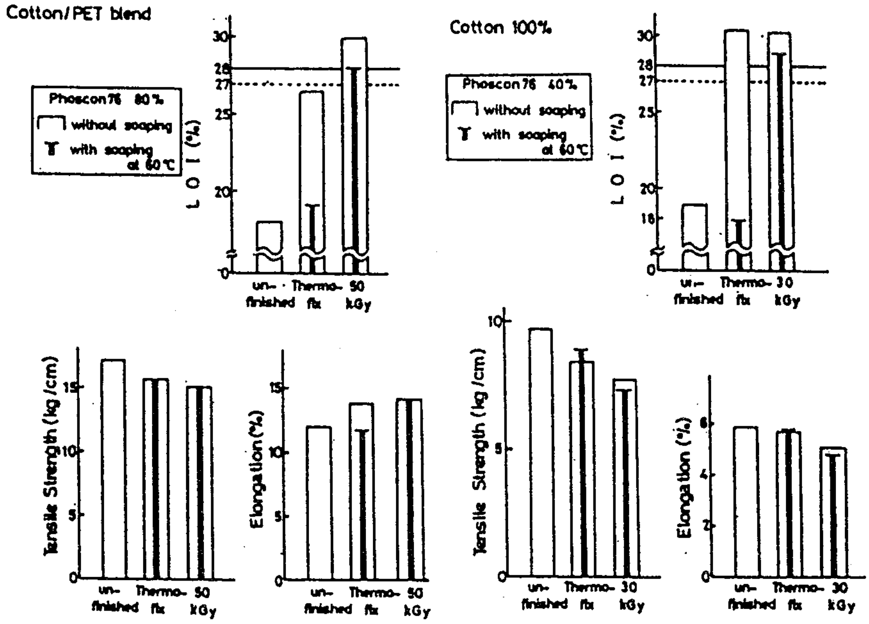


Fig. 3-52 Effect of soaping on flame retardance, tensile strength and elongation of C/P blend and cotton fabrics cured by thermo-fix and electron beam irradiation.

(ii) Decision of concentration of finishing solution

C/P blended, 100% PET and 100% cotton fabrics were treated with every finishing solution containing 40, 60 and 80% of Phoscon 76 respectively and cured by electron beam irradiation with 100 kGy for PET fabric and 50 kGy for other 2 fabrics followed by soaping. The results of determinations of LOI value, tensile strength and elongation are shown in Fig.3-53. As for LOI value, every sample showed reduction after soaping. C/P blended fabric with LOI values 27-28% keeping the flame retardance after soaping were those treated with 60% and 80% of Phoscon 76. Cotton fabric maintained LOI values 28% or higher after soaping in all cases treated with 40, 60 and 80% of Phoscon 76. The above results suggests that required concentration of Phoscon 76 for flame retardance of 100% cotton and C/P blended are at least 40% and 60-80% respectively. Whereas in the case of 100% PET, even with 80% of Phoscon 76 and 100 kGy of exposure dose, extremely large reduction of LOI value was observed after soaping, which disclosed that it would be very difficult to expect any favorable effect of electron beam irradiation to Phoscon 76 in the case of 100% PET.

On the other hand, tensile strength of 100% PET which denied any effect of electron beam irradiation showed entirely no change even by irradiation of 100 kGy dose followed by soaping, whereas 100% cotton which exhibited the best effect of the irradiation for the flame retardance were damaged to largest extent showing reduction of tensile strength down to 1/2 that of untreated sample. C/P blended sample also showed some reduction of tensile strength caused by coexistence of damaged cotton fiber, but the reduction ratio is thought to be reasonable when calculated from the blending ratio of C/P. The above results suggested that electron beam gives a large damage to ether bonding which form glycoside bond but not to ethylene bonding as well as to ester bonding.

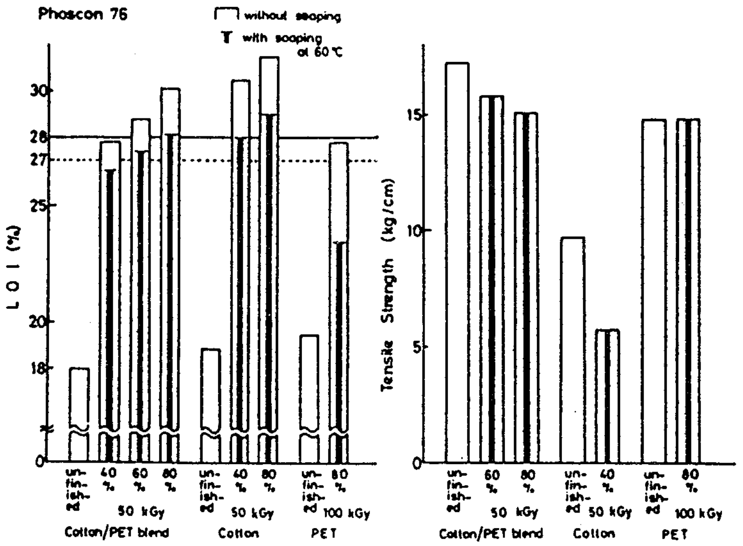


Fig. 3-53 Comparison of LOI value and tensile strength among C/P blended, cotton and PET fabrics unfinished and finished with different concentrations of Phoscon 76.

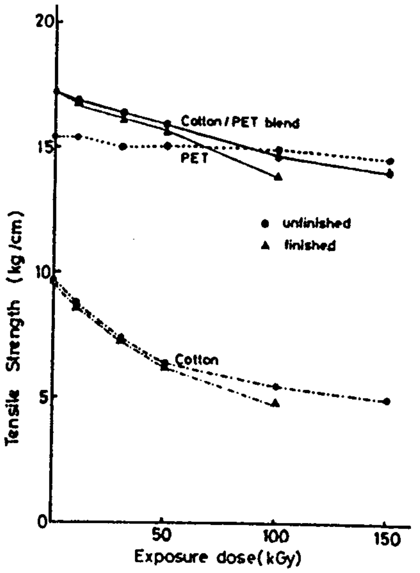


Fig. 3-54 Change in tensile strength with exposure dose of electron beam observed for Cotton, PET and C/P blended fabrics.

(iii) Effect of electron beam irradiation on tensile strength of each fabric sample

It has been proved from the above results that electron beam irradiation is applicable also to C/P blended fabrics. But a problem concerning the reduction of strength of cotton which affects C/P blended fabrics required a further investigation on tensile strength in more detail. Therefore, unfinished 3 kinds of fabrics were irradiated with 10-150 kGy exposure dose, which gave the results shown in Fig.3-54. Little change was observed in the tensile strength of 100% PET even with 150 kGy irradiation, in contrast, 100% cotton showed considerable reduction, specially, more steep in the initial dose range, 0-50 kGy showing a less slope in the latter range up to 150 kGy. In the case of C/P blended sample, the slope between 0-50 kGy irradiation is more gentle compared to that observed with 100% cotton because of the aid of 100% PET, but the slope between 50-150 kGy irradiation clearly disclosed the dominant influence of 100% cotton. Subsequently, the above results were compared with those of finished samples after the irradiation to see whether the observed reduction of tensile strength is caused only by electron beam or influence of the flame retardant itself is also participated in such degradation of cotton. It was found from the results that little change in the flame retardant was shown in a range of 0-50 kGy irradiation but finished sample irradiated with 100 kGy irradiation showed a decrease in tensile strength to some extent. Such results suggest that the influence of flame retardant on the degradation of cotton can be negligible in a range of 0-50 kGy irradiation but participation of the flame retardant can not be ignored when finished sample is irradiated with 100 kGy or more. Moreover, acidic finishing solution may be one of the reason for the degradation of cotton. From the above results, it was thought to be necessary for the inhibition of degradation of cotton cellulose to consider further investigation not only from the irradiation condition but also from the preparation of finishing solutions.

(iv) Improvement of finishing condition for inhibiting reduction of tensile strength

The above results were all obtained by one side-irradiation which brings about larger damage by irradiating a strong electron beam at one side of the fabric. Therefore, both side-irradiation of 1/2 dose of electron beam was attempted, the results of which showed as shown in Fig. 3-55 that both side-irradiation gave higher tensile strength, particularly larger rise was observed in the case of cotton which shows larger reduction by one side-irradiation. Moreover, higher tensile strength was shown by both-side irradiation after soaping. This is probably because of less degradation of fiber brought about by both side-irradiation resulting in less damage by soaping process. Also as to LOI value, both side-irradiation gave better results. Particularly the difference observed between one-side-irradiation and both side-irradiation are larger after soaping, which is due to the improvement of polymerization and cross-linking efficiencies brought by both side-irradiation.

Taking the above results into consideration, more detailed investigation was carried out by both side-irradiation with C/P blended fabric to see the relationship among LOI, tensile strength and elongation. As shown in Fig.3-56, both side-irradiation with 30 kGy (30 kGy × 2) gave LOI value 28% but LOI 30% was given with 50 kGy×2 showing very favorable flame retardance, which was leveled off with more exposure dose. On the other hand, tensile strength showed a little decrease in the initial range, up to 25 kGy, but considerable reduction was observed in a range of 30-50 kGy×2 leveling off in higher range of exposure dose. However, since irradiation of at least more than 30 kGy, e.g. 40-50 kGy at both sides are desirable for any sufficient flame retardance, another investigation on additives were attempted because of the limitation of improvement of irradiation condition.

Elongation increased to some extent by 10 kGy×2 irradiation but leveled off with more exposure doses.

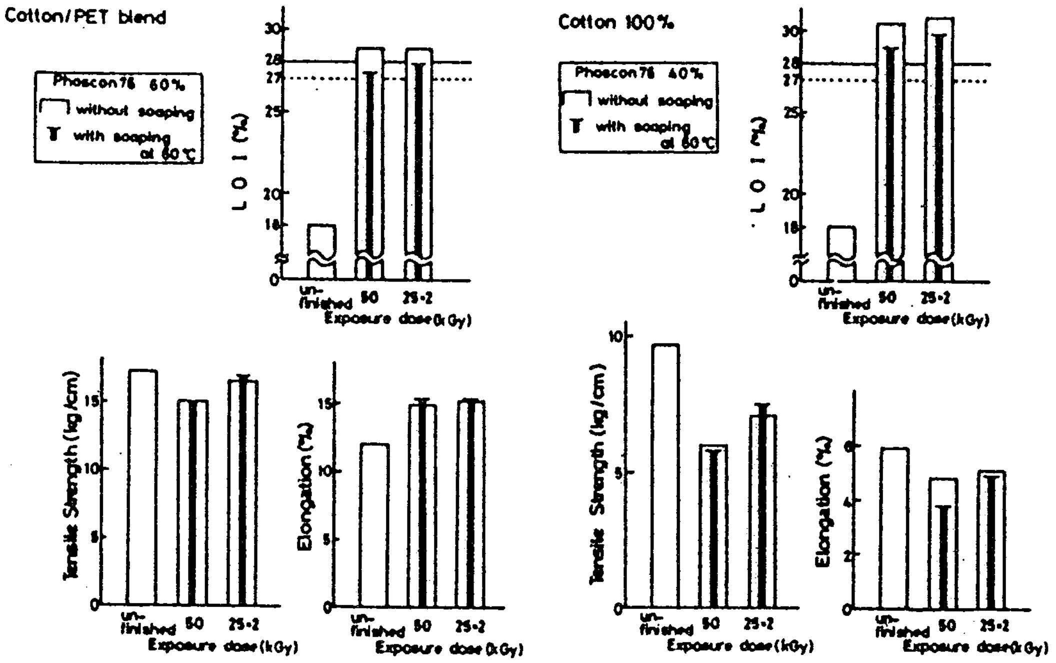


Fig. 3-55 Comparison between effect of one-side irradiation and that of both-side irradiation on LOI value, tensile strength and elongation.

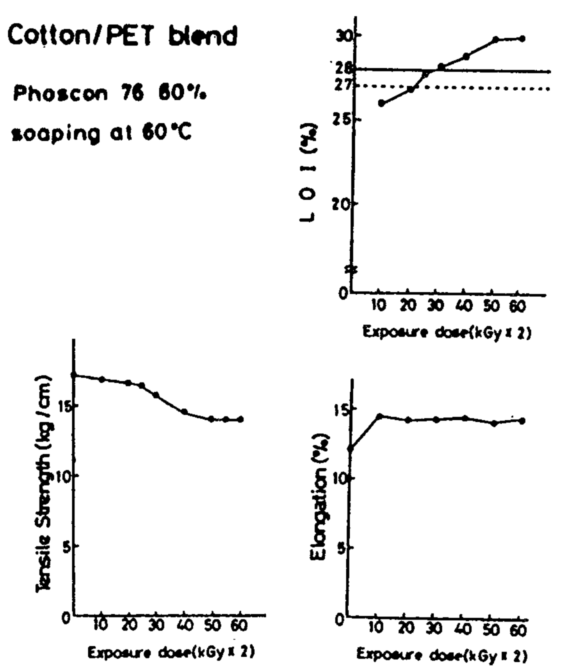


Fig. 3-56 Effect of exposure dose of electron beam (on both side) on LOI value, tensile strength and elongation.

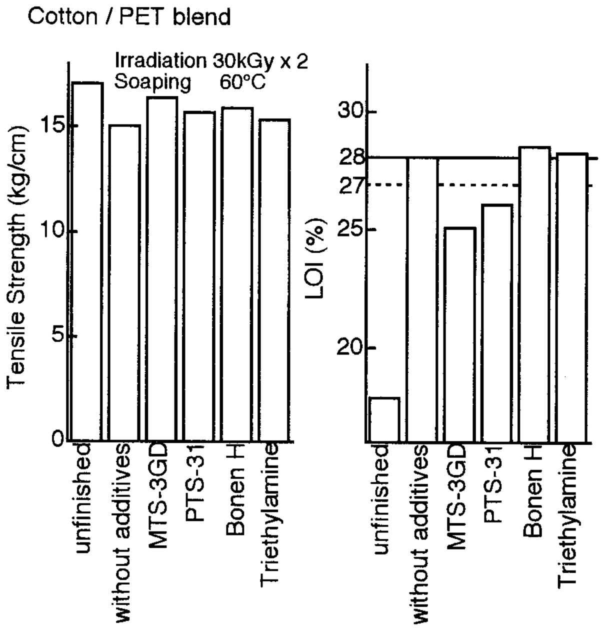


Fig. 3-57 Effect of additives on tensile strength and LOI values of C/P blend finished with Phoscon 76 (60%) and electron beam curing (conc. of each additive is 6% = 1/10 ×60%).

(v) Effect of additives

C/P blended fabric was treated with 6% of the additives (10% of the concentration (60%) of flame retardant) shown in Fig.3-57 and irradiated with 30 kGy at both sides.

As shown in Fig.3-57, every sample treated with the finishing solution containing each additive showed inhibiting effect on tensile strength compared with that treated in the absence of any additive. But, samples LOI values of which exceeded 28% were only those treated with flame retardant containing Bonen H or triethanolamine. As the results of the same investigation carried out for 100% cotton showed that samples treated with finishing solution containing Bonen H or triethanolamine also gave LOI values above 30% considerably higher than those treated without those additives, and Bonen H exhibited better result for inhibiting effect on reduction of strength. From the above results, the durability was tested with samples finished in the presence of Bonen H and triethanolamine separately for C/P blended fabric as well as with those finished with Bonen H for 100% cotton.

(vi) Durability test

C/P blended fabric was treated with 60% of Phoscon 76 containing 6% of Bonen H or triethanolamine and irradiated with 40 and 50 kGy of exposure dose in addition to 30 kGy, the result of which was that LOI was approximately 28% as already shown in Fig.3-56. As seen in Fig.3-58, LOI values were maintained at the level considerably higher than 28% even after 25 repetition of laundering, particularly 50 kGy irradiation gave higher LOI values. As for tensile strength, reduction observed after laundering with sample finished with Phoscon 76 alone is larger than that observed with unfinished sample, but addition of additives inhibited the reduction of tensile strength showing higher tensile strength than those of irradiated unfinished sample. Comparison of Bonen H and triethanolamine showed that, the former gave a little better results. As to exposure dose, 40 kGy which gave higher tensile strength and maintained higher LOI level exceeding 28% was thought to be most appropriate.

On the other hand, 100% cotton fabric was treated with 40% of Phoscon 76 containing 4% of Bonen, irradiated with 25 kGy at both side and followed by 25 time laundry.

After laundry, LOI values of both samples treated with and without the additive showed the same level, 29%. Tensile strength showed effect of additives by maintaining higher levels compared with that shown by sample treated without additives.

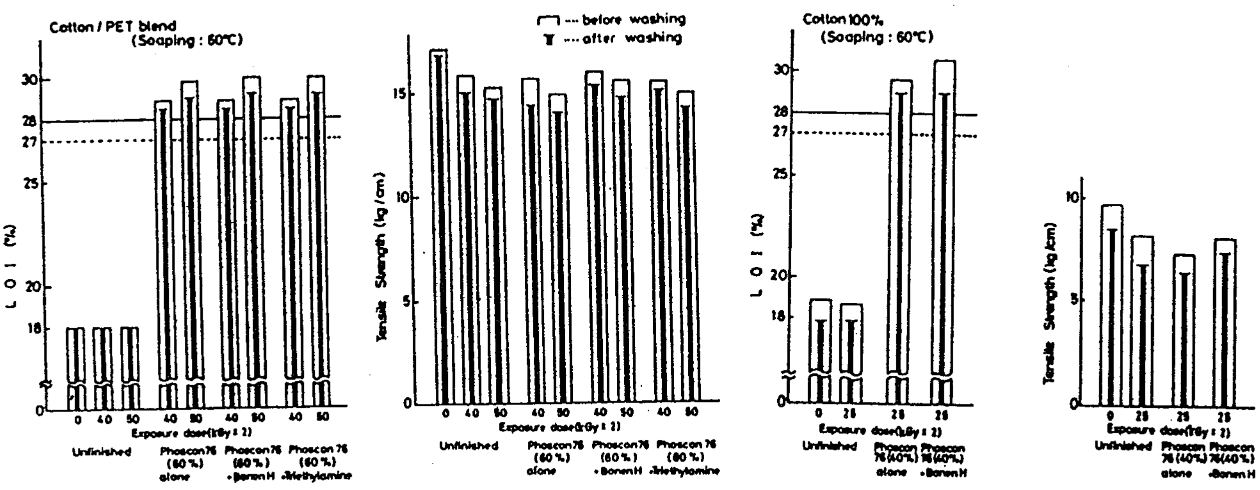


Fig. 3-58 Washability of C/P blend and Cotton fabrics treated with Phoscon 76 and cured by electron beam irradiation.

(vii) Relationship between flame retardance and add-on or water content

Add-on and water content were also investigated since these two factors were supposed to be related to the flame retardance of fabrics. As shown in Fig.3-59, add-on exceeding 30% (C/P blended sample) and 27-28% (100% cotton) showed 5-6% reduction after laundering. In this case, P content was also determined, but detected amount of P was only 1/2 compared with the amount calculated from P content in the molecule and add-on, which was thought to be attributed to the inhibition of coloration of P-molybdate in the presence of additive and evidenced experimentally. Relationship between add-on and flame retardance for C/P blended fabric and 100% cotton disclosed that the former requires add-on 1.2 times that for 100% cotton to acquire sufficient flame retardance.

As for water contents, finished C/P blended fabric showed nearly doubled water content than that of unfinished sample but it decreased to 1.5-1.8 times with liberation of the flame retardant fixed on the fabric after repetition of laundry, which is reflected on the flame retardance. On the other hand, water content of 100% cotton 2.5 times that of C/P blended fabric decreased by finishing, but increased by removal of the flame retardant after laundering. The above results suggests that relationship between flame retardance and add-on and water content would be observed in the case of C/P blended sample the water content of which is originally low, whereas change in water content, to some extent, would not affect flame retardance in the case of 100% cotton initially having high water content.

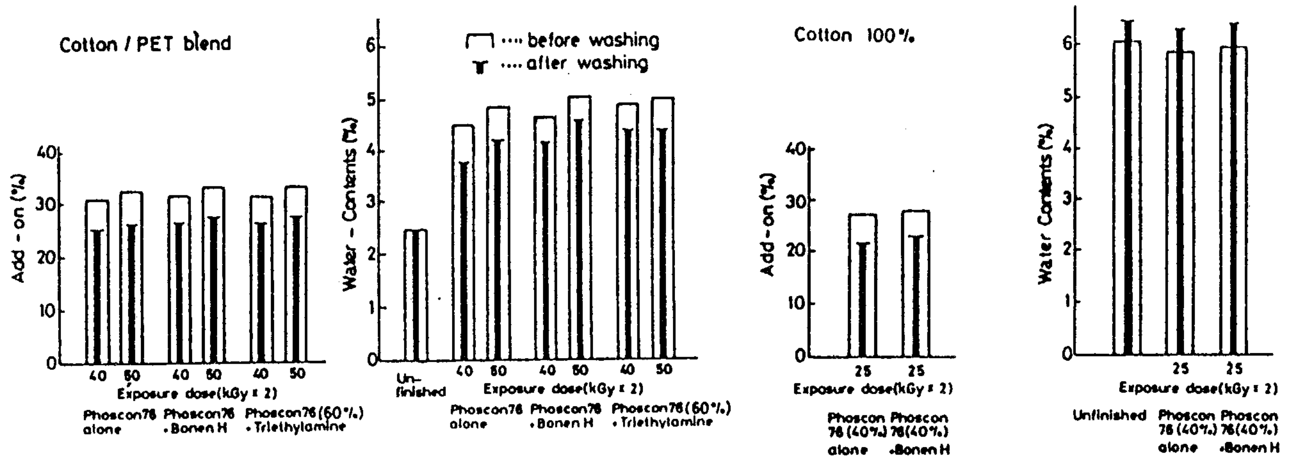


Fig. 3-59 Add-ons and water contents of C/P blended cotton 100% fabrics finished with Phoscon 76 with and without Bonen H (6%).

(viii) Comparison with samples finished by other methods

LOI values and tensile strength, the most important properties for the textile end-uses were compared between a flame retardant fabric finished with vinyl phosphonate oligomer, Phoscon 76, and cured by electron beam irradiation and that finished with Nonnen C-617 by heat cure described in 3-3-1. As shown in Fig.3-60, little difference was found in tensile strength between 2 samples, whereas LOI values showed a difference to some extent, i.e., LOI level of the thermo-fixed samples was little exceeded 28%. Such result suggests that the latter can be more highly hopeful. Furthermore, LOI values, tensile strength and detected HCHO levels were compared among samples finished by electron beam irradiation, treated with Pyrovatex CP as well as with PROBAN polymer. As seen on the right side of this figure, LOI value of the irradiated sample was little higher than Pyrovatex finished sample though a little lower than PROBAN finished sample.

Similarly, tensile strength of the irradiated sample was also higher than that of Pyrovatex finished-sample though lower than that of PROBAN finished-sample cured under the condition free from any damage by heat or electron beam.

Comparison of the flame retardance dominating factors for these flame retardant fabrics that the flame retardance of Pyrovatex finished fabric as well as of PROBAN finished fabric is the result of the synergistic effect of N and P, whereas the flame retardance is contributed by P alone in the case of electron beam irradiation. Moreover, formaldehyde, one of the important factors from the security, was not detect from Phoscon 76 as seen in Fig.3-60.

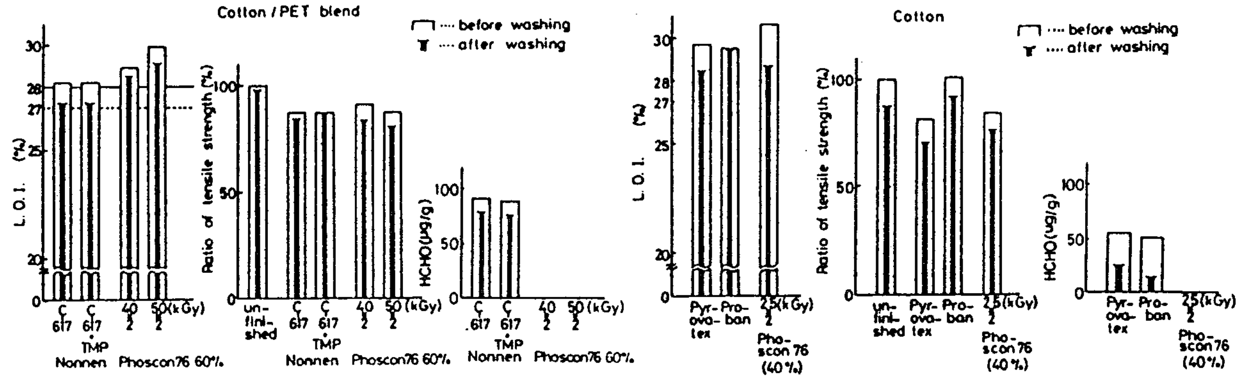


Fig. 3-60 Comparison of LOI value, tensile strength and HCHO deterced.

between cotton / PET blend finished by heat cure and that finished by electron beam curing.

among Pyrovatex-finished cotton, Proban-finished cotton and that finished by electron beam curing.

3) Conclusion

Minute investigations were systematically performed by the application of electron beam irradiation method to C/P blended fabric, particularly with higher ratio of PET, for which the flame retardant finish is difficult because of the combination of opposite, hydrophilic and hydrophobic properties.

It has been concluded that the most favorable results were obtained from the standpoints of flame retardance and strength when finished with 60% of Phoscon 76 (vinyl phosphonate oligomer), 40% for 100% cotton, in the presence of any additive 1/10 the concentrations of Phoscon 76 and irradiated with 40 kGy for C/P blend and 25 kGy for 100% cotton on both sides of the fabrics.

Comparison with the results obtained by the heat cure mentioned above reveals that LOI value shows considerable rise with similar tensile strength which proves improved performance as a flame retardant fabric. Cotton fabric finished with electron beam irradiation showed better results for LOI value and strength compared with Pyrovatex finished fabric and PROBAN finished fabrics. Furthermore, formaldehyde was not entirely detected. Such formaldehyde free finished sample has not been obtained from any other flame retardant finishes and can be highly evaluated from the standpoint of safety.

Therefore, it was proved by the comparison with other finished fabrics that application of electron beam irradiation to C/P blended fabrics as well as to cotton fabrics can be highly expected.

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Chapter 4

Chapter 4 Effects of Flame Retardant Finishes on Discoloration of Dyed Cotton Fabric Caused by Ultraviolet Irradiation

Introduction

Since a majority of fabrics dealt in the market and practically used by consumers are dyed, discoloration or fading of dyed fabrics may be unavoidably caused by any finishing process including flame retardant finishes, furthermore, any fabric is exposed to the sun light with high frequency.

The fastness of colors of dyed fabrics is one of the most important problems in the daily life from the practical standpoint, and considerable studies[1-6] have been achieved so far under the name of lightfastness, fading or photochemical decomposition of dyes together with the effect of sweat. It is also indispensable to pay attention to the effect of the flame retardant finish on dyed fabrics under such environmental condition as the ultraviolet irradiation. Although few information has been available for this point, dyestuff companies have collected data concerning the fastness of dye products to flame retardant finishes as well as to the irradiation for their own responsibility to keep the consumers' credit for the textile durabilities in the market. However, the evaluation for the fastness is merely based on the blue scale showing only grades, which may be useful as far as the practical use is concerned. But they lack not only of precision but also of any fundamental consideration resulting in little detailed comparison. Moreover, detailed information to be obtained by minute investigations are required to select the most favorable finishing condition.

Consequently, in a series of the studies on flame retardant finishes, it was thought that effects of flame retardant finishes on dyed fabrics in combination with ultraviolet irradiation should not be ignored.

Therefore, cotton fabric was dyed with different kinds of dyestuffs commercially used for textile goods on the market under the dyeing conditions specified by each maker, each of which was finished with durable flame retardants as well as with nondurable flame retardants followed by the ultraviolet irradiation. Coloration of each sample was observed before and after both flame retardant finish and the ultraviolet irradiation to see how it changed by the flame retardant alone as well as by combined effect of the finish and the irradiation.

4-1 Effects of Durable Flame Retardant Finishes

4-1-1 Effects of Pyrovatex Finish on Discoloration of Cotton Fabric Dyed with Reactive Dyes as well as on Discoloration to be Caused by Ultraviolet Irradiation

The present study deals with reactive dyes having different chromogens with the same or similar functional groups and with the representative durable flame retardant finish, Pyrovatex with additives. It is expected that this study will give a further information for selecting dyestuffs which show high fastness for flame retardant finish and ultraviolet irradiation, also for evaluating finishing conditions which can minimize discoloration.

1) Experimental

(a) Materials

(1) Fabric

One hundred % cotton the same as that described in 2-2-2 was used for this study.

(2) Dyes and additives for dyeing

The reactive dyes used for the present investigations are, as shown in Table 4-1, those having monoazo, bisazo, anthraquinone and phthalocyanine chromogens and triazinyl or pyrimidinyl functional groups with mono or tri halogen substituents in common. The structures of dyes, only 5 out of 14 kinds, are shown in Fig.4-1 since the chemical structures of the rests are unpublished.

Sodium sulfate and sodium carbonate were used as additives for dyeing.

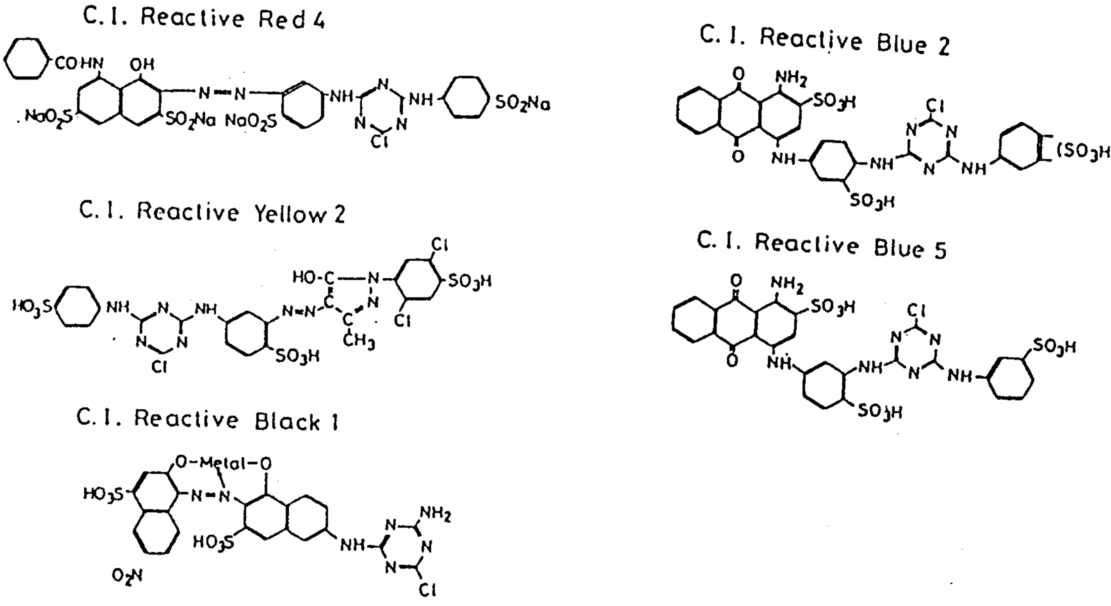
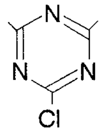
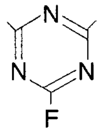
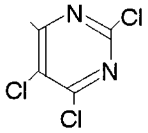


Fig. 4-1 Chemical structures of reactive dyes.

Table 4-1 List of reactive dyes used for this study.

Type of Dye	C. I. Name	Functional Group
Monoazo	Reactive Yellow 2	 (MCT)
	Reactive Red 4	〃
	Reactive Blue 13	〃
	Reactive Black 1	〃
	Reactive Yellow 143	 (MFT)
Bisazo	Reactive Red 120	MCT
	Reactive Brown 2	〃
	Reactive Brown 7	〃
	Reactive Blue 184	MFT
	Reactive Blue 52	 (TCP)
Phthalocyanine	Reactive Blue 41	MCT
	Reactive Green 5	〃
Anthraquinone	Reactive Blue 2	MCT
	Reactive Blue 5	〃

(3) Flame retardant and additives for finishing

Pyrovatex CP was used as the basic flame retardant and a glyoxal type resin (TS-10), hexamethylmelamine (M6), phosphoric acid, urea and ammonium chloride as additives for Pyrovatex finish.

(b) Methods

(1) Dyeing

Cotton fabric was immersed in each dye solution (5% o.w.f.) and temperature was raised linearly from room temperature up to 80°C within 50 min after the initiation of dyeing followed by the isothermal heating for 40-50 min at 80°C. The dyed fabric was rinsed with hot water and successively with tap water.

Table 4-2 Contents of treating baths for flame retardant finish for each dyed cotton fabric.

	Formulation	Concentration (%)	pH
B	Pyrovatex CP	32	4.00
C	Pyrovatex CP	32	4.63
	TS-10	8	
D	Pyrovatex CP	32	4.75
	M6	8	
E	Pyrovatex CP	32	2.00
	H_3PO_4	2	
F	Pyrovatex CP	32	2.10
	TS-10	8	
	H_3PO_4	2	
G	Pyrovatex CP	32	2.32
	M6	8	
	H_3PO_4	2	
H	Pyrovatex CP	32	4.20
	M6	8	
	$CO(NH_2)_2$	1	
	NH_4Cl	2	
I	Pyrovatex CP	32	2.32
	M6	8	
	H_3PO_4	1	
	$CO(NH_2)_2$	0.4	
	NH_4Cl	2	

(2) Flame retardant finish

Cotton fabric dyed with various kinds of dyes mentioned above were finished in the manner the same as described in 3-1-1 (Pyrovatex finish).

The formulations of the treating baths are shown in Table 4-2 with pH of each mixture.

(3) Ultraviolet(UV) irradiation

Carbon arc light was irradiated as a UV source using UV Regular Life Fade Meter Type FA 3 (Suga Shikenki K. K.).

(4) Evaluation of discoloration

The discoloration was evaluated by observing peak absorbances of each color from absorption curves in a range of 200-840 nm before and after the flame retardant finish and UV irradiation using a Ulbricht sphere attached to a spectrophotometer, Shimadzu UV 200S (double beam) followed by obtaining ratios of these peak absorbances of finished and irradiated samples to those of the unfinished and unirradiated dyed fabric.

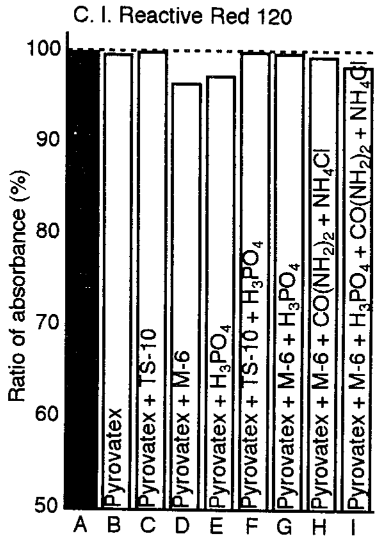
2) Results and discussion

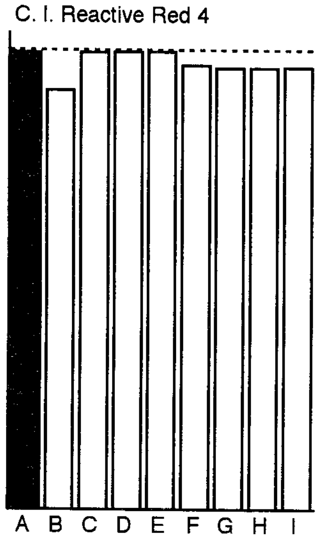
(a) Effects of flame retardant finishes on colors of cotton fabric dyed with reactive dyes

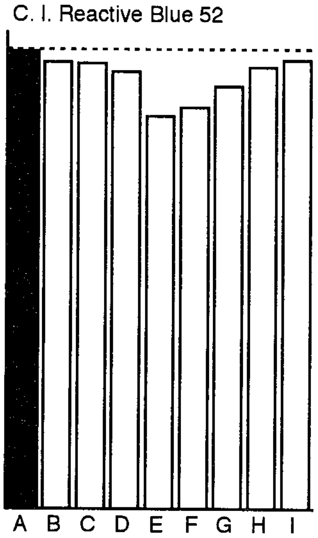
The flame retardant finish investigated this time also brought about the discoloration of dyed fabric, but considerable differences were observed in degrees of discoloration as shown in Fig.4-2. They are classified as follows:

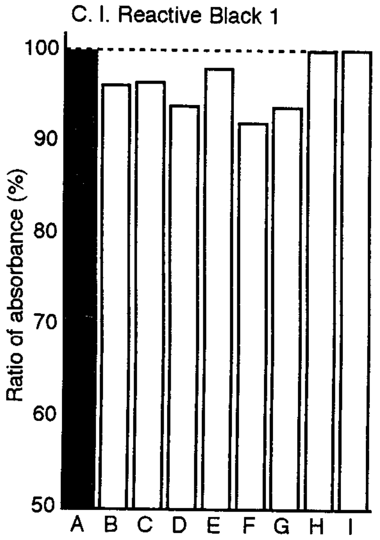
(1) C. I. Reactive Red 4 of monoazo type and Red 120 of bisazo type, both having monochlorotriazinyl group (MCT) as a functional group, kept the highest level, i.e., even 100%, 96% at lowest showing extremely strong resistance to the flame retardant finish with Pyrovatex CP.

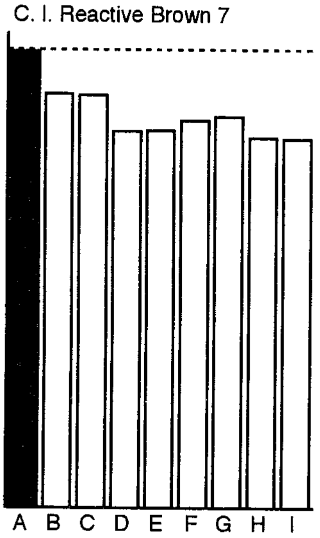
(2) The second level is between 90-95% or higher. The dyes which belong to this range are Black 1 of monoazo type, Blue 52 and Brown 7 of bisazo type and Green 5 of phthalocyanine type, all having MCT but Blue 52 having trichloropyrimidinyl ring as a functional group. In more details, these dyes showed different behavior depending upon the additives for finishing. For example, Blue 52 and Green 5 exhibited a similar tendency showing lower ratios by finishing in the treating baths containing phosphoric acid at low pH (samples E, F, G) though Blue 5 showed higher ratios in every case, whereas in the case of Black 1, ratios were lower when resins were added alone or with phosphoric acid (sample D, F, G) irrespective of pH, and Brown 7 showed little effect of additives.

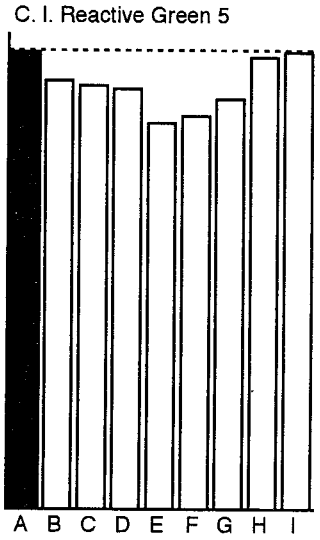


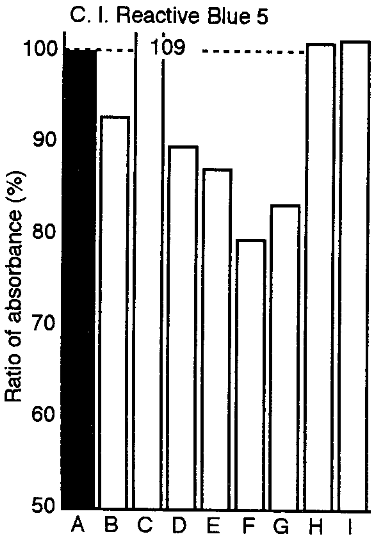


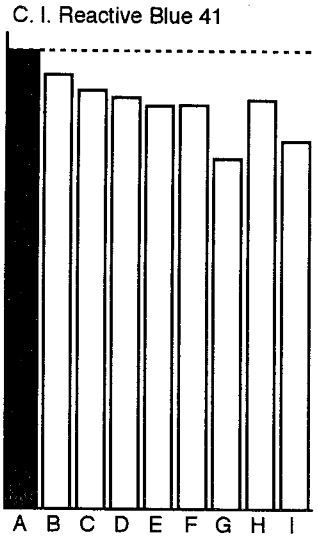


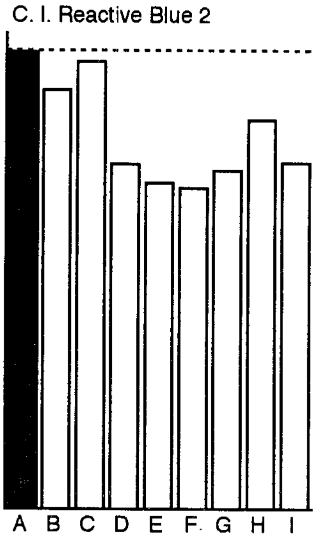












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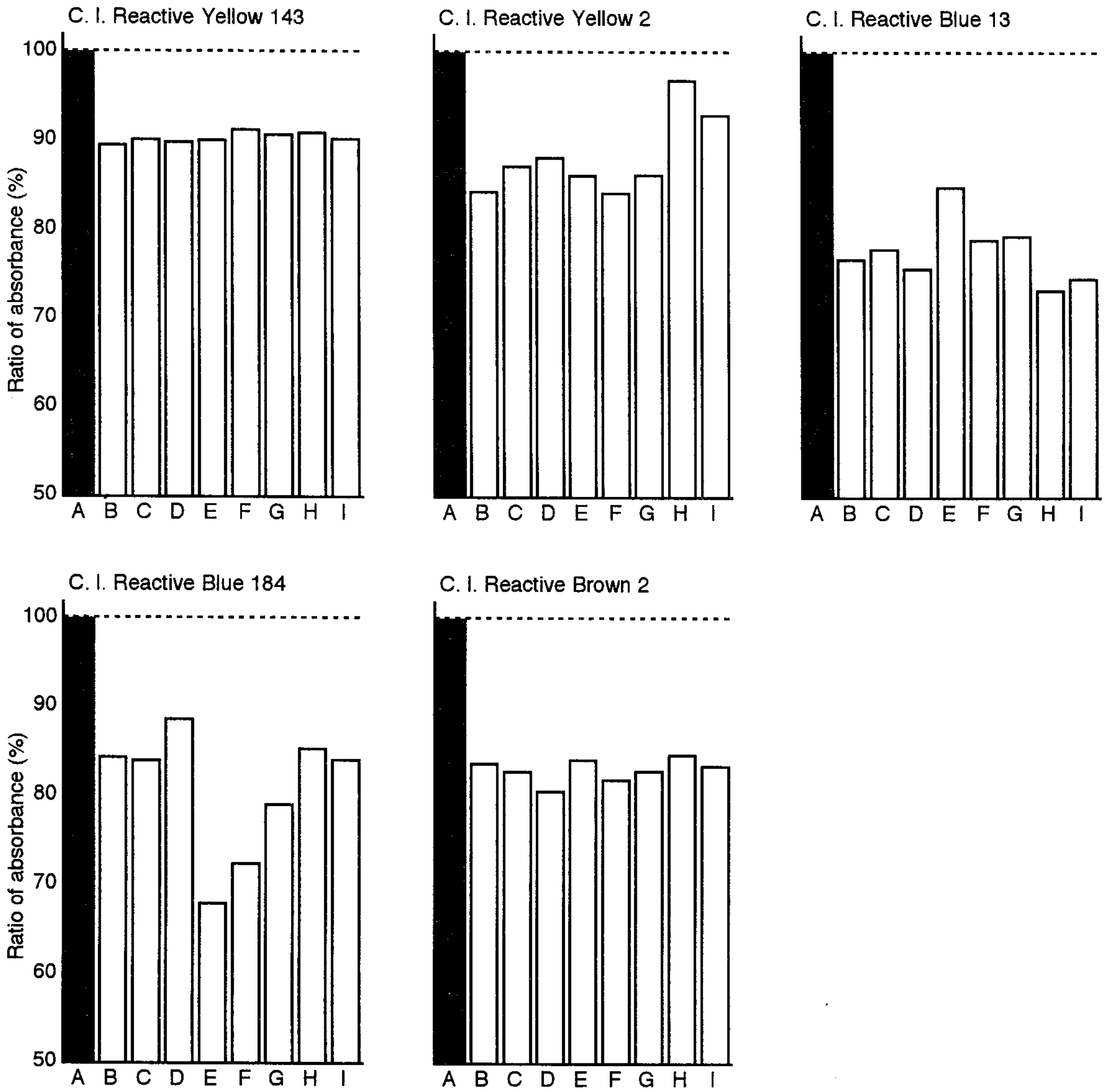


Fig. 4-2 Effect of flame retardant Pyrovatex finish with addives on colors of cotton fabric dyed with reactive dyes.

(3) Blue 41 of phthalocyanine type with MCT the same as Green 5 showed that the samples treated in baths containing M6 and phosphoric acid together (sample G, I) gave lower ratios, slightly above or below 90%, but the rests of them reached up to 95% or more showing similar behavior to that of Green 5 of the same type though the ratios of sample E and F are lower than those of Green 5. It likely seems that this dye is more influenced by combined effect of phosphoric acid and resin than by each single effect.

(4) A range of reduced ratios observed with Blue 5 extends over 20% or wider. This dye having anthraquinone ring (S) as the chromogen with MCT showed that the ratios of the samples treated in baths containing phosphoric acid (E, F, G) were low, between 80-90%, but those treated with flame

retardants containing glyoxal type resin (sample C) as well as containing urea and ammonium chloride (sample H, I) irrespective of the presence of phosphoric acid showed higher values even exceeding 100% level probably because of a deepening effect.

Blue 2 of the same type exhibited similar behavior, but the ratios of sample C, H and I were lower, whereas those of D, E, F and G were higher than those shown by Blue 5.

(5) Two dyes of Yellow type with the same chromogen and functional group showed similar but slightly different behavior, i.e., the ratios of Yellow 143 were all on a level of approximately 90% irrespective of additives, while in the case of Yellow 2, additives involving urea and ammonium chloride gave higher ratios exceeding 90% which were reduced to about 85% without these two additives.

(6) Brown 2 of bisazo type with MCT showed almost the same level between 80-85% under any finishing condition.

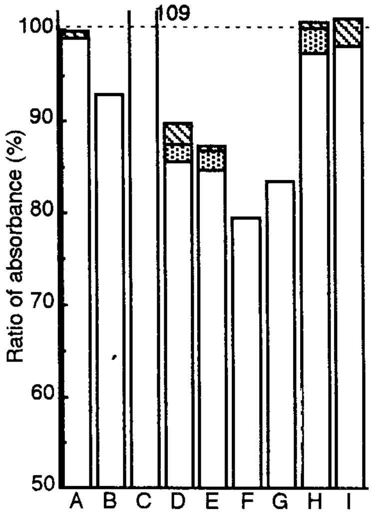
(7) The lowest range was from 68% for Blue 184 to 77% for Blue 13. Blue 13 belongs to monoazo type having MCT just as Red 4 which revealed the largest fastness showing the highest level. It is of interest that the dyes which have the same chromogen and functional group show such marked contrast. Moreover, comparing these two blue dyes, they showed another contrary result, i.e., Blue 184 was most largely discolored by the flame retardants of low pH containing phosphoric acid (E, F, G) but samples B, C, D, H and I showed ratios approximately 85% or higher. On the other hand, Blue 13 finished in the same treating baths exhibited that samples E, F and G gave higher ratios than those of the rest samples, which is contrary to what is observed in the case of Blue 184 and most of other dyes. Such result suggests that Blue 13 is more resistant to acid media as low as pH 2 rather than any pH higher than pH 4.

It is generally considered that the portion of the dye structure mainly affected by pH could be the functional group. In this case, a difference is that Blue 13 and Blue 184 have MCT and MFT respectively. But such difference between chlorine and fluorine probably make no difference after the chemical binding between cellulose and dye molecules.

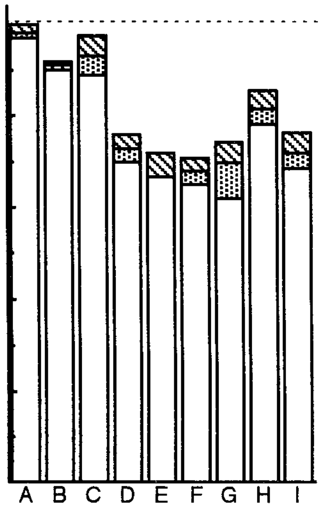
From the results mentioned above, as a whole, there arises an unavoidable question why much differences were found between Red 4 and Blue 13 as well as between Red 120 and Blue 184 even though they are constructed with the same chromogen and the same or similar functional groups.

After all, the above results leads us to a conclusion that little relationship is found between the functional group of the dye and the fastness to the flame retardant finish since the same functional group gives entirely different results even under the same finishing condition.

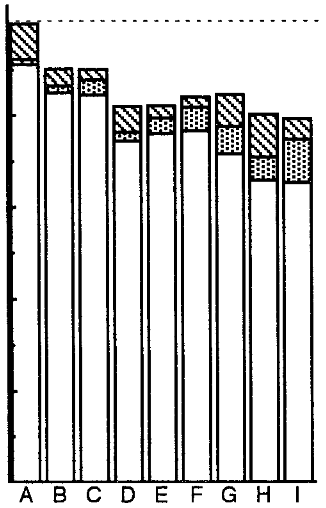
C. I. Reactive Blue 5



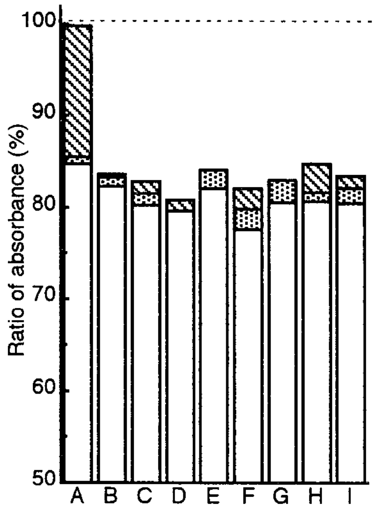
C. I. Reactive Blue 2



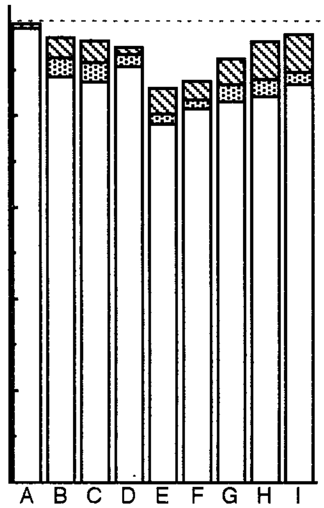
C. I. Reactive Brown 7



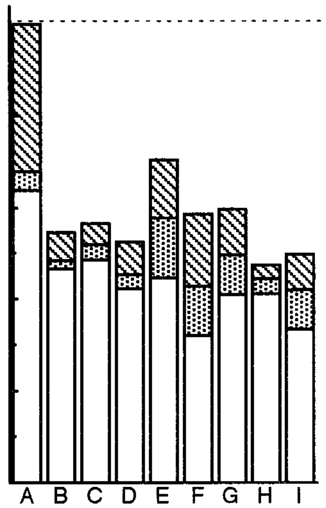
C. I. Reactive Brown 2



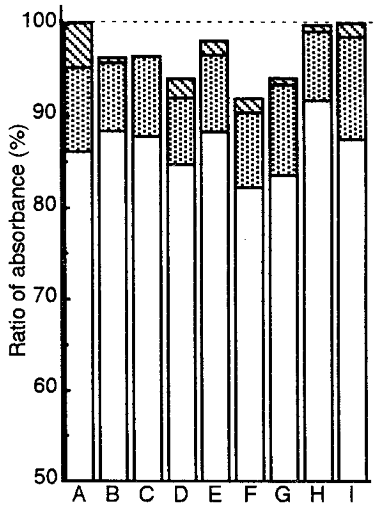
C. I. Reactive Blue 52



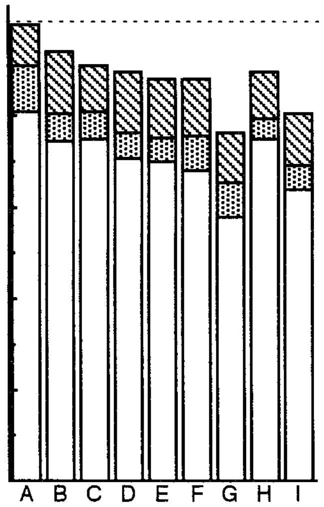
C. I. Reactive Blue 13



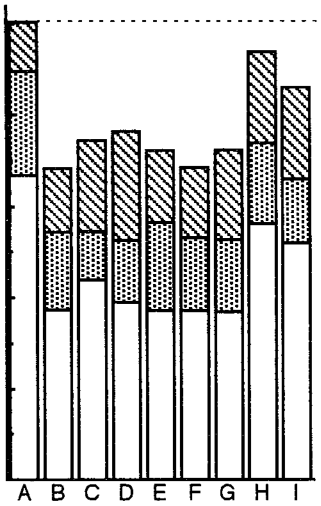
C. I. Reactive Black 1



C. I. Reactive Blue 41



C. I. Reactive Yellow 2



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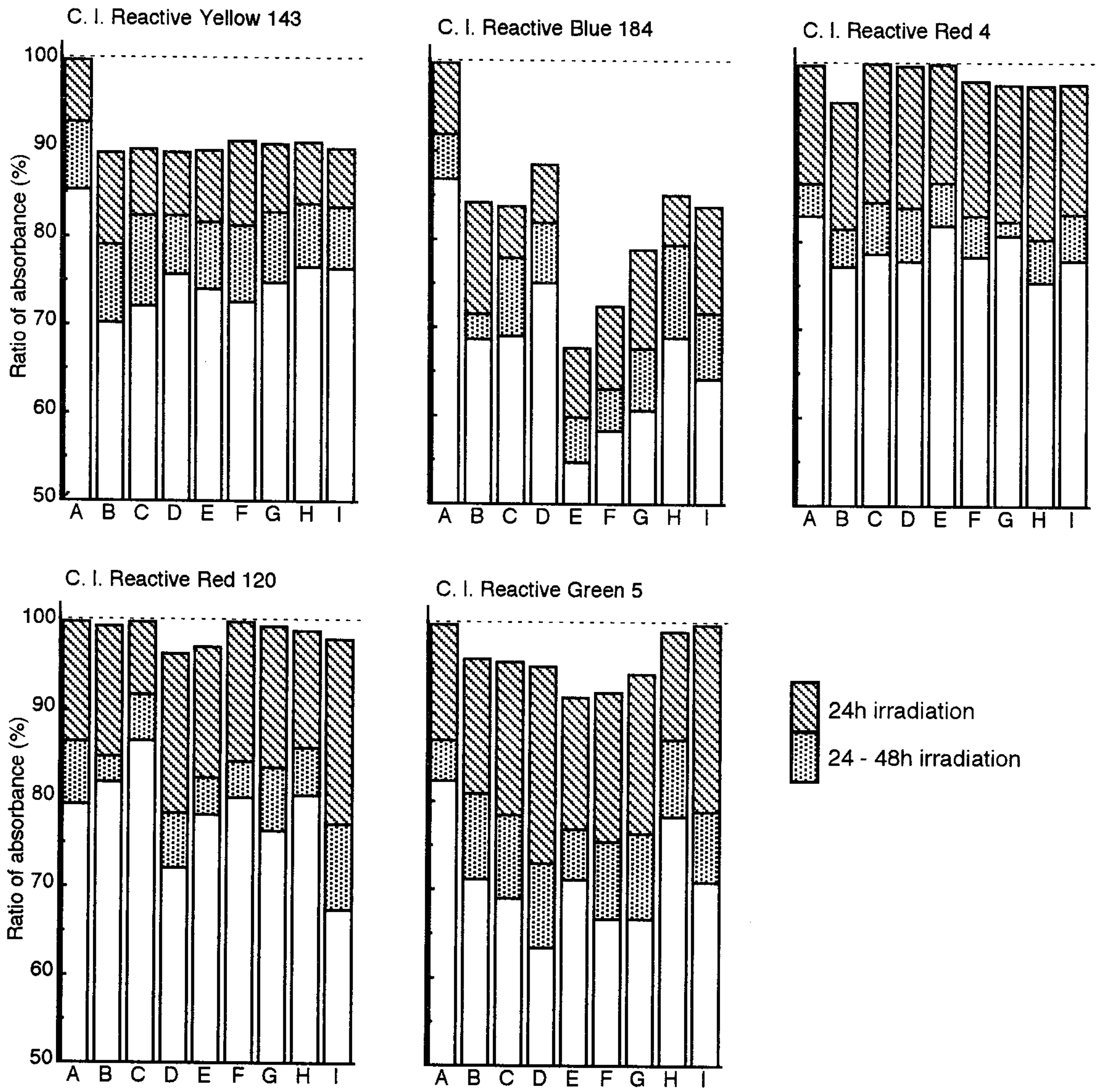


Fig. 4-3 Effects of ultraviolet irradiation on colors of unfinished and flame retardant finished cotton fabric dyed with reactive dyes.

(b) Effects of ultraviolet irradiation on flame retardant dyed fabric

The effect of ultraviolet irradiation which is reflected on the discoloration of dyed fabric were classified as follows as shown in Fig.4-3.

(1) The best lightfastness was shown by Blue 5, Blue 2, Brown 7, Brown 2 and Blue 52, a range of reduced ratios of which was 0-0.5%. Since the first two dyes belong to anthraquinone type, the unfinished dyed fabric showed only 1-2% reduction showing strong resistance to irradiation. The effects of the flame retardant finish on the lightfastness were that Blue 2 showed 2-3% reduction under the all finishing conditions (C-I) but B (0.5%), and in the case of Blue 5, B, C, F and G showed no reduction and the rests showed 3-4% reduction. These results suggests that the flame

retardant finish gives little effect on the lightfastness of, at least, anthraquinone type reactive dyes. However, the discoloration caused by the flame retardants containing phosphoric acid and resins (samples D, E and G) was considerable. Though the rest three dyes belong to bisazo type, lightfastness of these dyes were as high as that of the above mentioned anthraquinone type. Among these dyes, it seems worth paying attention to Brown 2, i.e., the unfinished fabric dyed with this dye showed considerable reduction (15%) while the flame retardant finished samples showed a little discoloration (less than 5%), which means that the flame retardants inhibit discoloration to be caused by the ultraviolet irradiation.

(2) The next grade is from less than 5% to about 15%, to which Blue 13 and Black 1 of monoazo type and Blue 41 of phthalocyanine type belong. The discoloration of Blue 13 was inhibited by the flame retardant finish as observed in the case of Brown 2. Black 1 after the flame retardant finish exhibited such typical behavior that the color reduction was a little in the first 24 h irradiation followed by 10-15% reduction during 24-48 h irradiation. In the case of Blue 41, all samples A-I showed almost the same degree of discoloration (about 10%), which means that the flame retardant finish under any condition with any additive give little effect on the lightfastness of the dye of this type.

(3) The next range of the reduction ratio is 13-20%. Yellow 2, Yellow 143 of monoazo type and Blue 184 of bisazo type belong to this range. A common behavior of these three dyes is that little difference was found between discolorations of each unfinished sample and those of the finished samples as observed in the case of Blue 41 mentioned above.

(4) The largest reduction range is 20-30% most of which was given during the first 24 h irradiation. Red 4, Red 120 and Green 5 showed such discoloration, of which Green 5 disclosed the worst lightfastness.

Attention should be paid to the fact that these three dyes showed the strongest resistance to the flame retardant finish. In these cases, the unfinished samples themselves showed considerably large reduction, e.g., 16.5% for Red 4, 18% for Green 5 and 20.2% for Red 120, and the discoloration of all finished fabric dyed with Red 4 and Green 5 were larger than those of the unfinished samples. But in the case of Red 120, finished samples B, C, E, F and H exhibited less reduction compared with the unfinished sample showing inhibiting effect of the flame retardant finish on the discoloration by the irradiation.

(c) Combined effect of flame retardant finish and ultraviolet irradiation

The effects of the flame retardant finish and the ultraviolet irradiation were discussed separately in the above clauses, but these effects will participate together in the practical use when dyed fabrics are finished and followed by the exposure of sunlight.

As the result of an overall observation by taking the both effects into consideration, the reactive dyes used for this study were classified into the following five types.

(1) Those showed strong resistance to flame retardant finish but very low lightfastness, to which Red 4, Red 120 and Green 5 belong.

(2) Those showed comparatively large discoloration by the flame retardant finish but little or a little discoloration by the irradiation are Blue 5, Blue 2 and Brown 2. Being anthraquinone type, Blue 5 and Blue 2 showed, as anticipated, favorable lightfastness. Whereas in the case of Brown 2, though the unfinished sample showed considerable discoloration by the irradiation, color reduction of every finished sample was much less than that of the unfinished sample. This fact probably means that the flame retardant finish inhibits the discoloration caused by the irradiation.

(3) A type which showed moderate discoloration by both flame retardant finish and irradiation, to which Brown 7 and Black 1 belong. The ratios of discoloration by the flame retardant finish were less than 10% and those by the irradiation were not more than that shown by the unfinished samples.

(4) The worst type was such that showed the large discoloration by both flame retardant finish and ultraviolet irradiation. Yellow 2, Yellow 143, Blue 13 (monoazo type) and Blue 184 (bisazo type) having MCT or MFT showed such unfavorable behavior.

(5) The best type was that showed high fastness to both flame retardant finish and ultraviolet irradiation. Blue 52 of bisazo type having TCP is an example. As to the effect of flame retardant finish on this dye, samples E and F, especially E showed larger discoloration than the rests because of low pH caused by addition of phosphoric acid. But, such results does not involve any problem practically since phosphoric acid is not used neither alone nor with glyoxal type resin TS-10 in any practical use.

It is noteworthy that this dye has high fastness both to the flame retardant finish and the ultraviolet irradiation even though not belonging to anthraquinone type but to azo type.

From the overall standpoint, Table 4-3 is shown for a quick and comprehensive evaluation and mutual comparison of the fastness to both finish and irradiation, which will concretely illustrate what were described above.

Table 4-3 A grading of color fastness for gaich evaluation of reactive dyes.

	Flame retardant finish	Ultraviolet irrdiation		Finish + Irradiation
		24h irradiation	48h irradiation	
	B C D E F G H I	A B C D E F G H I	A B C D E F G H I	B C D E F G H I
Red 120	◎◎◎◎◎◎◎◎	○○○△○△△○△	△△○△△△△△×	△○△△△△△×
Red 4	◎◎◎◎◎◎◎◎	○○○△○○○△○	△△△△△△△△△	△△△△△△△△
Blue 52	◎◎◎○○◎◎◎	◎◎◎◎◎◎◎◎◎	◎◎◎◎◎◎◎○○	○○◎○○○○○
Black 1	◎◎○◎○○◎◎	◎◎◎◎◎◎◎◎◎	○○○○○○○○○	○○△○△△○○
Brown 7	◎○○○○○○○	◎◎◎◎◎◎◎◎◎	◎◎◎◎◎◎○○○	○○○○○○△△
Green 5	◎◎◎○○○◎◎	○△△△○△△○△	△△△×△△△△△	△××△××△△
Blue 41	◎◎◎○○○○○	◎○○○○○○◎○	○○○○○○○○○	○○○○△△○△
Blue 5	○◎○○△△◎◎	◎◎◎◎◎◎◎◎◎	◎◎◎◎◎◎◎◎◎	○◎○○△△◎◎
Blue 2	◎◎○○○○○○	◎◎◎◎◎◎◎◎◎	◎◎◎◎◎◎○◎◎	◎○○△△△○○
Yellow 143	○○○○○○○○	○○○○○○○○○	△△△○△△△○○	△△△△△△△△
Yellow 2	△○○○△○○○	○○○○○○○○○	△△△△△△△△△	×△××××△△
Brown 2	△△△△△△△△	○◎◎◎◎◎◎◎◎	△◎◎◎◎◎◎◎◎	△△△△△△△△
Blue 184	△△○×△△○△	○○○○○○○○○	○△○○○○△△△	××△×××××
Blue 13	△△△○△△△△	△◎◎◎○○◎◎◎	△◎◎◎○○○◎○	△△△△×△△×

Ratio of discoloration : ◎) 0~5%, ○) 5~15%, △) 15~30%, ×) 30~100%

As a final point, another attention should be focused to the comparison between Blue 52 and Blue 184. These two blue dyes showed entirely different, even contrary attitudes to the flame retardant finish as well as to the ultraviolet irradiation, i.e., the former exhibited the best result and the latter the worst fastness though they both possess the same chromogen. Therefore, it is supposed that not only chromogen or functional group but also the whole chemical structure may participate in the fastness, e.g., Blue 52 may contain in its structure a kind of auxiliary group which effectively exert to avoid any damage to the dye structure, but nothing can be evidently described since the chemical structures of the dyes used for this study are unfortunately unpublished except those shown in Fig. 4-1.

(d) Effects of additives for Pyrovatex finish on discoloration of dyed fabric

It is also important to select the most favorable finishing condition as well as additives for Pyrovatex finish to minimize the discoloration caused by the flame retardant finish and by the ultraviolet irradiation.

As the results of the investigation carried out this time, it has been clarified that the discoloration was most largely caused by the addition of phosphoric acid which acts an important role for the flame retardant finish with Pyrovatex, whereas the addition of urea and ammonium chloride decreased discoloration. Moreover, according to our previous study, the flame retardance can be also improved by addition of these additives. Therefore, it can be concluded that the addition of urea and ammonium chloride is necessary for the flame retardant finish with Pyrovatex from the standpoints of the flame retardant finish and color stabilization of dyed fabrics.

3) Conclusion

From the results of the observation mentioned above, it is difficult to deduce any clear conclusion concerning what kinds of dyes would be recommendable, i.e., any significant regularity or universal validity could be hardly available for the relationship between structure and fastness of dyes. One of the reason is attributed to lacking in information about the structures of dyes used for this study. However, the following tendencies were found at least from what were investigated this time.

As to the relationship between the dye structures and fastness to the flame retardant finish, dyes the structures of which are similar to each other showed similar behavior for the discoloration, and halogens (chlorine in this case) at positions other than the functional group (MCT) or a five membered ring consisting of C and N gave larger discoloration.

The investigations for the effect of additives for the flame retardant finish clarified that the addition of phosphoric acid gave an enhancement of discoloration probably because of acidity.

The most important finding is that the addition of urea and ammonium chloride inhibits the discoloration to be caused by phosphoric acid and resins otherwise, which is very advantageous also from the practical standpoint since the addition of urea and ammonium chloride contributes to the improvement of the flame retardance.

As for the lightfastness, dyes of anthraquinone type showed the best fastness followed by bisazo type even after the flame retardant finish just as universally observed with unfinished dyed fabrics in almost all cases. The finishing conditions gave little effect on the lightfastness.

The overall evaluation led us to conclude that as illustrated in Table 4-3, the worse effect becomes dominant to keep the discoloration at the level of larger reduction when the flame retardant finish is followed by the ultraviolet irradiation and the both effects are combined.

As far as Pyrovatex finish is concerned, if the finishing condition H or I is selected, dyes of anthraquinone type would be most recommendable after all.

4-1-2 Effects of PROBAN Finish on Discoloration of Cotton Fabric Dyed with Vat Dyes as well as on Discoloration Caused by Ultraviolet Irradiation in Comparison with the Results Obtained from Pyrovatex Finish and Reactive Dyes

The dyes used for this study are 15 kinds of reactive dyes having each of monoazo, bisazo, anthraquinone or phthalocyanine type chromogens with vinyl sulfonyl group (VS) in addition to the aforementioned MCT, MFT and TCP, and also 8 kinds of vat dyes of anthraquinone type with different kinds of substituents. As the flame retardant finish, another representative universally used durable flame retardant finish, PROBAN finish was also adopted in comparison with Pyrovatex finish. The discoloration was evaluated by K/S values derived from the Kubelka-Munk's function this time.

Thus, the investigation was carried out aiming to reveal what kinds of dyes would show the most favorable fastness to the flame retardant finishes and the lightfastness to obtain some helpful information for the practical uses.

1) Experimental

(a) Materials

(1) Fabric: 100% cotton fabric was the same as described in 2-2-2.

(2) Dyes: Reactive dyes and vat dyes used for this study are shown in Table 4-4 and 4-5 and Fig.4-4. Of these dyes, C.I. Reactive Blue 19 and Red 22 were obtained from 2 different companies {Hoechest Co. (Remazol) and Sumitomokagaku Co. (Sumifix)}, Blue 21 from Hoechest Co., Red 4, Yellow 143, Brown 7, Blue 2, Blue 52 and Green 5 from Ciba-Geigy Co. (Cibacron), Yellow 37, Yellow 42, Black 5 and all of the vat dyes from Sumitomokagaku Co. (Sumifix).

Table 4-4 Mark style illustration for fastness of reactive dyes evaluated on the basis of reduction ratios obtained from K/S value.

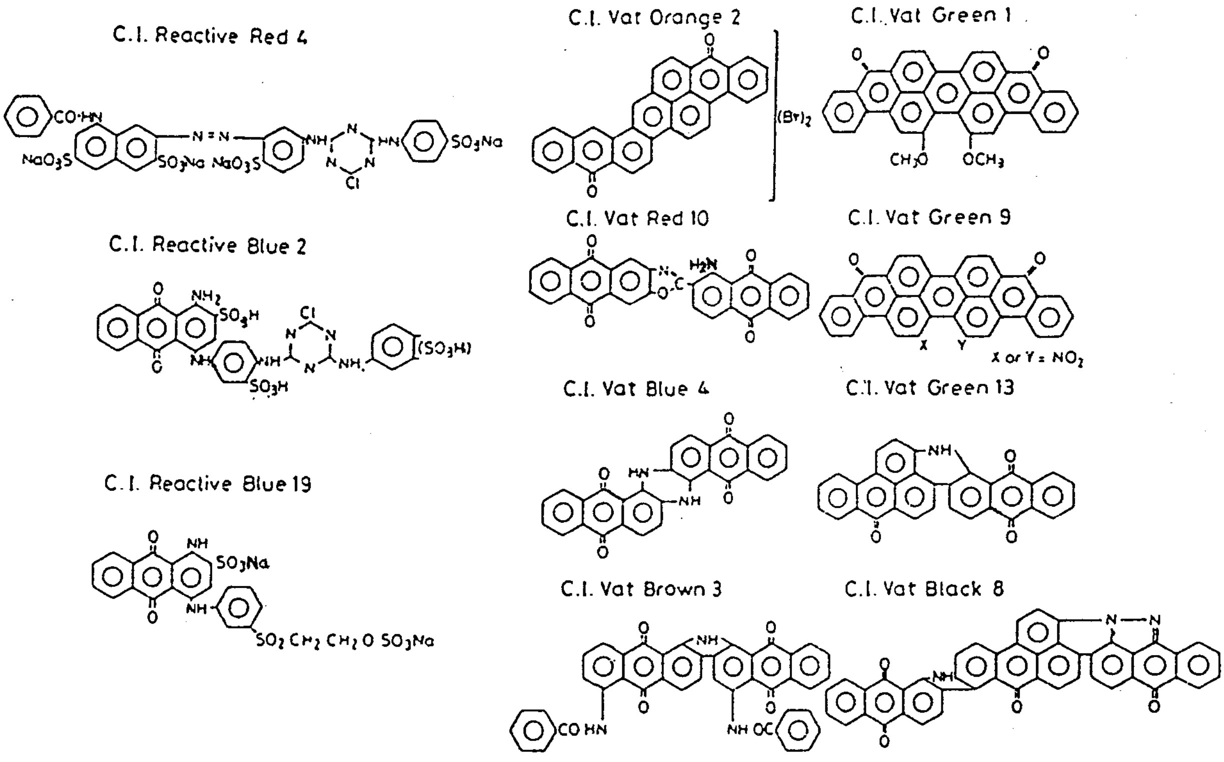
◎) 0~10%, ○) 10~30%, △) 30~50%, ×) 50%~

C. I. Name	Type of dye (Functional group)	Retardant		Irradiation					
		Pyrovatex	Proban	unfinished		Pyrovatex		Proban	
				24h	48h	24h	48h	24h	48h
Yellow 143	Monoazo (MFT)	○	△	△	×	△	×	×	×
Yellow 37	Monoazo (VS)	○	○	○	△	○	△	×	×
Yellow 42	Monoazo (VS)	○	△	△	×	△	×	×	×
Red 4	Monoazo (MCT)	○	×	○	○	◎	△	×	×
Red 22 (R)	Monoazo (VS)	◎	○	○	△	△	△	×	×
Red 22 (S)	Monoazo (VS)	○	○	○	△	○	△	×	×
Violet 22	Anthraquinone (VS)	○	△	◎	◎	◎	◎	×	×
Blue 52	Bisazo (TCP)	○	○	◎	◎	◎	◎	×	×
Blue 2	Anthraquinone (MCT)	○	○	◎	◎	◎	◎	◎	○
Blue 19 (R)	Anthraquinone (VS)	◎	○	◎	◎	◎	◎	○	○
Blue 19 (S)	Anthraquinone (VS)	○	○	◎	◎	◎	◎	○	○
Blue 21	Phthalocyanine (VS)	◎	△	◎	△	○	△	△	×
Green 5	Phthalocyanine (MCT)	○	○	△	×	△	×	×	×
Brown 7	Bisazo (MCT)	○	×	◎	○	◎	○	△	×
Black 5	Bisazo (VS)	○	△	○	○	○	○	×	×

Table 4-5 Mark style illustration for fastness of vat dyes evaluated on the basis of reduction ratios obtained from K/S value.

◎) 0~10%, ○) 10~20%, △) 20~40%, ×) 40%~

C. I. Name	Type of dye (Functional group)	Retardant		Irradiation					
		Pyrovatex	Proban	unfinished		Pyrovatex		Proban	
				24h	48h	24h	48h	24h	48h
Orange 2	Anthraquinone	◎	◎	△	△	◎	◎	○	○
Red 10	〃	○	○	○	○	◎	◎	◎	◎
Blue 4	〃	◎	○	○	○	◎	◎	◎	◎
Green 1	〃	◎	◎	○	△	◎	◎	◎	◎
Green 9	〃	×	×	○	○	◎	○	◎	◎
Green 13	〃	△	△	○	○	◎	◎	◎	◎
Brown 3	〃	△	△	○	○	◎	○	○	○
Black 8	〃	△	△	◎	○	◎	◎	◎	◎


C.I. Reactive Red 4

C.I. Reactive Blue 2

C.I. Reactive Blue 19

C.I. Vat Orange 2

C.I. Vat Red 10

C.I. Vat Blue 4

C.I. Vat Brown 3

C.I. Vat Green 1

C.I. Vat Green 9

C.I. Vat Green 13

C.I. Vat Black 8

Fig. 4-4 Chemical structures of reactive dyes and vat dyes used for the present study.

(3) Flame retardants: Pyrovatex CP and THPS precondensate were used for Pyrovatex finish and PROBAN finish respectively.

(b) Methods

(1) Dyeing

(i) Reactive dyes: The exhaustion method was used in all the cases as described in the previous section.

(ii) Vat dyes: IW method was applied to Vat Brown 3 and IN method was used for other 7 kinds of vat dyes under the following condition.

Concentration of dyes: 2% o.w.f.

Additives: 3-5 ml of sodium hydroxide (S. G. 1.385) were added for IW method, 10-20 ml for IN method, 1.5 g/l of sodium hydrosulfite for both methods, 10 g/l of sodium sulfate only for IW method.

Temperature: 45-50°C for IW method, 50-60°C for IN method.

Time: 60 min in both cases.

Ratio of liquid to fabric: 100:1

(2) Flame retardant finishes

(i) Pyrovatex finish: Cotton fabric dyed with the above mentioned dyes was immersed in a bath containing 32% Pyrovatex CP, 8% hexamethylolmelamine together with 0.24% of its catalyst, 1% urea and 0.5% ammonium chloride for 40 min and 10 min consecutively padding after each immersion, cured and soaped as described in 3-1-1.

(ii) PROBAN finish (THPS ammonia cure): Each dyed cotton fabric was treated with THPS-precondensate containing 2.6% sodium acetate and 0.2% nonionic surfactant for 10 min, padded, preliminarily dried, cured by exposure to ammonia and soaped as mentioned in 3-1-2.

(3) Ultraviolet irradiation

The dyed samples were irradiated before and after each finish with ultraviolet ray for 24 and 48 h by using Regular Life Fademeter FA type (Suga Shikenki Co.) with a carbon arc light source.

(4) Evaluation of discoloration

The discoloration was evaluated for each sample by the spectrophotometric measurement of the reflectance (R) before and after the flame retardant finishes and the ultraviolet irradiation using Spectrophotometer Shimadzu UV2000 equipped with Ulbricht sphere in a range of 200-840 nm, from which K/S value was calculated for each sample from Kubelka-Munk's function $(1\text{-}R)^2/2R$. The ratio of the value for each treated and/or irradiated sample to that for the untreated and / or the unirradiated sample was compared to each other.

2) Results and Discussion

Prior to discuss about the result of the discoloration brought about by the flame retardant finish and the ultraviolet irradiation, it seems necessary to consider how to express the degree of discoloration for the comparison of the effects of the finish and irradiation between unfinished and finished samples as well as between Pyrovatex finished and PROBAN finished samples. In general, the discoloration observed with the dyed fabric is attributed to the structural modification of each dye molecule having an absorption at each specific wavelength to be caused by the effect of the flame retardant finish and / or the energy of the irradiated ultraviolet ray. Therefore, we adopted Kubelka-Munk's K/S function derived from the spectral reflectance R which is proportional to the amount of dyes fixed on the fabric to calculate $K/S = (1\text{-}R)^2/2R$ for each sample from the value of R. This is because the most adequate way to express the degree of the structural modification observed before and after the flame retardant finish and / or the ultraviolet irradiation is thought to be the relative change in the amount of the dye molecule exhibiting the unmodified or modified structures respectively before and after the finish and the irradiation. K/S is a function established on the bases of the Kubelka-Munk's two constant theory which defines that nonfluorescent lamella substances which absorb and scatter the light can be identified by an absorption coefficient (K) and a scattering coefficient (S) as a function of wavelength (λ) of the visible spectrum. It is generally recognized that this is applicable to any sample in which K and S are homogeneous material but not to any inhomogeneous material like fabrics. However, we used this function sine the object of this investigation is not to observe the amount of the dye itself but the relative comparison such as changes observed between finished and unfinished samples as well as between irradiated and unirradiated samples. Moreover, this function is widely used for the quantitative evaluation of dyestuffs fixed on the fabric.

(a) Effects of flame retardant finishes on dyed fabric

Fig.4-5 shows the relative comparison of the ratios of K/S (finished/unfinished) observed among the dyes as well as between Pyrovatex finished samples and PROBAN finished samples.

In the case of reactive dyes, Pyrovatex finished fabric showed comparatively small or moderate reduction in a range of 5% (Blue 19, Blue 21 and Red 22) - 25% (Black 5). Comparing two types of Blue 19 as well as of Red 22, Remozol type from Hoechest Co. gave better results, less reduction (5%), while Sumifix type from Sumitomokagaku Co. showed higher reduction (15-16%). The dyes which gave the best result, only 5% reduction, all have VS group though with three different chromogens (Blue 19, Red 22 and Blue 2), whereas a dye showing the largest reduction also possess VS group (Black 5). Moreover, comparing Green 5 and Blue 52, these two dyes show little different values though they have different functional groups and chromogens. Such result may suggest that the effect of the flame retardant finish on the discoloration, that is, the fastness to the flame retardant finish little depends on the structure of dye molecule, and the discoloration by Pyrovatex finish maintains at a level of 15% in average which will not bear any serious problem.

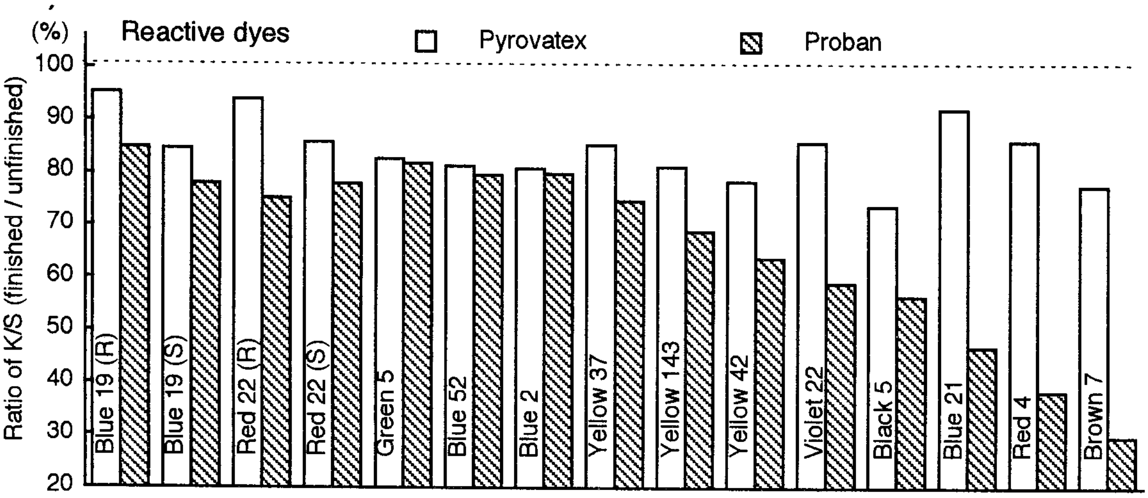


Fig. 4-5 Effects of flame retardant finishes, Pyrovatex finish and Proban finish, on reactive dyes expressed by change in K/S values.

As to PROBAN finish, on the other hand, Blue 19 showed the highest fastness also in this case, but the reduction is 15%, much larger than that given by Pyrovatex, while Red 4 and Brown 7, azo type having MCT group showed awful reduction, even 60-70%. But those having VS or TCP group showed less reduction even with azo type chromogen, and those of anthraquinone or phthalocyanine types exhibited around 20% reduction though they have MCT group. Such findings suggest that the combination of azo type chromogen and MCT are strongly affected by PROBAN finish.

Since Pyrovatex finish is carried out in acid medium while PROBAN finish in alkaline atmosphere, almost every dye may have larger acid resistance than the alkali resistance, but Blue 19 (Remazol) which consists of anthraquinone and VS has comparatively strong resistance to both acid and alkali, on the other hand, Blue 21, Red 4 and Brown 7 are acid resistant but not alkali resistant. An attention is also drawn to the fact that Green 5, Blue 52 and Blue 2 exhibit little or a little difference between the effect of Pyrovatex finish and that of PROBAN finish, which probably means that these 3 dyes consisting of a combination of bisazo type chromogen and TCP, phthalocyanine type chromogen and MCT as well as of anthraquinone type chromogen and MCT have similar degree of acid and alkali resistances showing such moderate discoloration as around 20%.

The results mentioned above can be summarized as follows:

PROBAN finish extremely affects the reactive dyes whereas Pyrovatex finish gives much less effect confirming that the reactive dyes can not be used in combination with PROBAN finish in the practical use. As to the respective effects of the chromogens and the functional groups, VS gave the better result than the chlorinated azine groups among the functional groups while the anthraquinone type chromogen was recognized to show the highest fastness as the result of comparing various kinds of chromogens with the same functional group (each of VS or MCT). The above facts led us to conclude that Blue 19 consisting of anthraquinone type chromogen and a functional group VS gave the best result from the standpoints of both Pyrovatex and PROBAN finishes.

In the case of vat dyes, a characteristic finding for this kind of dyes which first draws our attention is that only a little difference is observed between the effect of Pyrovatex finish and that of PROBAN finish though the former is slightly less than the latter, which suggests that vat dyes have the same degree of sensitivities to both acid and alkaline media. The dyes which gave the most favorable result were Green 1 and Orange 2 showing K/S even exceeding the unfinished sample probably because of a little shading effect, followed by Blue 4 which showed a comparatively allowable discoloration less than 10%. On the other hand, Green 9, Brown 3 and Black 8 showed the most undesirable results even 30-40% reduction. When the degree of the discoloration shown in Fig.4-6 is considered with the chemical structures of dyes illustrated in Fig.4-4 in which Green 3 is substituted for unpublished Green 13 because of the similarity of both structures, many-numbered anthraquinone type ring with methoxy groups (Green 1) or skeletal structure without any substituent other than =O (Orange 2) showed the best results whereas those with NO_2 group or CO-NH group exhibited the worst fastness. It is of interest that a substitution of NO group (Green 9) for CH_3O group (Green 1) gives marked reduction of the fastness, whereas those having the same substituent =NH group reveals considerably different discoloring behaviors depending upon other constitutional components involved in the structures as observed among Blue 4, Brown 3 and Black 8.

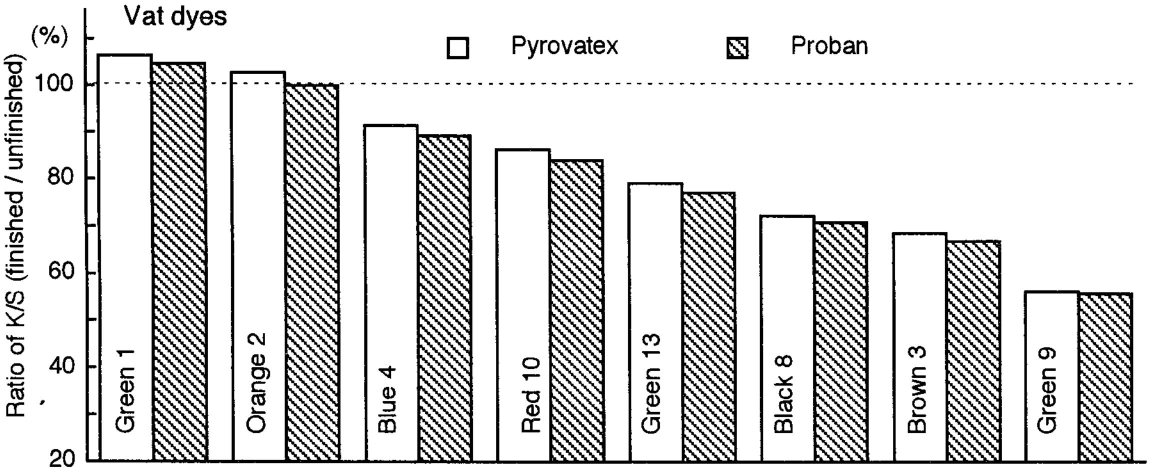


Fig. 4-6 Effects of Pyrovatex finish and Proban finish on vat dyes shown by change in K/S values.

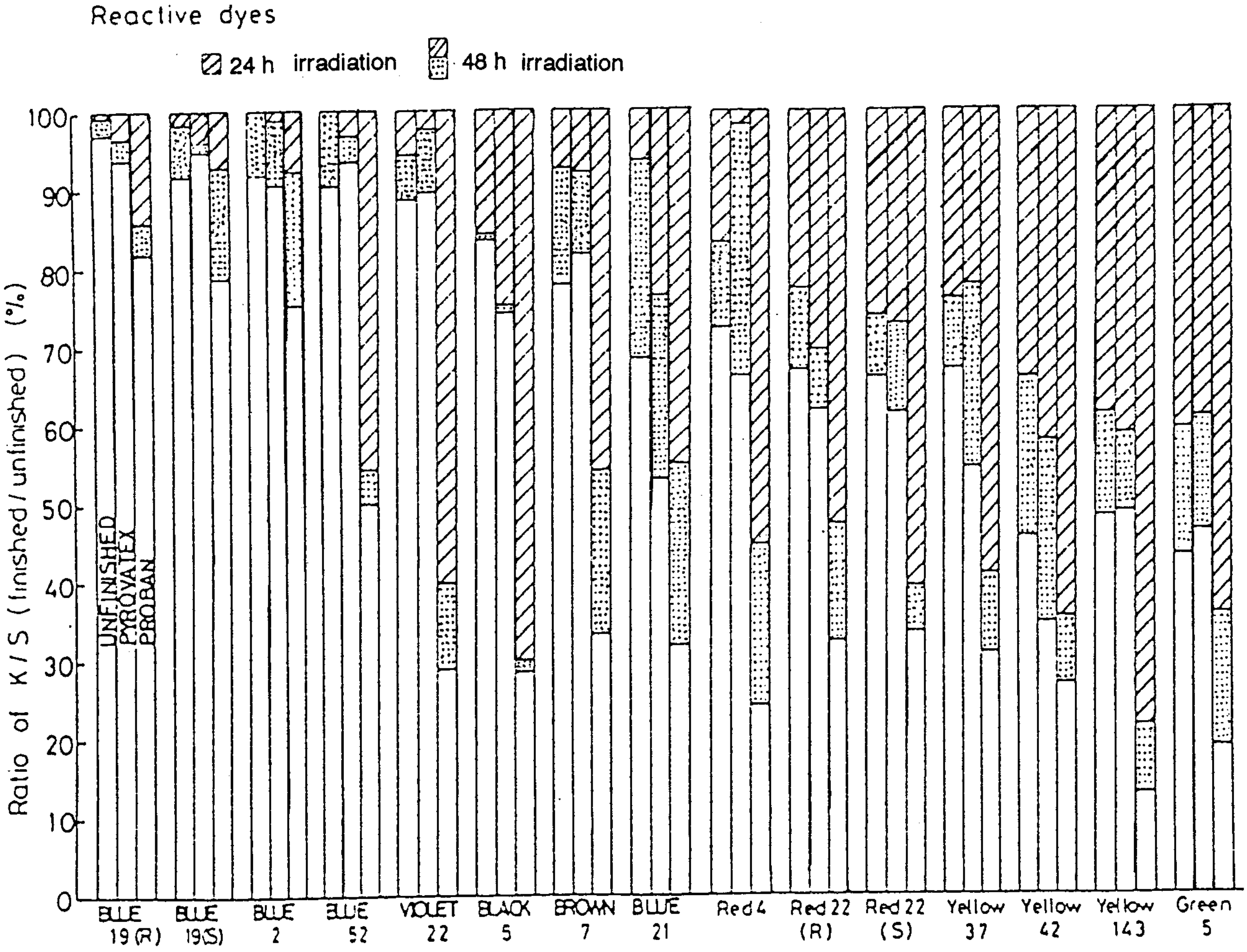


Fig. 4-7 Effect of ultraviolet irradiation on reactive dyes observed with and without flame retardant finish, Pyrovatex finish or Proban finish.

(b) Effect of ultraviolet irradiation on dyed fabric

Fig.4-7 shows the ratio of K/S value of the irradiated sample to that of the unirradiated sample obtained for each dyed fabric. The values for the unfinished, Pyrovatex finished and PROBAN finished samples of each dyed fabric are shown together for easier comparison.

(1) In the case of reactive dyes

The unfinished dyed samples should be first compared one another before comparing between unfinished and finished samples as well as between Pyrovatex finished and PROBAN finished samples. Blue 19 and Blue 2 are both anthraquinone type with different functional groups, VS and MCT, showed the best lightfastness as expected and followed by Blue 52 (bisazo type with TCP) and Violet 22 (monoazo type with VS). On the other hand, Yellow 42, Yellow 143 and Green 5 exhibited extremely large discoloration e.g., 52% (Yellow 42) - 57% (Green 5) which is the worst range. Such difference in the lightfastness observed between blue color and yellow color is also reasonable when the energy absorbed by dyes is taken into consideration in addition to the dependence on the type of chromogen. The medium reduction, around 20% is observed for Black 5 and Brown 7 which are both bisazo type, and 30% for Red 4, Red 22 and Yellow 37, all monoazo type, as well as for Blue 21, phthalocyanine type.

(i) Effect of Pyrovatex finish

Even after Pyrovatex finish, Blue 19 and Blue 52 showed the best result, only 5% reduction, confirming that the characteristic of the anthraquinone type chromogen for the resistance to the ultraviolet ray favorably works even with Pyrovatex finish. Whereas the worst discoloration, 45-55% reduction, was observed for Blue 21 and Green 5, both phthalocyanine type, and Yellow 37, 42, 143, all monoazo type. The medium discoloration, 15-25% reduction was shown by Black 5 and Brown 7, around 37% by Red 22. Thus, the tendency exhibited by Pyrovatex finished samples is similar to that shown by the unfinished samples which suggests that Pyrovatex finish little affects the effect of ultraviolet irradiation on the reactive dyes.

(ii) Effect of PROBAN finish

It is obviously shown that PROBAN finish gave tremendously large discoloration to almost all kinds of the dyes extending over 18-87%. Blue 19 showed the least reduction but around 20% followed by Blue 2, about 30%, and Violet 22, Black 5, Red 4, Yellow 143 and Green 5 exhibited the largest discoloration ratio in an unexpectedly large range, 70-87%, especially Black 5 and Yellow 143 showed this much already during 24 h irradiation. The rests are Blue 52 (50%), Brown

7, Blue 21, Red 22 and Yellow 37 (65-70%) respectively. Such finding will explain here again why reactive dyes are seldom used practically in combination with PROBAN finish, and the results obtained here have confirmed such ill effects of PROBAN finish in comparison with Pyrovatex finish empirically and numerically.

(2) In the case of vat dyes

Comparing the ratios of K/S values among the unfinished samples, little difference was observed among them in a range of 15-20% with one exception 28% shown by Orange 2 which showed a very favorable fastness to the flame retardant finish. The result of the observation for the effect on the flame retardant finishes on the discoloration caused by the ultraviolet irradiation disclosed unexpectedly that the all finished samples showed remarkably less discoloration than that of the unfinished samples as shown in Fig.4-8, which means that both flame retardant finishes protect the dyes from the ultraviolet ray and inhibit the discoloration caused by the irradiation. A phenomenon different from what was shown by the reactive dyes is that PROBAN finish gave less discoloration than that given by Pyrovatex finish in some cases, e.g., Green 13, Blue 4 and Green 9, especially even no discoloration was observed for Green 9. Thus, as far as the effect of the ultraviolet irradiation on the fabric dyed with some selected vat dyes is concerned, the flame retardant finish gives some protective effect at least apparently.

Table 4-4 and 4-5 are lists of the evaluation on the basis of grades determined by the reduced ratios of K/S values obtained after each flame retardant finish followed by the ultraviolet irradiation for 24 and 48 h. The grades are indicated by the respective symbol marks. According to the tables, apparent but quick evaluation can be done as follows: In the case of reactive dyes, Red 22 shows fairly good fastness to the finish but not to the irradiation. Violet 22 and Blue 52 exhibit remarkable lightfastness for Pyrovatex finished fabric but worst result for PROBAN finished fabric. Blue 2 and Blue 19 show not only much favorable lightfastness for both Pyrovatex and PROBAN finished samples but also fairly good fastness to both finishes.

In the case of vat dyes on the other hand, all finished samples dyed with vat dyes examined this time showed favorable lightfastness, but it is unexpected that the lightfastness of the unfinished dyed sample was not so desirable though the dyes used this time have the anthraquinone type chromogen. As to the fastness to the flame retardant finish, Orange 2, Green 1, Blue 4 and Red 10 showed high fastness, specially the first 2 are the best, while Green 9, Green 13, Brown 3 and Black 8 exhibited unfavorable results, particularly Green 9 or Brawn 3 was the worst case.

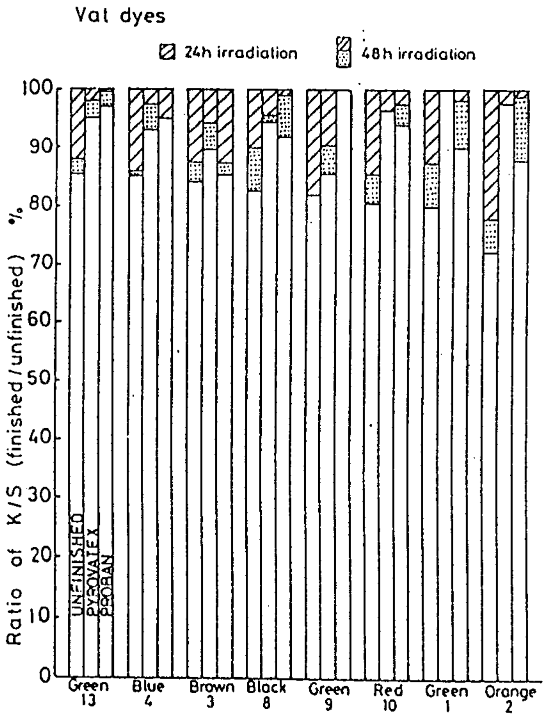


Fig. 4-8 Effect of ultraviolet irradiation on vat dyes observed with and without flame retardant finish, Pyrovatex finish or Proban finish.

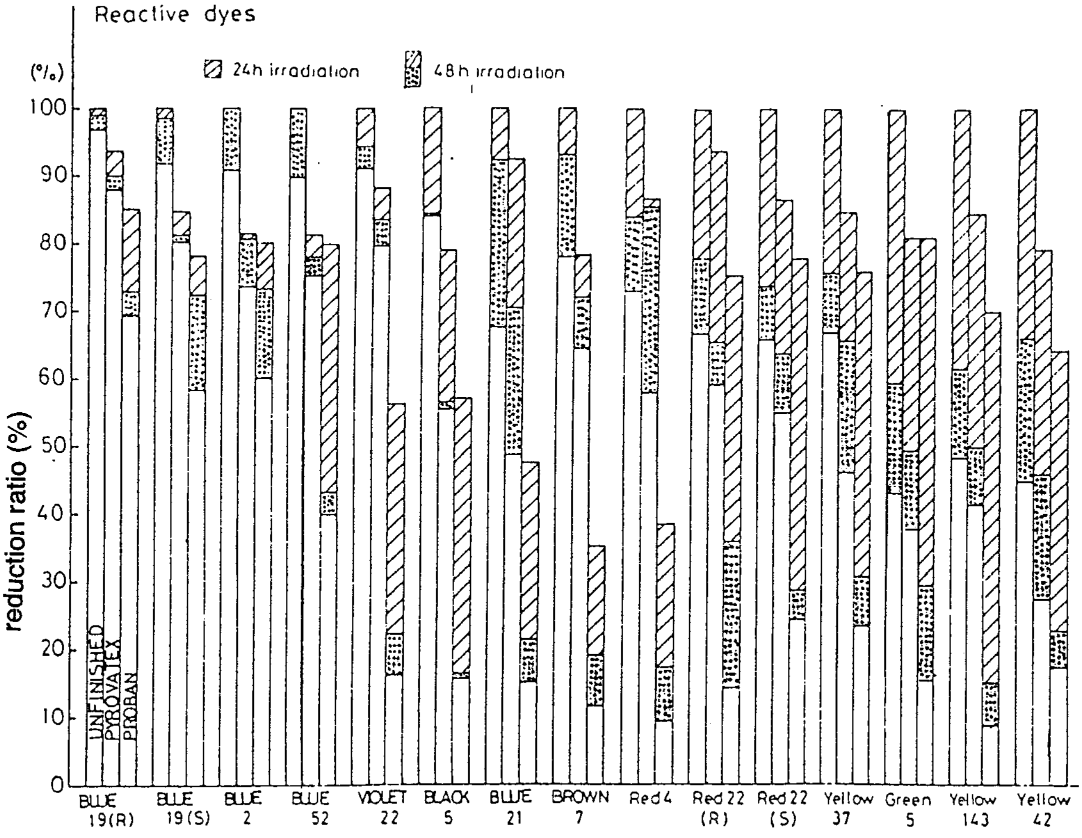


Fig. 4-9 Effect of flame retardant finish in combination with ultraviolet irradiation on reactive dyes.

(c) Effects of flame retardant finishs in comfination with ultraviolet irradiation

(1) In the case of reactive dyes

(i) Effect of Pyrovatex finish and ultraviolet irradiation

As shown in Fig. 4-9, Blue 21 and Red 22 showed comparatively high fastness to Pyrovatex finish. After all, only Blue 19 (R) and Violet 22 showed allowable result, specially the discoloration of Blue 19 (R) observed after 48 h irradiation is 10-12%, which is very much recommendable for practical use though Blue 19 (S) showed larger reduction (about 20%) similar to that given by Violet 22.

(ii) Effect of PROBAN finish and ultraviolet irradiation

It is clearly evident from Fig.4-9 that almost all PROBAN finished samples showed awful discoloration as large as 90% reduction or more. Even Blue 19 and Blue 2 which have the highest lightfastness showed 30-40% reduction. Blue 52 and Violet 22 also exhibited extremely large reduction when combined with PROBAN finish though they showed comparatively favorable results in the case of Pyrovatex finish.

(iii) Comparison of effects of Pyrovatex finish and PROBAN finish on color reduction of reactive dyes

The overall observation of the discoloration of the reactive dyes caused by Pyrovatex finish or PROBAN finish in combination with the ultraviolet irradiation have disclosed that PROBAN finish much largely affected the reactive dyes and gave extremely larger reduction than that given by Pyrovatex. Such result is probably attributed to that the acid resistance of the reactive dyes is predominant, whereas the alkali resistance is much inferior, since cotton fabric is treated in acidic bath for Pyrovatex finish and in the alkaline atmosphere for PROBAN finish.

(2) In the case of vat dyes

In comparison with the results observed in the case of the reactive dyes, it is really worth paying attention to that the flame retardant finished samples showed remarkable lightfastness even much better than that of the unfinished dyes samples as illustrated in Fig.4-10. This means that the flame retardant finishes, both Pyrovatex and PROBAN finishes inhibit the discoloration caused by the ultraviolet ray, which is the very meritorious effect of the flame retardant finish.

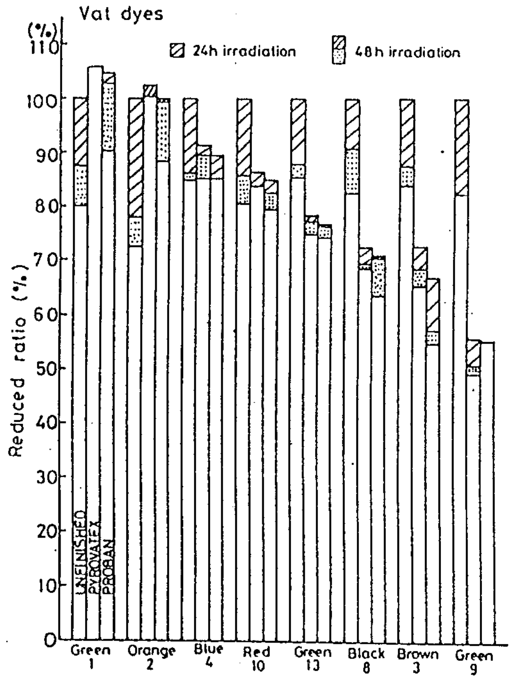


Fig. 4-10 Effect of flame retardant finish in combination with ultraviolet irradiation on vat dyes.

3) Conclusion

The results obtained for the present study led us to conclude as follows:

(a) In the case of reactive dyes

(1) As to the fastness to the flame retardant finish, Pyrovatex finish gave fairly favorable results to all samples examined, specially those having VS as the functional group showed better fastness irrespective of the chromogen.

(2) On the other hand PROBAN finish gave much larger discoloration than that observed with Pyrovatex finish in all cases. Also in this case, those having VS showed the best result though 15-20% reduction at best, whereas 60-70% reduction was exhibited by MCT functional group as the worst case.

(3) As for the effect of the ultraviolet irradiation, dyes of anthraquinone type showed remarkably favorable lightfastness in the case of Pyrovatex finish, e.g., the ratio of discoloration was less than 10% even after 48 h irradiation, while those possessing MCT functional group exhibited 50-60% reduction.

On the other hand, PROBAN finish gave extremely large discoloration except for anthraquinone type dyes, e.g., the largest reduction reached 85-90%.

(4) The combined effect of finish and irradiation is that anthraquinone type dyes with VS functional group showed the best results in both Pyrovatex and PROBAN finishes also in the present study, i. e., only 10-20% reduction was observed in the case of Pyrovatex while PROBAN finish gave larger reduction 30% or more. The worst results were given by monoazo type dyes irrespective of the functional group, e.g., both finishes gave the discoloration larger than 85%. After all, reactive dyes are not applicable to PROBAN finish.

(b) In the case of vat dyes

(1) The dyes which showed the most favorable fastness to the flame retardant finish were those having the structure without any substituent on benzene ring or having methoxy groups, while those with NO_2 or NH-CO showed the worst result.

(2) Since the vat dyes used for this study are all anthraquinone type, every sample showed considerably favorable lightfastness, better than that of the unfinished sample, e.g., no reduction was observed with a few samples and the discoloration was only 5% for Pyrovatex finish or 10% for PROBAN finish even in the worst case.

(3) It was disclosed that the combined effects of finish and irradiation depended on that of the flame retardant finish since the lightfastness was extremely favorable in every case, even better than that of the unfinished samples.

After all, it was empirically evidenced that vat dyes were much more applicable to the flame retardant finished fabric specially in the case of PROBAN finish.

4-2 Effects of Nondurable Flame Retardant Finishes on Discoloration of Dyed Cotton Fabric Caused by Ultraviolet Irradiation

In addition to the durable flame retardant finishes, nondurable flame retardant finishes can not be ignored for unwashable materials for which washing is unnecessary, e.g., interior materials not only for residences but also for offices, e.g., cloths for walls and furnitures or papers for walls and ceilings, or those for which cleaning is required only once or twice a year and refinishing after cleaning is possible, such as curtains, since nondurable flame retardant finishes possess merits from standpoints such as low cost, easy availability and less pyrolytic gas formation etc.

Therefore, the studies on the effects of durable flame retardant finishes described in 4-1 are continued to see the effects of nondurable flame retardant finishes on dyed fabric as well as on the discoloration of dyed fabric to be caused by the ultraviolet irradiation.

4-2-1 Effects of Nondurable Flame Retardant Finishes with Inorganic Compounds Containing N, P, S, Halogens and B on Cotton Fabric Dyed with Reactive Dyes and Vat Dyes.

1) Experimental

(a) Materials

(1) Fabric

Sample fabric used for this study was the same as that described in 4-1.

(2) Dyestuffs

Reactive dyes and vat dyes used for this study are listed in Table 4-6. The structures of dyes published are shown in Fig.4-11.

Table 4-6 List of dyes used for the present investigation.

Type	C. I. Name	Functional Group	Chromogen
Reactive Dye	Blue 171	Monochlorotriazinyl (MCT)	Disazoic type (Naphthalene sulfonic acid)
	Blue 82	Dichlorotriazinyl (DCT)	
	Blue 120	Dichloromonofluoro pyridine (DCMFP)	
	Red 22	Vinyl Sulfonic acid (VS)	Monoazoic type
	Violet 22		Unpublished Disazoic type
	Black 5		
	Blue 19		Anthraquinone
	Blue 194	VS + MCT	Disazoic type
Vat Dye	Vat Red 16	Structures shown in Fig. 4-11	Anthraquinone
	Vat Orange 2		
	Vat Green 1		
	Vat Black 8		

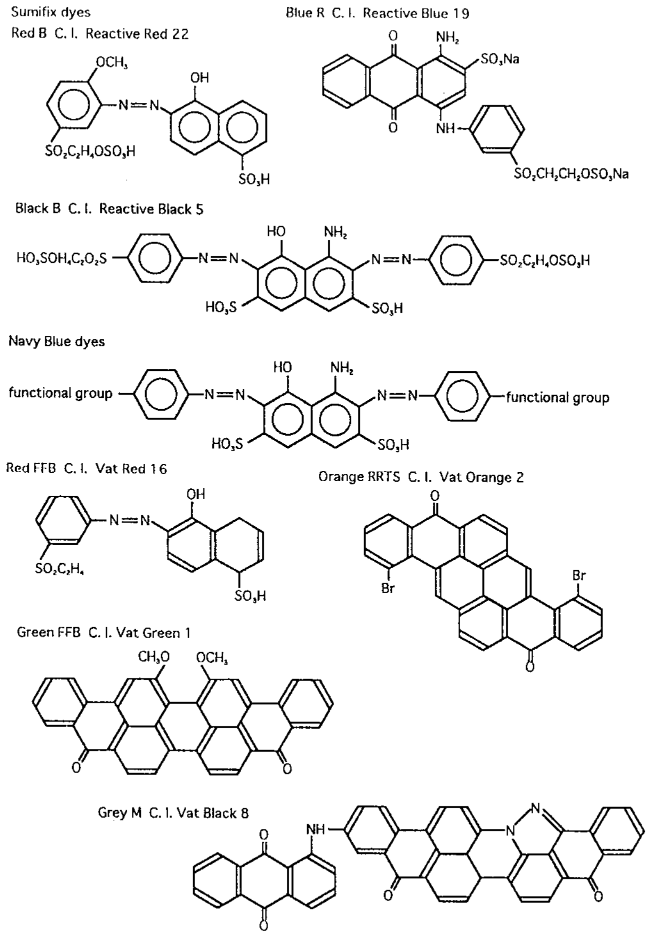


Fig. 4-11 Chemical structres of reactive and vat dyes used for the present investigations (C. I. Reactive Violet 22 : azoic-type with vs group containing Cu but structure not published).

(3) Flame retardants

Nondurable inorganic flame retardants used for the present study are listed in Table 4-7 and a durable flame retardant Pyrovatex CP and additives used for the comparison with the nondurable flame retardants are shown in Table 4-8.

(b) Methods

(1) Dyeing methods

Cotton fabric was dyed and washed according to the methods shown in Table 4-9 and air dried.

(2) Flame retardant finish

For nondurable flame retardant finish, each dyed fabric was impregnated with each treating solution listed Table 4-7 for 10 min, padded to 90% pick up after 2 dip - 2 nip process and air dried. Durable flame retardant finishes were carried out according the manner described in 4-1-1 above.

Table 4-7 List of nondurable flame retardant used for the Present Study.

Nondurable inorganic compound	Conc. (%)	Weight ratio
Diammonium hydrogen phosphate	20	
Ammonium sulfamate	20	
Ammonium bromide	20	
Ammonium chloride	20	
Ammonium sulfate + Ammonium chloride	20	1 : 1
Boric acid + Borax	20	3 : 7
Boric acid + Borax + diammonium hydrogen phosphate	20	3 : 7 : 5

Table 4-8 Durable flame retardant used for comparison with nondurable flame retardant.

Flame Retardant & Additive	Conc. (%)
Pyrovatex CP	32
Hexamethylolmelamine	8
Ortho-phosphoric acid	2
Catalyst	3
Pyrovatex CP	32
Hexamethylolmelamine	8
Urea	1
Ammonium chloride	0.5
Catalyst	3
Pyrovatex CP	32
Hexamethylol melamine	8
Urea	1
Ammonium chloride	0.5
Ortho - phosphoric acid	2
Catalyst	3

Table 4-9 Dyeing methods for dyestuffs used for the present study.

Dyes	Conc. o. w. f.	Additive	Temperature and Time		Rinsing and Soaping
Red 22	5 %	Na_2SO_4 50 g/l Na_2CO_3 20 g/l		Heat up to 50°C, Na_2SO_4 added at 50°C, allowed to stand for 30min, Na_2CO_3 added allowed to stand for 60min (bath ratio : 50)	Rinsed with water for 5 min, washed with hot water for 5 min. Soaped with 3 g/l soap for 15 min at 90 °C (bath ratio : 50) Rinsed with hot water (50 °C) for 5 min, with water for 5 min.
Blue 19					
Black 5					
Violet 22					
Blue 82	1.5%	Na_2SO_4 50 g/l Na_2CO_3 20 g/l	40°C	Na_2SO_4 added at each temperature allowed to stand for 20 min. Na_2CO_3 added, allowed to stand for 60 min. (bath ratio : 20)	the same as mentioned above
Blue 120	1.5%		40°C		
Blue 171	1.3%		80°C		
Blue 194	1.3%		60°C		

(3) Observation of color change after flame retardant finishes

(i) Determination of spectral reflectance factor

The spectral reflectance factor of each dyed sample was measured by Ulbricht sphere attached to Shimadzu double beam spectrophotometer UV-200S in a range of 350-800 nm before and after flame retardant finishes.

In addition to the determination of reflectance, color concentration was $K/S = (1-R)^2/2R$ described above in 4-1-2.

(ii) Color difference was determined for each sample by a color tester (Suga Shikenki Co.)

(iii) Lab chromaticity diagram was prepared for each sample according to the conventional manner.

2) Results and Discussion

(a) Effects of nondurable flame retardant finishes on dyed fabric

(1) Effects on reactive dyes

Comparison among colorations of dyes possessing the same functional group VS and different types of chromogens, anthraquinone, monoazoic and bisazoic types on cotton fabric, finished with 7 kinds of the above mentioned treating solutions were expressed by ratios of K/S value of each dyed and finished sample to that of the same dyed unfinished sample, which is shown in Fig.4-12.

As seen here, the least reduction was observed with samples finished with boric acid and borax in every dye only decreasing less than 5% except for Violet 22, still less than 10% also in this case. Other dyes also kept a level at least 85%, which suggests that nondurable inorganic flame retardants do not affect dyes so significantly and little difference is observed in effect of flame retardants among different kinds of dyes, particularly boric acid and borax showed an attractive and encouraging result.

Another comparison was attempted by using dyes with the same chromogen, bisazoic type and different types of functional groups, MCT, DCT, DFCP of MCT + VS. As flame retardants, 3 kinds out of 7, boric acid and borax which showed the best result, diammonium hydrogen phosphate containing P and ammonium chloride containing a halogen were selected as representative for the nondurable flame retardant and Pyrovatex finished samples were also selected as a representative durable flame retardant finish for a comparison with the results of nondurable flame retardant finishes to see how the effects of nondurable flame retardant is different from those of durable flame retardant finishes. The ratio of K/S values obtained by (K/S value finished)/(K/S value unfinished) as used above was illustrated in Fig.4-13.

Nondurable flame retardants showed a similar tendency compared with that observed in Fig.4-12, whereas marked reduction was observed with samples treated with durable flame retardants.

To see if such reduction by durable flame retardant finish is due to only reduction of color or also to any participation for color change, attention was paid to chromaticity diagrams shown in Fig.4-14. From these diagrams, it is clearly disclosed that durable flame retardants gave significant color change (○→□), i.e., from blue to red purple (Blue 82), to grayish blue (Blue 120) or to purple (Blue 171 and Blue 194). Blue 171 and Blue 194 showed a similar tendency probably because of possessing a common functional group MCT. Blue 82 showed a marked change on the diagrams though much less reduction of K/S values compared with other dyes. Comparison among the 3 kinds of Pyrovatex flame retardants used for the present study, those containing ortho-phosphoric acid gave larger change than that without it, which was probably attributed to lower pH affecting the dissociation of functional groups of dyes. From the above results, the relationship between dye structure and resistibility to flame retardant finish can be deduced as follows:

Dyes possessing VS group with the same chromogen showed the least effect with favorable resistibility to the flame retardant finish also in this case.

Comparison among 4 kinds of Blue type dyes having different functional groups revealed that the order of the resistibility of functional groups were DCT > MCT + VS > MCT > DFCP. MCT + VS was better than MCT because of the aid of VS. As for the participation of rings, triazinyl ring showed higher resistibility compared with pyrimidinyl ring. The number of Cl was thought to be responsible to some extent, i.e., dye having only 1 Cl showed very low resistibility which rose with increase in Cl to 2 molecules.

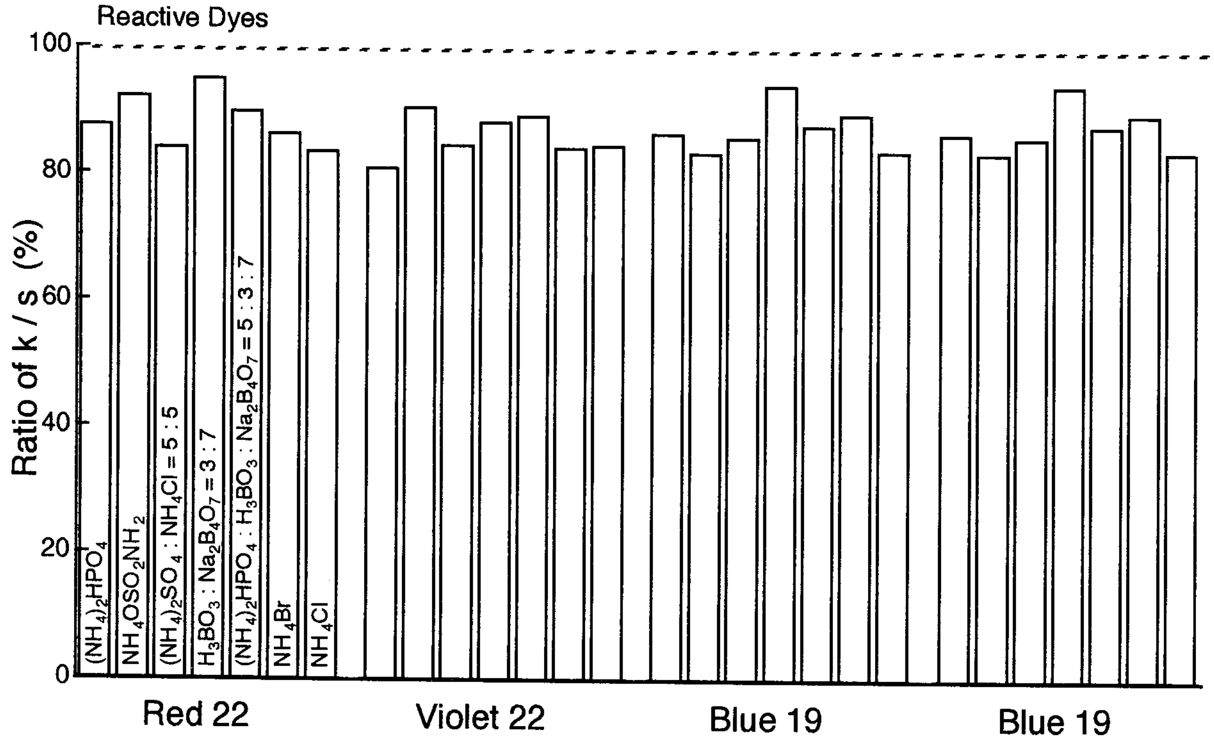


Fig. 4-12 Effects of flame retardant finishes on reactive dyes with the same functional group (VS group) and different chromogens observed by ratios of K/S values (ratios of K/S of finished samples to those observed before finishing).

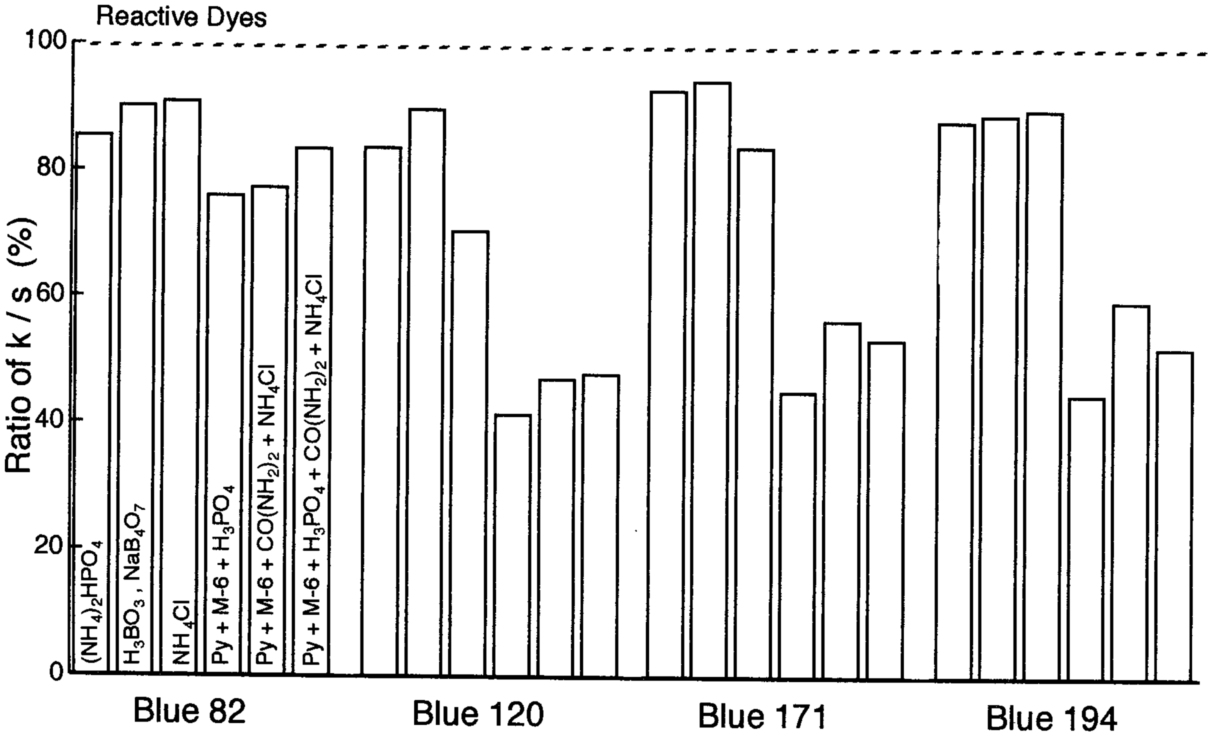


Fig. 4-13 Effects of flame retardant finishes on reactive dyes with the same bisazoic chromogen and different functional groups observed by ratios of K/S.

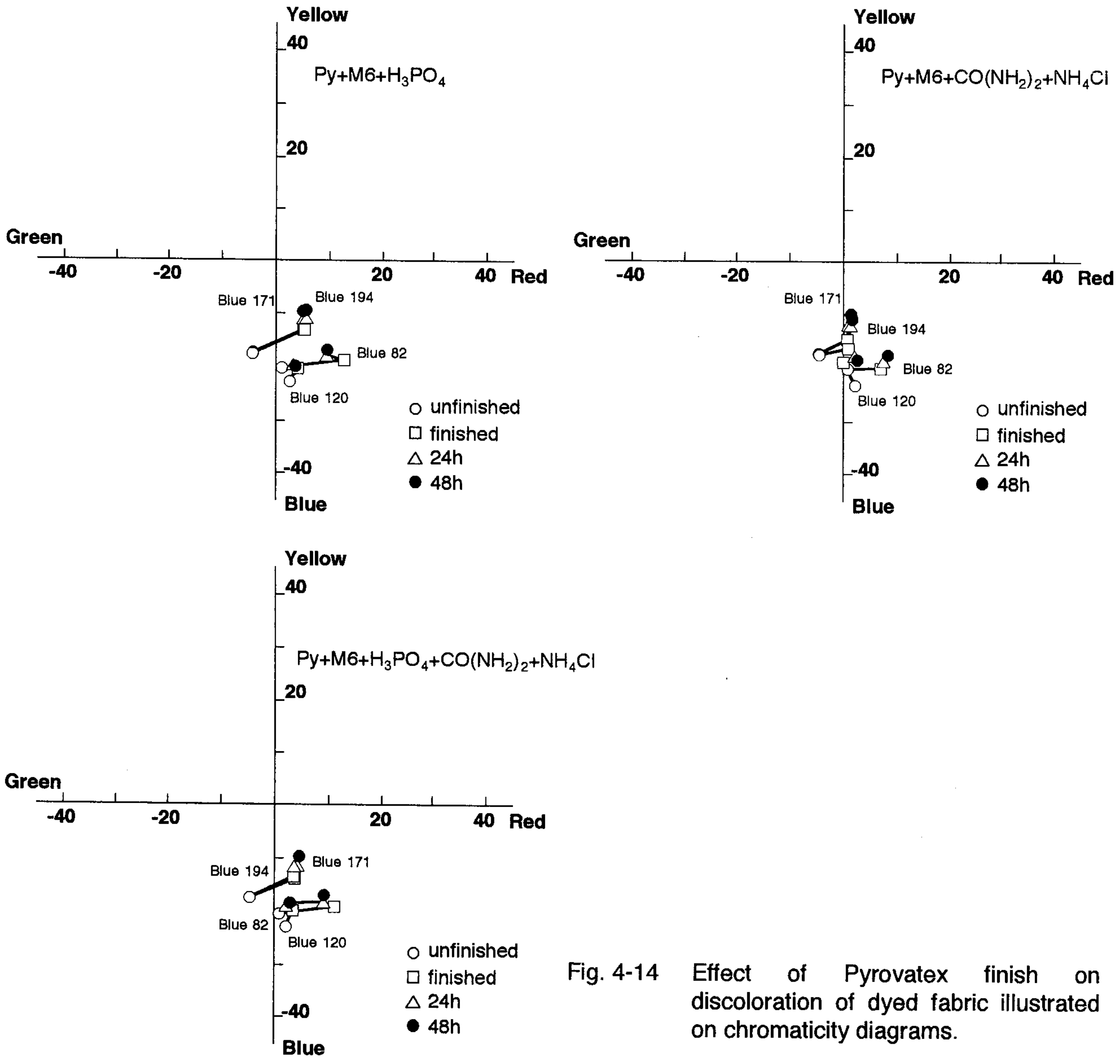


Fig. 4-14 Effect of Pyrovatex finish on discoloration of dyed fabric illustrated on chromaticity diagrams.

(2) Effects on vat dyes

Cotton samples dyed with 4 kinds of vat dyes with different types of structure, possessing methoxy groups, sulfonic group and hydroxy group, Br or -NH- bond were finished with the same flame retardant solutions mentioned above. Ratios of K/S values of these finished samples to those of unfinished dyed samples are shown in Fig.4-15. Also in this case, boric acid and borax showed the least reduction, even no change for Green 1, and little difference was observed among flame retardant finishes as well as among dyes showing decrease less than 13% except that Black 8 showed slightly larger reduction probably owing to -NH- bond between anthraquinone and heterocyclic portion.

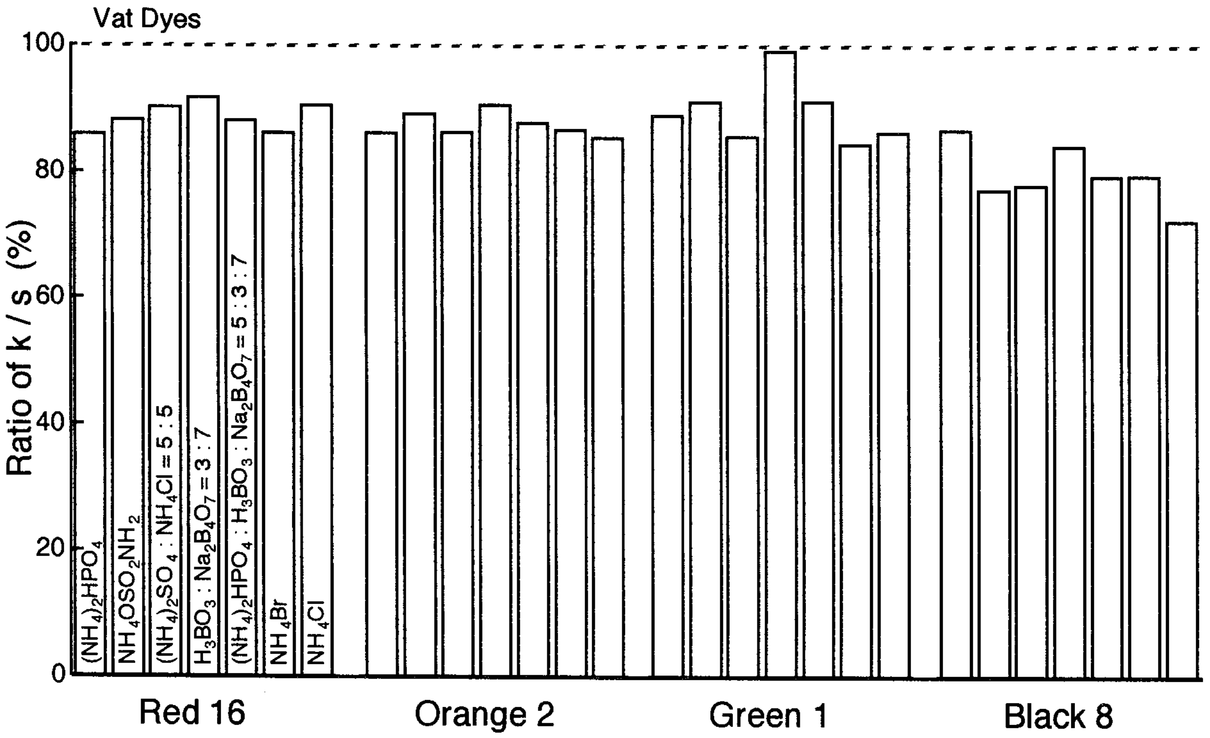


Fig. 4-15 Effects of flame retardant finishes on vat dyes of different structures observed by ratios of K/S values observed by ratios of K/S values of finished samples to those of unfinished samples.

3) Conclusion

Overall conclusion is that effects of nondurable inorganic flame retardant finishes on dyed samples were not significant much less than those given by durable flame retardant finishes.

Among nondurable flame retardants, boric acid and borax showed the most desirable behavior even entirely harmless under some condition.

4-2-2 Effects of Nondurable Flame Retardant Finishes on Discoloration of Cotton Fabric Dyed with Reactive and Vat Dyes to be Caused by Ultraviolet Irradiation

1) Experimental

The fabric material, dyestuffs and flame retardants were all the same as those used in the previous study described in 4-2-1. The dyed and finished materials used for this investigation were prepared under the conditions the same as described in the previous section.

These samples were irradiated with ultraviolet ray by using UV Regular Fademeter Type FA (Suga Shikenki Co.) with a UV carbon arc light source for 24 h and 48 h.

At the end of each irradiation time, spectral reflectance of these irradiated dyed and finished samples were measured as described in the previous section 4-2-1.

2) Results and Discussion

(1) Effects on discoloration of reactive dyes

Cotton samples dyed with dyes possessing VS group as the functional group and finished with the above flame retardants were exposed to ultraviolet ray for 24 h and 48 h, spectral reflectance of which was measured and K/S value is shown in Fig.4-16 as a ratio of irradiated value to unirradiated value for each sample. As seen in the figure, significant differences were observed among dyes as well as among flame retardants. Considering from chromogen, Blue 19 showed the least reduction because of anthraquinone in the structure of this dye as the chromogen. In contrast, Black 5 exhibited the largest reduction, particularly when finished with flame retardants containing ammonium halides. Such instability of this dyes is supposed to be due to bisazoic type chromogen. Also in this case, samples finished with flame retardants containing boric acid and borax gave the most favorable results inhibiting the discoloration of dyes caused by the ultraviolet irradiation. Paying attention to the chromaticity diagrams, all samples showed discoloration (Fig.4-17) shifting to yellow region in all the cases except that samples finished with boric acid and borax showed little shift even after 48 h irradiation (Fig.4-18) proving the inhibiting effect of this flame retardant on the discoloration by the ultraviolet irradiation.

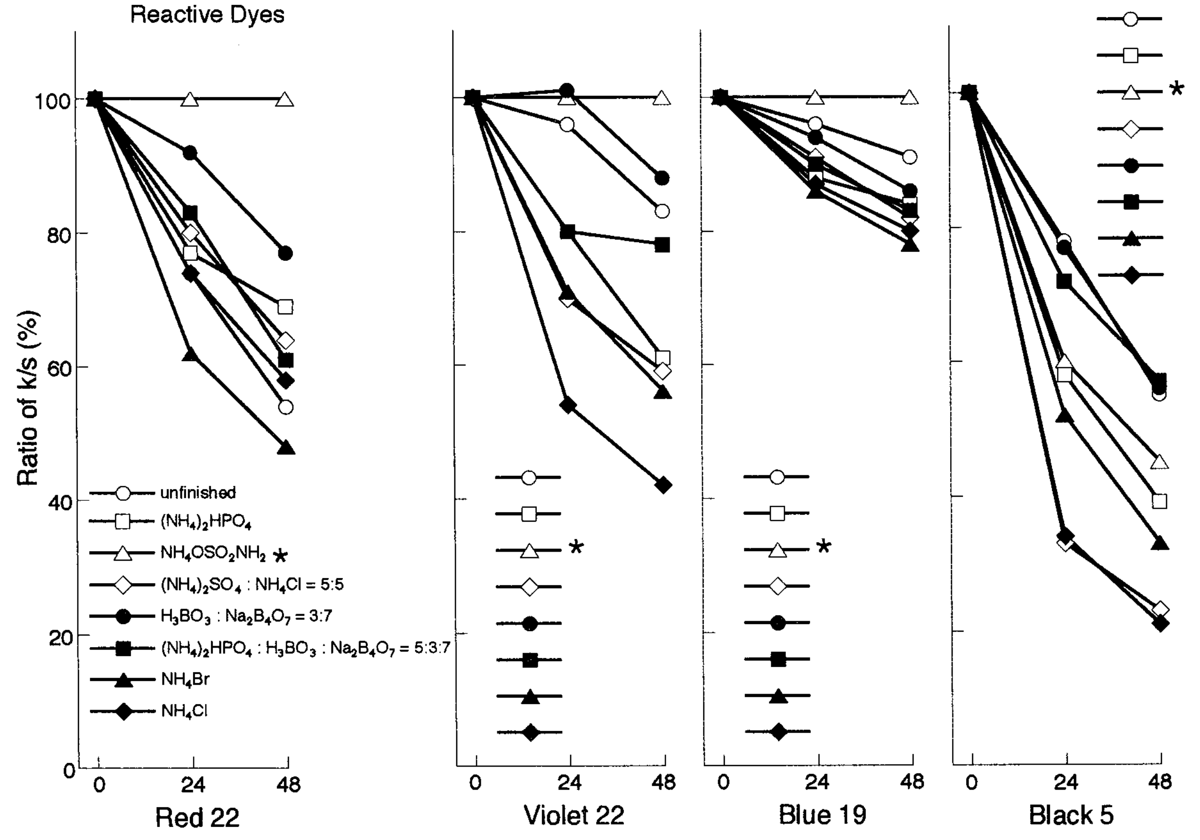


Fig. 4-16 Effect of ultraviolet irradiation on reactive dyes with vinyl sulfonic group and different chromogens by ratios (%) of K/S values observed after irradiation to those obtained before irradiation (* indicated results affected by browning discoloration).

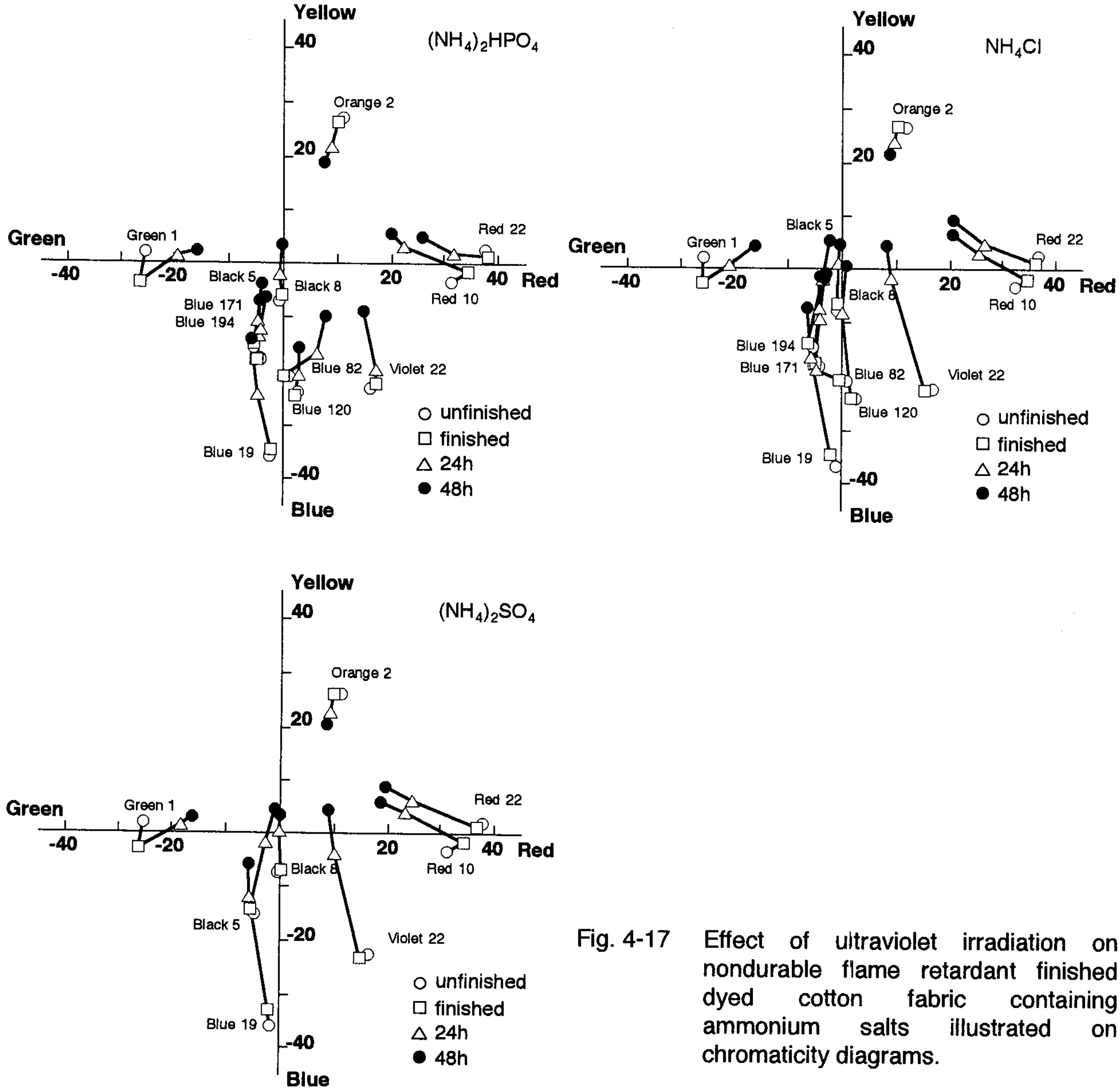


Fig. 4-17 Effect of ultraviolet irradiation on nondurable flame retardant finished dyed cotton fabric containing ammonium salts illustrated on chromaticity diagrams.

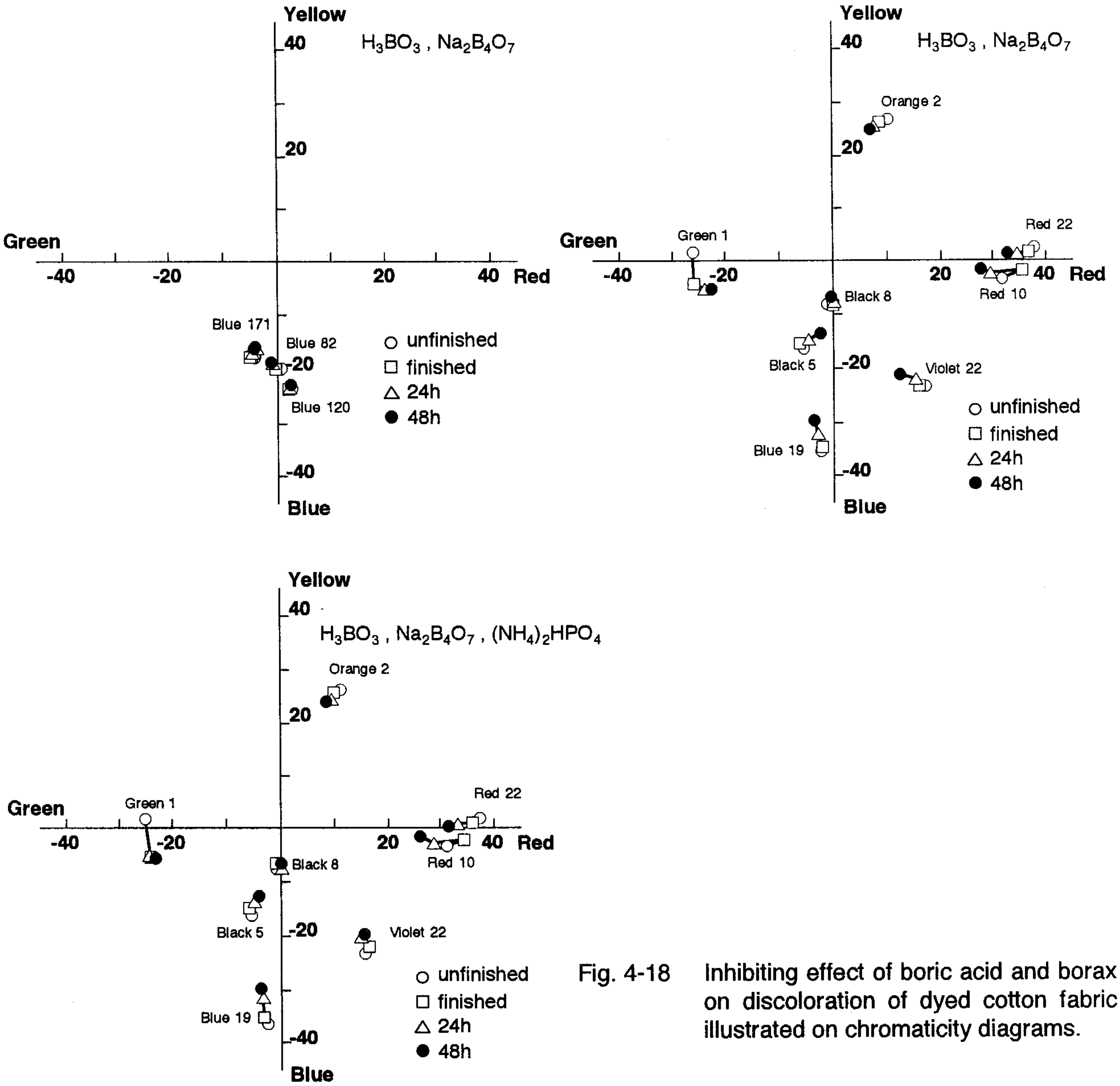


Fig. 4-18 Inhibiting effect of boric acid and borax on discoloration of dyed cotton fabric illustrated on chromaticity diagrams.

Considering from the color tone, resistance of blue color was highest and decreased in the order of violet, red and black. It has been also found that red type color which absorbs a shorter wavelength range and black color absorbing the whole wavelength range have weak lightfastness. Such tendency was observed not only with nondurable flame retardant finished samples but also with unfinished samples. Therefore, nondurable flame retardant finishes change the effect of ultraviolet irradiation on the discoloration of dyed fabric except that boric acid and borax is very capable to inhibit the discoloration of ultraviolet irradiation.

Another comparison of effects of flame retardants on the discoloration of dyes with the same bisazoic type chromogen having different functional groups is shown in Fig.4-19, in which unfinished samples, samples finished with represented flame retardants selected and those finished with Pyrovatex are exhibited for comparison between nondurable flame retardants and durable flame retardants. This figure also clearly shows that boric acid and borax showed the most favorable results inhibiting the discoloration of dyes to be damaged by the irradiation. Detailed observation of effects of diammonium hydrogen phosphate and ammonium chloride was revealed that the latter showed larger reduction ratios, the largest reduction in all cases, as shown below.

C. I. Name	Functional group	(NH4)2HPO4	NH4Cl
Blue 82	DCT	34%	47%
Blue 120	DCMFP	35%	72%
Blue 171	MCT	46%	70%
Blue 194	MCT + VS	61%	70%

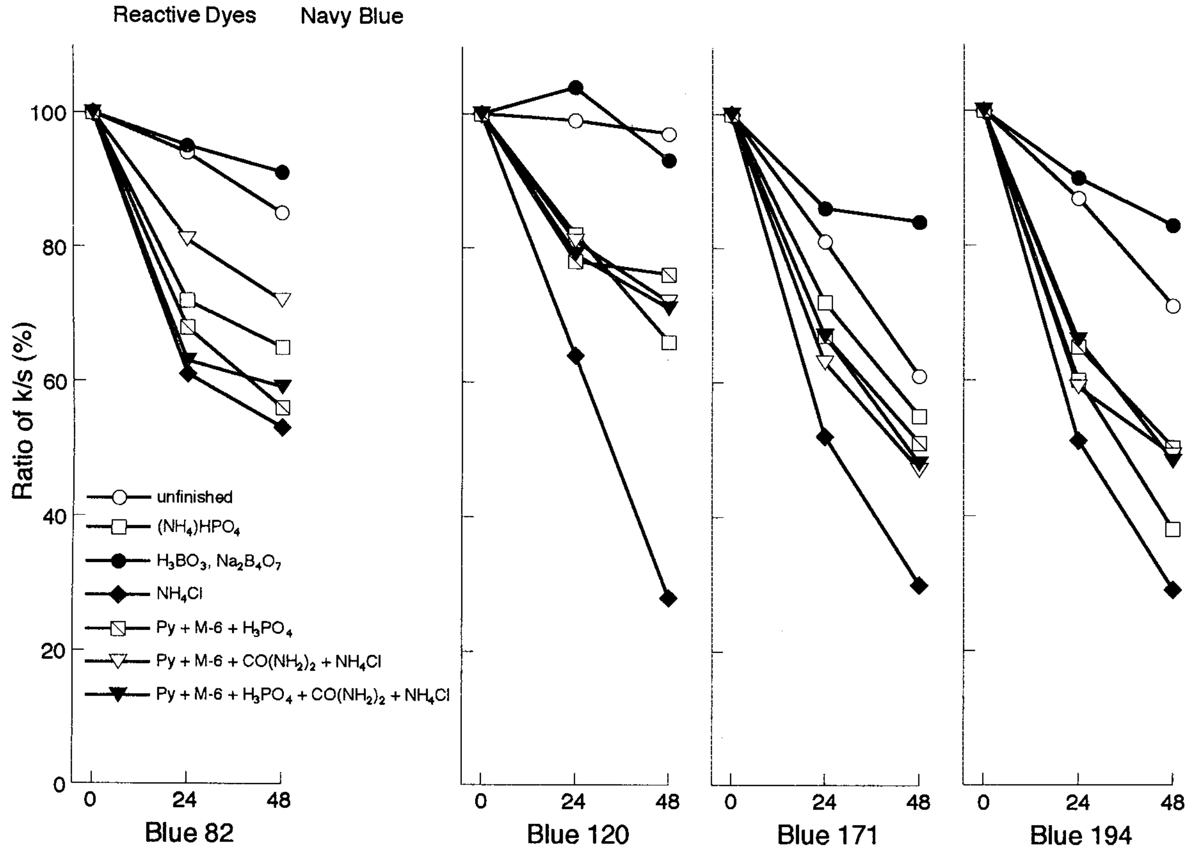


Fig. 4-19 Effect of ultraviolet irradiation on reactive dyes having bisazoic chromogen and different functional groups and inhibiting effect of H_3BO_3 + $Na_2B_4O_7$ observed by ratios (%) of K/S values obtained after irradiation to those obtained before irradiation.

The reason for the larger reduction by NH4Cl is of course that hydrochloric acid is a stronger acid than phosphoric acid produced after volatilization of ammonia.

DCT gave better effect compared with MCT, which is a similar tendency as observed in the case of the effect of flame retardant finishes mentioned above (4-2-1).

Comparison between the effect of Blue 171 with MCT and Blue 194 having MCT + VS finished with diammonium hydrogen phosphate suggests that additional VS group in the structure may give some extra damage to dyes, by which the considerable reduction of all dyes but Blue 19 shown in Fig.4-16 is now understandable since these dyes shown in Fig.4-16 possess 1-2 VS groups. Thus, VS group has favorable resistibility for flame retardant finish but not for ultraviolet irradiation.

As for comparison with effects of durable flame retardant finish, durable flame retardant finished samples showed rather less reduction compared with those of nondurable ammonium salts. Such phenomenon is contrary to the results observed in the case of effects of flame retardant finishes alone to which the irradiation is not involved as shown in Fig.4-13 in which durable flame retardant finishes showed large reduction twice as much as that shown by nondurable flame retardant finishes.

Comparison of the lightfastness among different functional groups with the same chromogen, bisazoic type disclosed that Blue 120 with DCMFP group as a functional group which showed the worst resistibility for finishing gave the best result. Thus, flame retardant finishes and ultraviolet irradiation gave the opposite effects to the same dye. The difference observed between MCT group alone and MCT group in combination with VS group in the case of nondurable flame retardant finishes was not found in these durable flame retardant finishes.

Generally, the lightfastness or the effect of ultraviolet irradiation is dominated by chromogens in the structures of dyes, effects of functional groups may participate in discoloration when chromogens are the same.

(b) Effects of discoloration of vat dyes

Cotton fabric samples dyed with vat dyes and finished with the above mentioned 7 kinds of nondurable flame retardant solutions were irradiated with ultraviolet ray for 24 and 48 h, the results of which are shown in Fig.4-20. It should be noted that samples finished with flame retardants except for those containing boric acid and borax gave browning to every dyed fabric resulting in the reduction of reflectance of any brownish sample which made K/S values larger (indicated by ※ mark).

Samples finished with ammonium sulfamate or ammonium chloride showed specially significant and browning reflectance of which was undetectable, out of scale for the measurement. Such browning was expressed on the chromaticity diagram as shown in Fig.4-17. Considerable shifts are shown from position of flame retardant finishes to 24 h irradiation toward the direction of yellow.

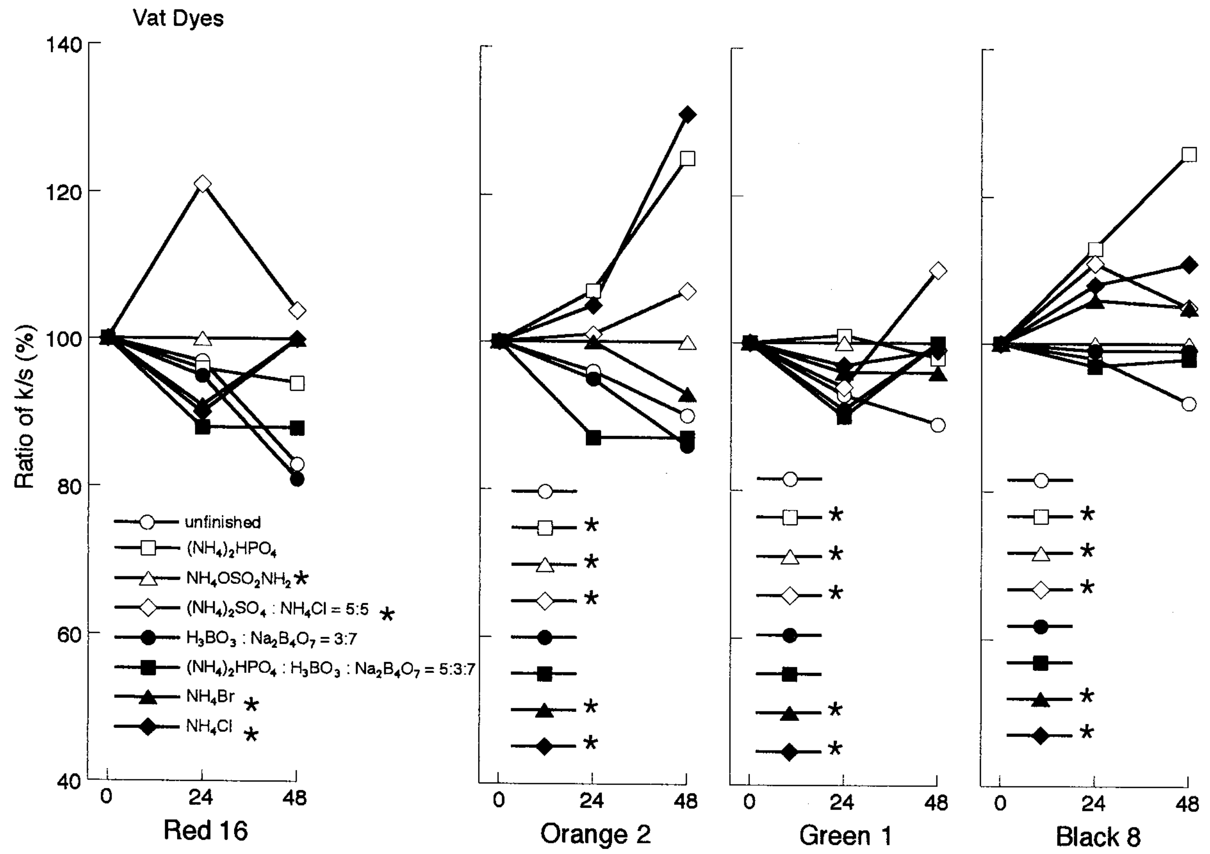


Fig. 4-20 Effect of ultraviolet irradiation on vat dyes of different structures observed by comparing K/S values between unirradiated samples (100) and irradiated samples (%) (* indicates unreasonably higher values owing to brawning discoloration caused by ammonium salts).

(c) Effects of nondurable flame retardant finishes in combination with ultraviolet irradiation on dyed fabric

Overall results of investigations on effects of nondurable flame retardant finished in combination with those of ultraviolet irradiation on dyed fabric, i.e., effects of nondurable flame retardant finishes on discolorations of dyed fabric caused by the ultraviolet irradiation are shown in Fig.4-21 for reactive dyes having the same VS group as the functional group and different chromogens, anthraquinone, monoazoic and bisazoic types, in Fig.4-22 also for reactive dyes possessing the same bisazoic type chromogen and different types of functional group, MCT, DCT, DCMFP and MCT + VS groups. From these figures, inhibitng effect of H_3BO_3 and $Na_2B_4O_7$ on discoloration of dyes by UV irradiation is noticeable.

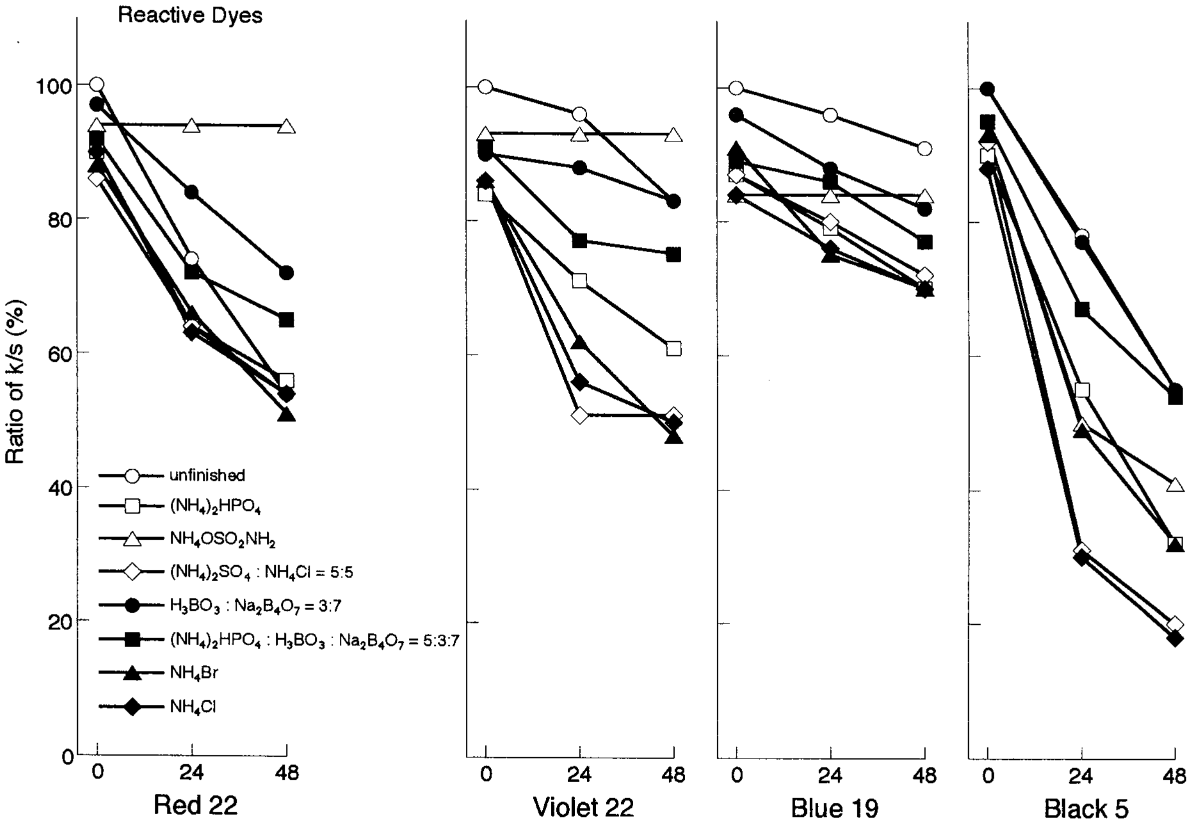


Fig. 4-21 Effects of flame retardant finishes in combination with ultraviolet irradiation on reactive dyes with vinyl sulfonic group and different chromogens observed by ratios of K/S values of irradiated finished samples to those of unirradiated unfinished samples.

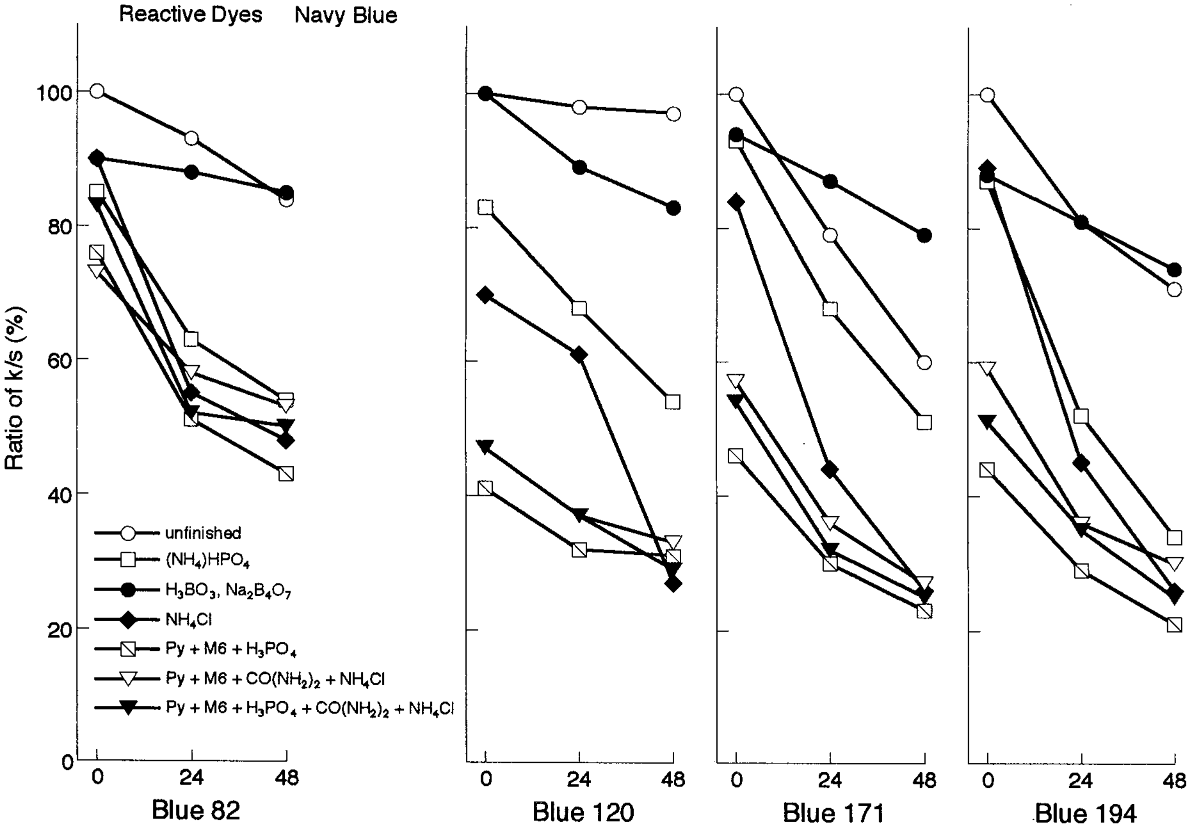


Fig. 4-22 Effects of flame retardant finishes followed by ultraviolet irradiation on reactive dyes with bisazoic chromogens and different functional group observed by ratios of K/S values of irradiated finished samples to those of unirradiated unfinished samples.

3) Conclusion

From the above figures, the results are summarized as follows.

From the structure of dye, Blue 19 which has anthraquinone as the chromogen and VS groups as the functional group showed the best results from resistibility to finishing as well as from lightfastness, followed by Red 22 and Violet 22 having monoazoic type chromogen and VS group, and Black 5 possessing the same VS group and bisazoic type chromogen showed the worst result from resistibilities of both flame retardants and the ultraviolet irradiation.

From the standpoint of flame retardants, boric acid and borax showed the best results giving the least influence to dyed samples and inhibiting the discoloration of dyes caused by the UV irradiation.

Ammonium salts of P, S and halogens were very effective as flame retardants, but caused significant discoloration by finishing and accelerated discoloration by UV irradiation. However, these harmful influences were inhibited by addition of boric acid and borax.

Combined effects of durable flame retardants on dyed fabric were extremely larger compared with those of nondurable flame retardants showing even 80% reduction.

Vat dyes showed significant browning, which results in awful discoloration, but ratio of K/S value showed higher levels. Thus, ammonium salts are not recommendable for vat dyes. Boric acid and borax showed the best results also in this case.

From the results obtained this time, any dye possessing -NH- group (Black 8) showed favorable lightfastness but little resistibility to flame retardants, and other vat dyes also showed better results compared with those observed in the case of reactive dyes, only except for the problem of browning caused by ammonium salts when irradiated.

4-2-3 Effects of Nondurable Flame Retardants on Discoloration of Cotton Fabric Dyed with Direct Dyes, Basic Dyes and Fluorescent Brightener Caused by Ultraviolet Irradiation

In this section, cotton fabric was dyed with dyes for cellulosic fiber only, i. e., direct dyes, a basic dye and a fluorescent brightener followed by flame retardant finishes with inorganic compounds. The reason for adopting a fluorescent brightener this time is that majority of commercial detergents are formulated with this dye.

Furthermore, methods other than those used in the previous sections were adopted in this section to express the discoloration for better understanding.

1) Experimental

(a) Materials

(1) Fabric

One hundred % cotton fabric used for this study was the same as that described in 2-2-2.

(2) Dyes and additives for dyeing

Dyestuffs used this time were 7 kinds of azoic direct dyes, a basic dye and a triazinyl stilbene type fluorescent brightener (F. B.) shown in Fig. 4-23.

As additives, tannic acid, tartar emetic and acetic acid were used for the basic dye and sodium sulfate was added to other direct dyes.

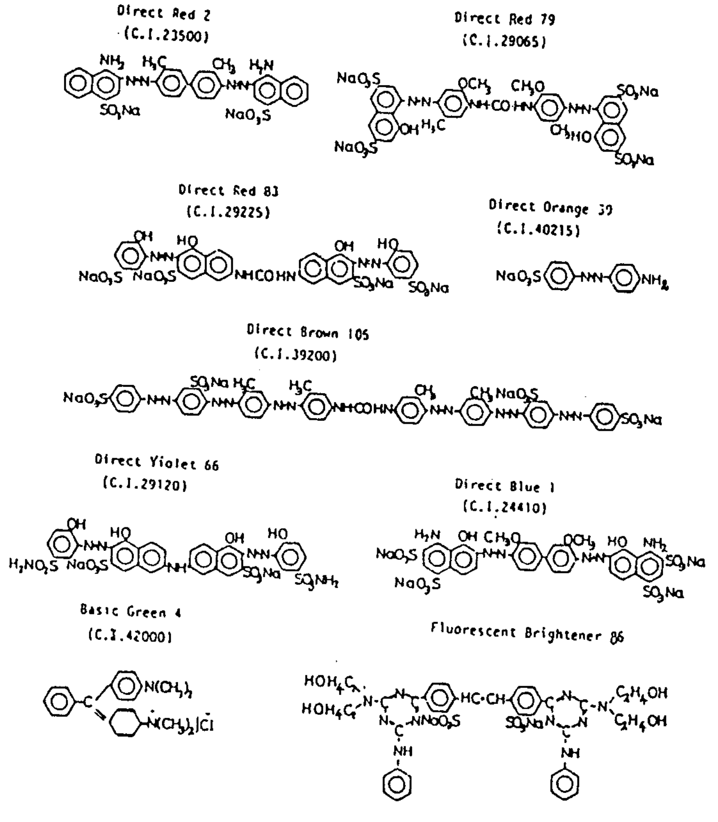


Fig. 4-23 Structural formulas of dyes used for the present studies.

(3) Flame retardants

Diammonium hydrogen phosphate, a mixture (1:1) of polyphospho-carbonate and guanyl methylol phosphate (to be called polyphosphate below) as compounds containing N and P, ammonium sulfamate as a compound containing N and S, a mixture (1:1) of ammonium sulfate and ammonium chloride as a reagent containing N, S and a halogen Cl were used as flame retardants containing representative flame retardant elements N, P, S and a halogen Cl. In addition, mixtures of boric acid and borax containing B but without any one of the above mentioned flame retardant elements were used as a mixture (3:7) alone and mixtures with other compounds (3:7:5), i.e., with diammonium phosphate, with ammonium sulfamate, with a mixture (1:1) of ammonium sulfate and ammonium chloride, 8 kinds in total were used for the preparation of 10, 20 and 30% of treating solutions.

(b) Methods

(1) Dyeing

Cotton fabric was dyed in 0.4% (o.w.f.) of each direct dye solution containing 20% (o.w.f.) of sodium sulfate with bath ratio of 50:1 by raising temperature up to 90-95℃ taking 20 min, allowed to stand at this temperature for 30 min and air dried after rinsing with tap water for 10 min. In the case of the basic dye, the fabric was pretreated with 3% (o.w.f.) of tanning acid and 1.5% (o.w.f.) of tartar emetic for the fixation of tannic acid followed by the conventional mordanting method with 1% (o.w.f.) of the basic dye, to which 1-2 drops of acetic acid was added to avoid uneven fixation of dye by reducing the dyeing rate.

(2) Flame retardant finishing

Cotton fabric was immersed in each treating solution mentioned above for 1-2 min, padded to 80-90% pickup after 2 dip- 2 nip process and air dried.

(3) Each sample was irradiated with carbon arc light for 10-48 h by UV Regular Light Fademeter Type FA3 (Suga Shikenki Co.) as mentioned above.

(4) Discoloration of dyed samples were observed before and after the irradiation by the following processes.

(i) Spectral reflectance factors extending over 200-700 nm were observed by using a Ulbricht sphere attached to a Spectrophotometer, Shimadzu UV 200S as mentioned in 4-1.

(ii) Tristimulus values X, Y and Z of the same samples were measured by a color difference meter (Type Au-CH-1, Suga Shikenki Co.) to calculate Lab color difference.

(iii) For a F.B., fluorescence intensity was determined by a fluorescence color difference meter and xenon standard white light source.

2) Results and Discussion

(a) Effect of ultraviolet irradiation on unfinished dyed fabric samples

Before observation of any effect of flame retardant finishes, effects of ultraviolet irradiation on unfinished cotton fabric dyed with the above mentioned dyestuffs were observed.

As shown in Fig.4-24, azoic dyes, Red 2, Blue 1 and basic dye Green 4 showed a considerable reduction of peaks and F.B. exhibited inversion of curve after irradiation. The rest 5 dyes showed little reduction because of favorable lightfastness of these dyes.

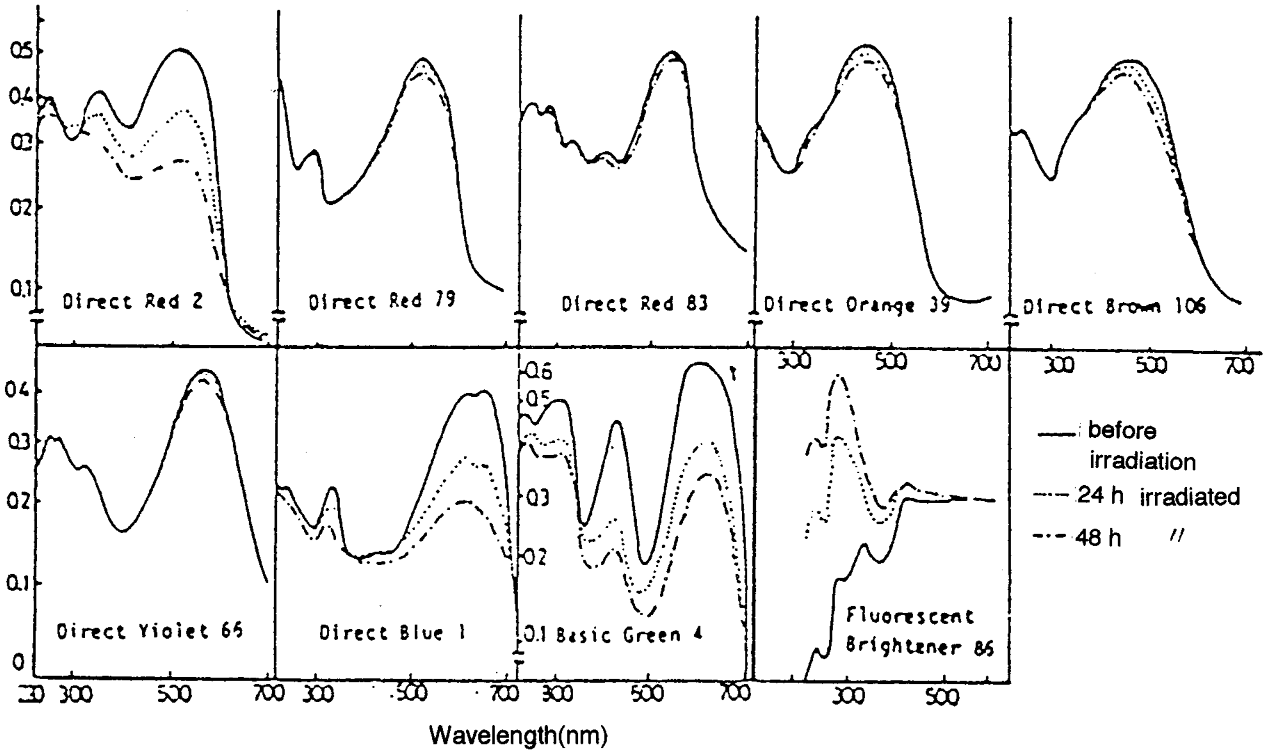


Fig. 4-24 Discoloration of unfinished dyed fabrics observed by Ulbright sphere after ultraviolet irradiation.

The results obtained by Ulbricht sphere were also observed by color difference and shown in Fig.4-25.

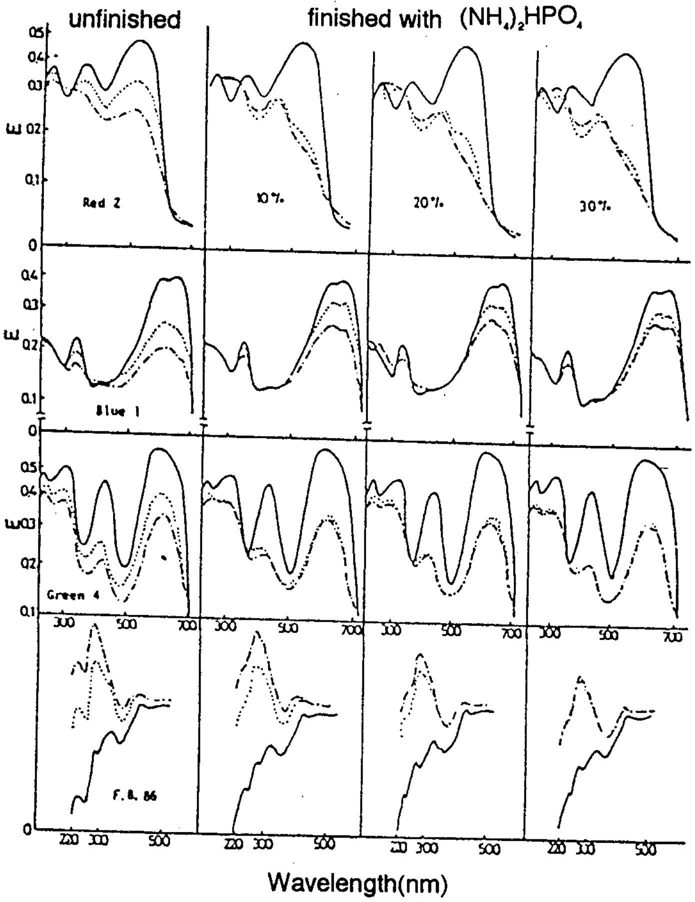


Fig. 4-25 Effect of $(NH_4)_2HPO_4$ on discoloration observed after ultraviolet irradiation for fabrics dyed with Red 2, Blue 1, Green 4 and F. B. 86 followed by finishing with $(NH_4)_2HPO_4$.

(b) Effects of flame retardants on discoloration of dyed fabric samples observed after ultraviolet irradiation

(1) Effect on absorption spectra observed by Ulbricht sphere

(i) Effect of diammonium hydrogen phosphate

As the result of irradiating dyed samples finished with 10, 20 and 30% solutions of this flame retardant, Red 2, Blue 1 and Green 4 and F. B. 86 showed obvious reductions as shown in the case of unfinished samples, but the reduction behavior of each finished sample was different from those observed with the unfinished samples as shown in Fig.4-25. The results shown by other finished samples were omitted in this figure because of little difference in the reduction behavior from those of the unfinished samples shown in the above figures.

Comparison with the results of unfinished sample for each dyed sample is as follows.

Unfinished sample dyed with Red 2 showed reduction from E=0.503 down to 0.263 at the same peak 518 nm, whereas in the case of flame retardant finished samples, a peak shift was shown from 518 nm to 448 nm after 24 h and even further to 434 nm after 48 h with much larger reduction at 518 nm, and such reduction was enhanced with increase in the concentration of flame retardant.

Blue 1 showed such entirely different discoloration behavior that finished samples showed as inhibiting tendency with less reduction decreasing with increase in the concentration of the flame retardant, which means that diammonium hydrogen phosphate inhibited discoloration of Blue 1 caused by the ultraviolet irradiation, i.e., unfinished sample showed reduction of optical density at 656 nm from 0.405 to 0.246 after 24 h and 0.190 after 48 h irradiation, whereas reduction of the optical density of sample finished with 10% solution was from 0.405 to 0.319 after 24h and to 0.253 after 48h and that of sample finished with 30% solution was to 0.290 even after 48 h, which means that the reduction was inhibited to about 50%.

Green 4 showed a little larger discoloration after 24 h irradiation in the case of finished sample, but any further change was not observed after 48 h and little difference was shown with increase in the concentration of the flame retardant.

In the case of F. B. 86, samples treated with 20% and 30% of the flame retardant showed inhibiting effect though spectra of sample treated with 10% solution were similar with those of unfinished sample.

As mentioned above, both accelerating or inhibiting effects were shown on the discoloration of dyed fabrics depending on dyes having different types of structures.

(ii) Effect of polyphosphate

Such phenomenon that one flame retardant showed both accelerating and inhibiting effects depending on dyes was observed also in the case of polyphosphate, but accelerating effect of discoloration was larger than that observed in the case of diammonium hydrogen phosphate, i.e., Red 2, Red 79 and Brown 106 finished with polyphosphate showed larger reduction compared with unfinished samples, particularly, the largest discoloration was observed with sample dyed with Red 2 with a shift of the peak from 518 nm to 445 nm (Fig.4-26). In contrast, Blue 1, Green 4 and F. B. 86 showed inhibiting effect though the degree of inhibition differed depending on the concentration of polyphosphate, i.e., samples treated with 10-20% solutions showed inhibiting effect but that treated with 30% solution showed less effect (Fig.4-27).

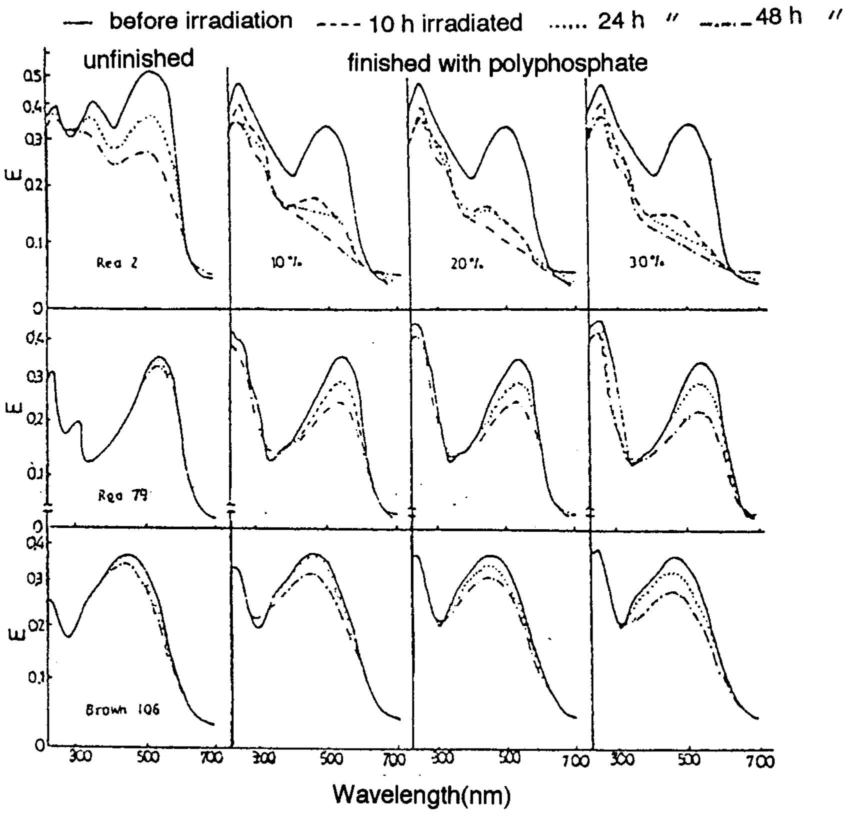


Fig. 4-26 Accelerating action of polyphosphate to discoloration observed after ultraviolet irradiation for fabrics dyed with Red 2, Red 79 and Brown 106 followed by finishing with polyphosphate.

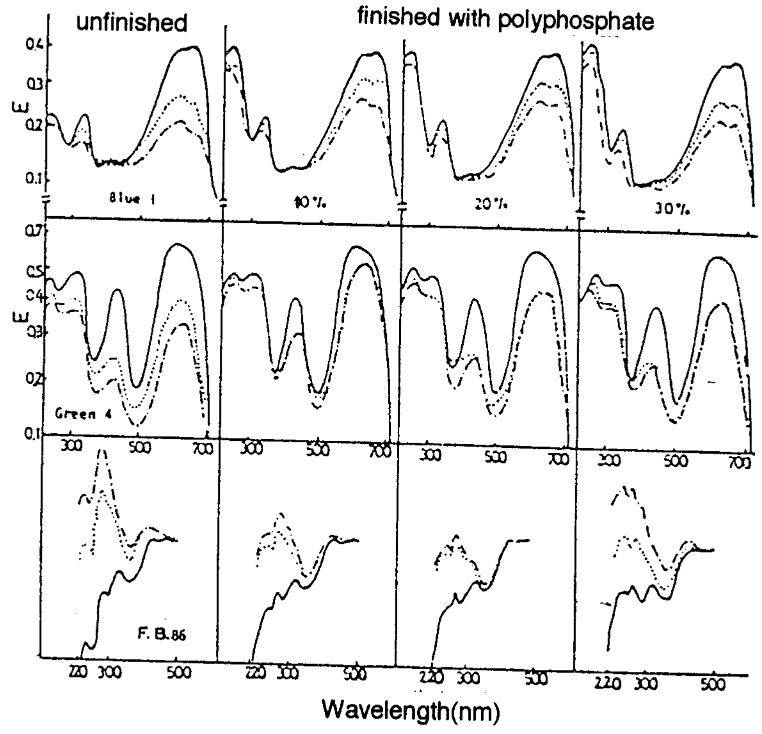


Fig. 4-27 Inhibiting effect of polyphosphate on discoloration observed after ultraviolet irradiation for fabrics dyed with Blue 1, Green 4 and F. B. 86 followed by finishing with polyphosphate.

(iii) Effects of ammonium sulfamate and a mixture of ammonium sulfate and ammonium chloride

Effect of flame retardant containing N and S was investigated in contrast to that of a flame retardant containing N and P, of which only the results from samples dyed with Red 2 and F. B. 86 showing the largest effect of ultraviolet irradiation are illustrated in Fig.4-28. The both flame retardants gave similar effects, i.e., a slight inhibiting effect on F. B. 86 but accelerating effect on Red 2 with a hypochromic effect to 452 nm after 24 h and to 428 nm after 48 h.

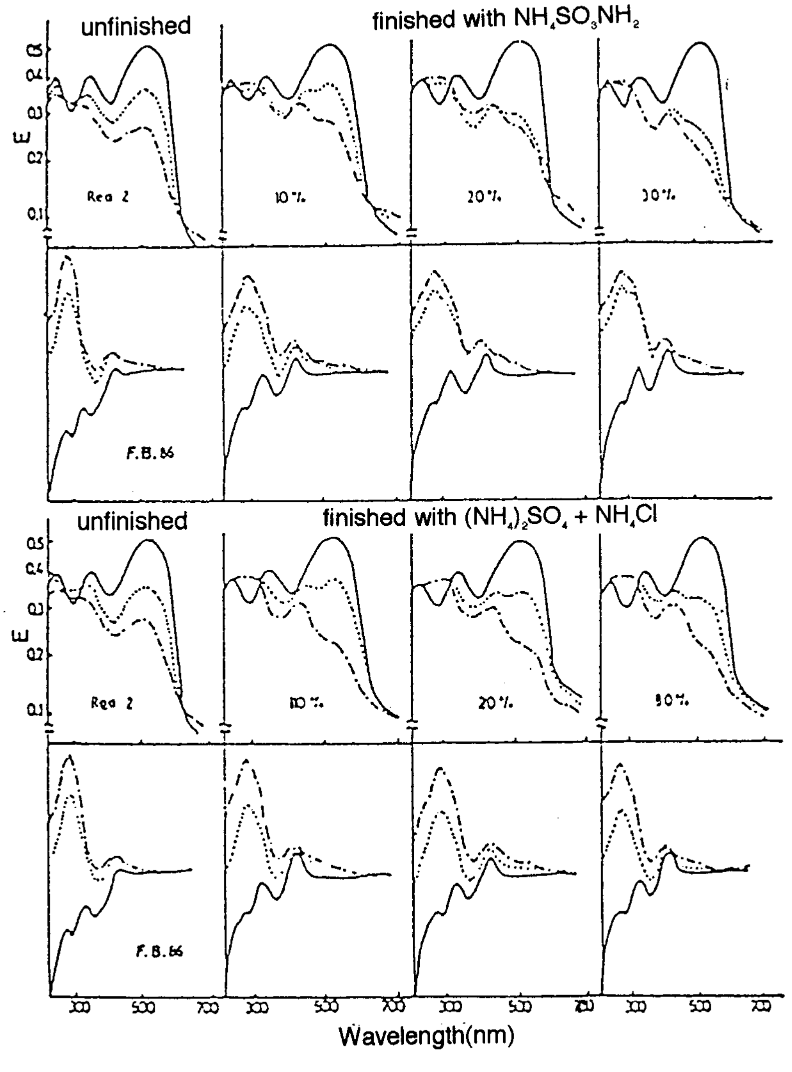


Fig. 4-28 Effect of $NH_4SO_3NH_2$ and $(NH_4)_2SO_4$ + NH_4Cl on discoloration observed after ultraviolet irradiation for dyed fabrics finished with $NH_4SO_3NH_2$ or $\{(NH_4)_2SO_4 + NH_4Cl\}$.

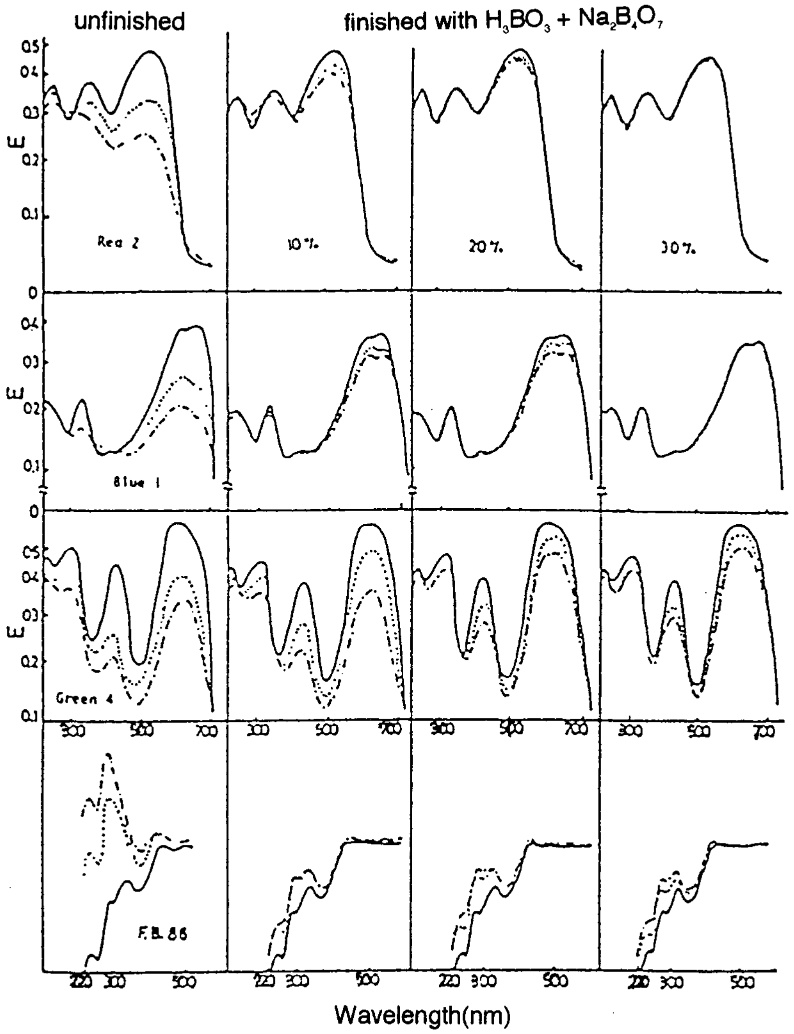


Fig. 4-29 Remarkable inhibiting effect of H_3BO_3 + $Na_2B_4O_7$ on discoloration observed after ultraviolet irradiation for fabrics dyed with Red 2, Blue 1, Green 4, and F. B. 86 foloowed by finishing with H_3BO_3 + $Na_2B_4O_7$.

(iv) Effect of boric acid and borax

Since a mixture of boric acid and borax is a very favorable flame retardant from flame retardance as well as from pyrolytic gas generation though not containing any one of N, P, S and halogens, the effect of this flame retardant on the discoloration of dyed fabric to be caused by ultraviolet irradiation was also investigated with a big expectation.

The most characteristic finding was that this flame retardant showed an extremely remarkable inhibiting effect on every dyed fabric. It is also worthy of special mention that boric and borax markedly inhibited discoloration of Red 2 for which all other flame retardants not only failed to inhibit discoloration but also even accelerated.

Fig.4-29 shows the inhibiting effect of boric acid and borax on 4 kinds of dyes which showed the largest discoloration, in which results of other dyes having good lightfastness are omitted because finished fabric showed no discoloration even 48 h irradiation. As clearly seen in the figure, samples treated with 30% solution showed no change in Red 2, Blue 1 and F. B. 86 after 48 h, 10% and 20% solutions exhibited less but sufficient inhibition except for Green 4 treated with 10% solution. It was also found that this flame retardant was most effective on F. B. 86. Such fact is practically convenient since white cloths which frequently require treatment with F. B. for visible whitening are unavoidably exposed to sunlight. Treatment with this flame retardant will contribute to act not only as a flame retardant for safety but also as an inhibitor for the discoloration of F. B. to protect from yellowing which is otherwise caused by the ultraviolet irradiation.

From the above results, further investigations were attempted by mixing boric acid and borax with other flame retardants which otherwise showed accelerating effects on the discoloration.

(iv-1) In the case of addition to diammonium hydrogen phosphate

Samples dyed with Red 2, Blue 1, Green 4 and F. B. 86 respectively were finished with 10% of diammonium hydrogen phosphate alone and the same concentration of a mixture of this compound and boric acid and borax prepared as mentioned above (Experimental).

As seen in Fig.4-30 discoloration of Red 2, Blue 1 and F. B. 86 by irradiation was considerably inhibited by addition of boric acid and borax though less inhibition was observed after 48 h with sample dyed with Green 4 probably because of a complicated participation of mordanting for this dye.

(iv-2) In the case of addition to ammonium sulfamate and a mixture of ammonium sulfate and ammonium chloride

In this case, Red 2 and F. B. 86 which exhibited the largest discoloration were selected, the results of which are shown in Fig.4-31. Also in these cases, boric acid and borax acted as a inhibitor for discoloration by the irradiation. Comparison of these three cases showed that boric acid and borax was most effective on diammonium hydrogen phosphate. Effect on a mixture of ammonium sulfate and ammonium chloride is less than that on ammonium sulfamate alone probably because a doubled ratio (5+5) is contained in the same amount of boric acid and borax in the former case. At any rate, remarkable inhibiting effect of boric acid and borax was clearly disclosed on the discoloration of dyed fabrics by the ultraviolet irradiation.

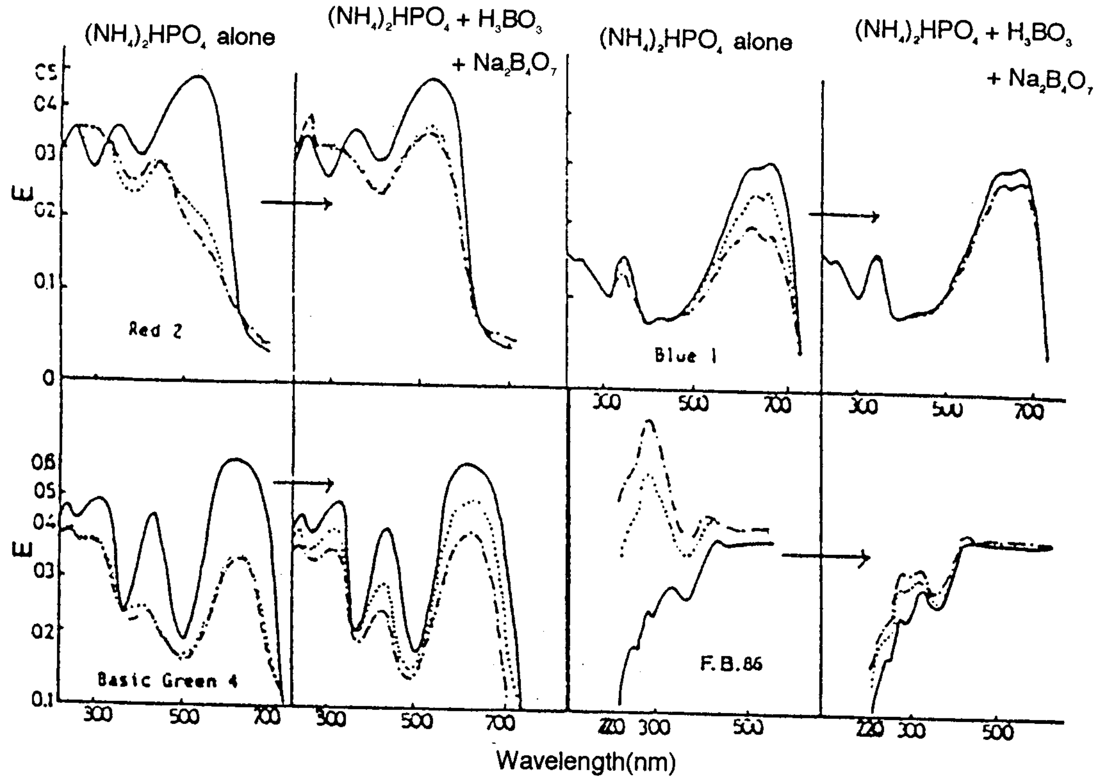


Fig. 4-30 Inhibiting effect of addition of (H_3BO_3 + $Na_2B_4O_7$) on discoloration of irradiated dyed fabrics finished with $(NH_4)_2HPO_4$.

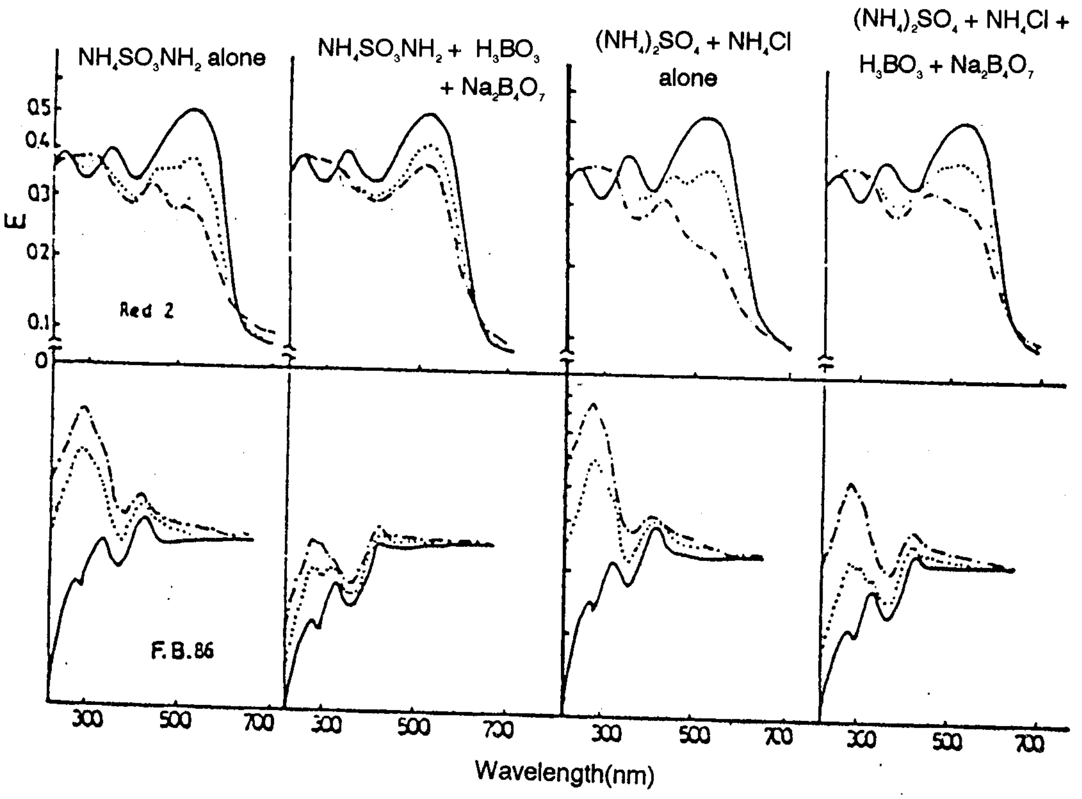


Fig. 4-31 Effect of addition of (H_3BO_3 + $Na_2B_4O_7$) on discoloration of irradiated dyed fabrics finished with {$(NH_4)_2SO_4$ + NH_4Cl}.

(2) Effects of flame retardants observed by color difference and fluorescence intensity

In addition to the observation of discoloration behavior extending from the ultraviolet range to the visible range, change in the reduction ratio of color difference or fluorescence between before and after the irradiation was observed for Red 2 and F. B. 86 as representatives. The results are shown in Fig.4-32 and 4-33. In the case of Red 2, diammonium hydrogen phosphate, polyphosphate and ammonium sulfamate and ammonium sulfate + ammonium chloride all brought about extremely large accelerating effects but addition of boric acid and borax showed remarkable inhibiting effect on these reduction of coloration also in this figure, specially, an effect on diammonium hydrogen phosphate was most outstanding. On the other hand, F. B. 86 showed considerable reduction in the case of unfinished sample and polyphosphate rather inhibited discoloration in contrast to the result observed in the case of Red 2. Other 3 flame retardants gave discoloration similar to that of unfinished sample. Addition of boric acid and borax also showed marked inhibiting effects, particularly on ammonium sulfamate.

In general, azoic compounds are reduced to amines by four electron reduction. The flame retardants used this time are ammonium salts acting as H^+ donors, which probably participated in reduction of dyed fabric.

As for the inhibiting effect on discoloration, boric acid and borax may contribute to disperse the excited energy to bring down to the stationary state acting as a UV absorbent or a complex formed by any dye and boric acid and borax may inhibit the degradation of structures of dyes. Thus, some possibilities can be considered, but nothing can be the right answer at present.

In the case of F. B., it can be considered that the discoloration by the irradiation (yellowing) will be attributed to the isomerization from trans-form to cis-form at a double bond loosened by the irradiation. Boric acid and borax can fasten the double bond by fixation or absorb the irradiation energy to protect from the ill effect on the double bond.

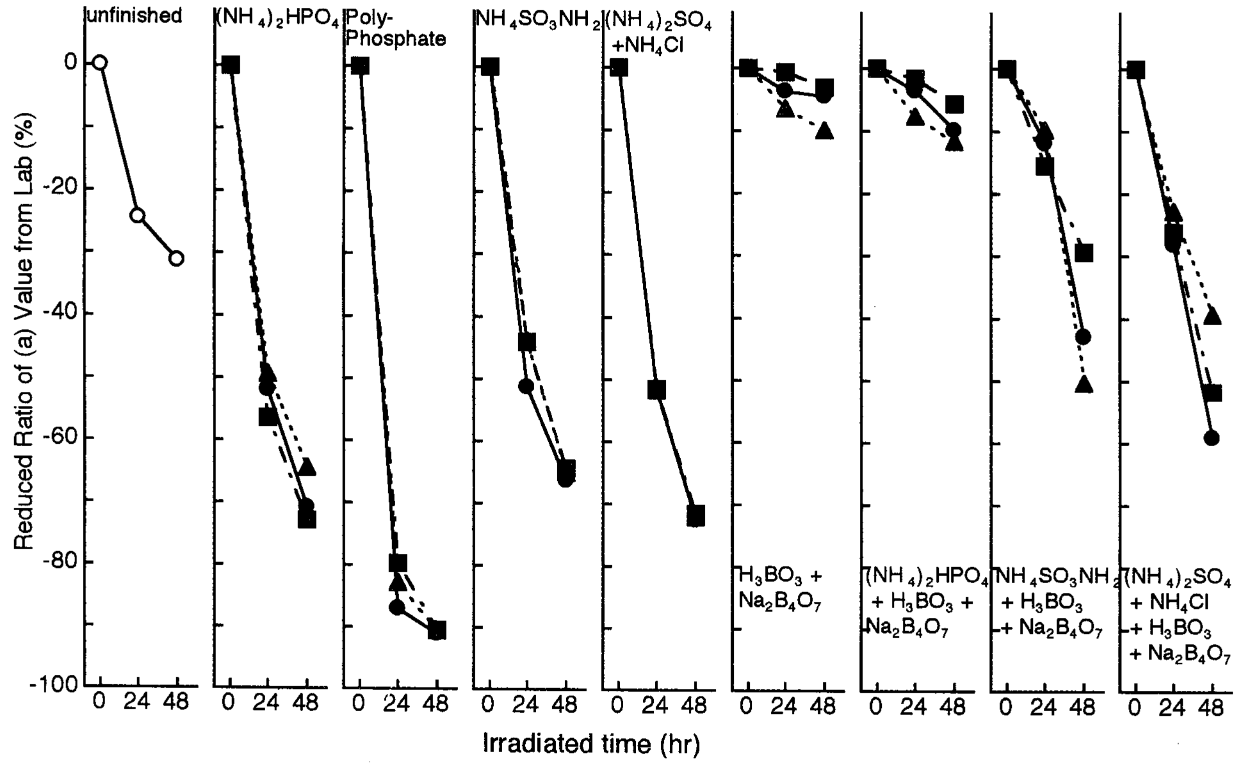


Fig. 4-32 Reduction of color difference observed after ultraviolet irradiation for fabric dyed with Red 2 and finished with various kinds of flame retardants.

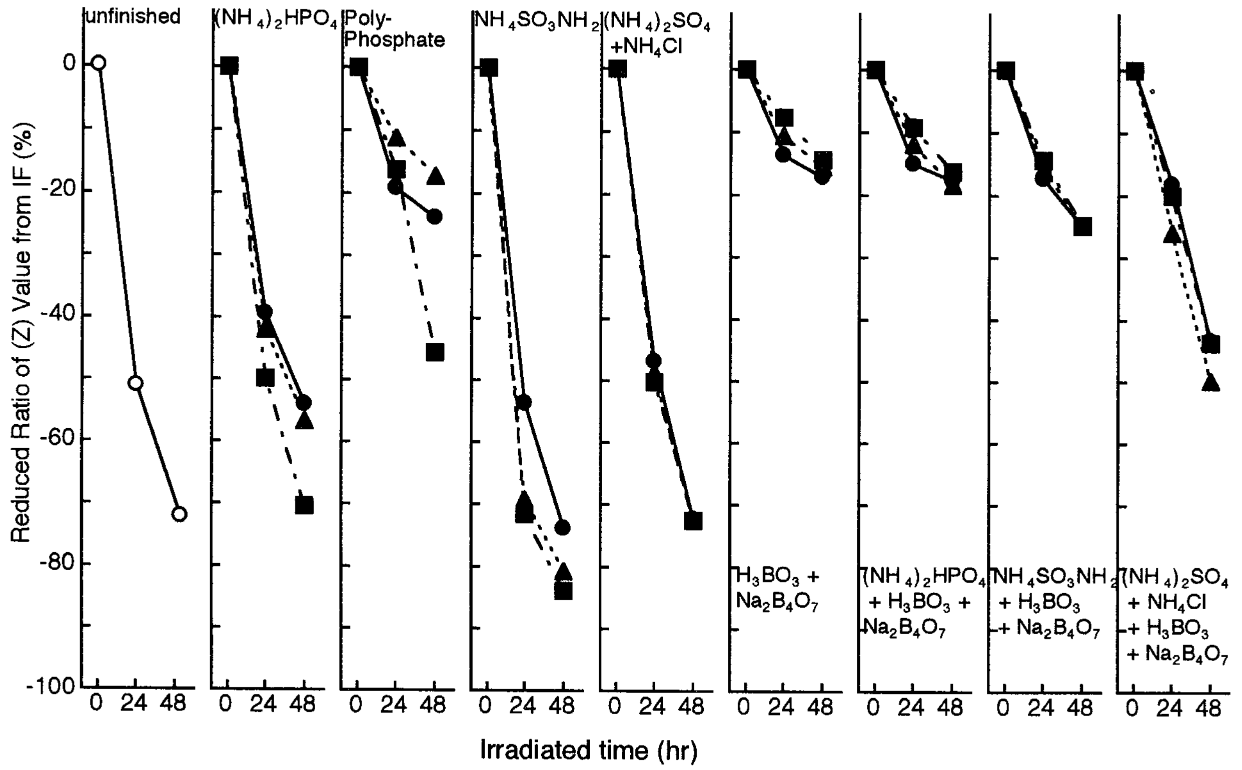


Fig. 4-33 Reduction of intensity of fuluorescence observed after ultraviolet irradiation for fabric dyed with F. B. 86 and finished with various kinds of flame retardants.

3) Conclusion

In addition to reactive dyes and vat dyes used for the previous investigation, different kinds of dyes, azoic direct dyes, a basic dye and a fluorescent brightener were used together with additives for further investigation. Effects of flame retardants containing N, P, S, Cl and B each alone and 2-3 together were observed in combination with effect of ultraviolet irradiation. It was found that discoloration behavior varied with dyes themselves as well as with flame retardants, but attention should be paid to the fact that boric acid and borax depressed discoloration in every case and even when added to flame retardants which accelerate discoloration by themselves. Boric acid and borax always strongly maintained high flame retardance and color stability in every case, which proves the important and useful role of this nondurable flame retardance in contrast to any durable flame retardant having no such merit.

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Chapter 5

Chapter 5 Propagation Behavior of Smoldering Observed in Fiber Assemblies and Effects of Flame Retardant Finishes on Smoldering and Heat of Combustion

5-1 Propagation Behavior in Fiber Assemblies and Effects of Flame Retardant Finishes

Introduction

According to a white paper on fire defense, burning cigarettes comes first as a cause of the fire except for the incendiary fire which is intentional,i.e., the primary hazards associated with fires where beddings or upholstered furnitures would be first initiated are burning cigarettes.

In foreign countries, attention has been seriously paid to burning cigarettes as igniters for beddings or upholstered furnitures, and studies and burning tests have actively achieved in large scale[1-12]. The fire from burning cigarettes is initiated by an instantaneous ignition at a time when heat from a burning cigarette propagates through fiber assemblies and accumulated heat exceeds the critical heat level[13,14].

The recent society with increasing population of aged people is unavoidably involved by such serious problem of much possibility that aged persons smoke in beds or on sofas or carpets, specially much more dangerous when they live alone. There have been some cases that isolated aged persons living alone often place cooking heat sources by their own beds in daily life.

Therefore, we investigated to analyze how the heat of burning cigarette propagates in fiber assemblies to observe propagation behavior of the heat from burning cigarettes under different conditions.

Smoldering has been recognized as a phenomenon burning by an exo-thermic reaction accompanied with the thermal degradation caused by reaction of incombustible residues and char remaining after pyrolytic gas generation with oxygen on the surface[15], which increases the number of fire outbreak as the initial phenomenon of fire though without flaming. It exists even in the growing period and the maximum stage of the fire. Characteristic of the smoldering is to generate large amounts of toxic gases and smoke which can be a direct cause of poisoning and suffocation resulting in death[16], and when temperature and concentration of mixture of flammable gases and air become to meet the condition for onset of fire, the simultaneous flame formation transfers the smoldering to flaming combustion to induce the fire[12-14]. Thus there are many cases in which the smoldering can be a trigger for the fire and involves much hazard to extend over the big fire because of difficulty to detect such smoldering in the initial stage which results in retardation of fire fighting activities. Particularly, smoldering within any limited narrow space can be mortal.

From the above facts, the flame retardation of fiber assemblies is considerably important to protect them from the smoldering by burning cigarettes. Therefore, the investigation this time was started with preparation of flame retardant fiber assemblies followed by observations of smoldering and burning behavior of these flame retardant finished fiber assemblies in comparison with those of unfinished fiber assemblies. Furthermore, different effects were observed between unfinished and flame retardant finished fiber assemblies or cotton fabric (for ticking of Futon) on smoldering phenomenon and burning behavior of miniature Futons prepared according to JIS L 4403-1974.

In addition, resistibilities to dry cleaning of flame retardant finishes used for Futon were tested according to JIS L 0860-1974.

5-1-1 Heat Propagation Behavior in Fiber Asseblies from Burning Cigarette

1) Experimental

(a) Materials

(1) As fiber assemblies, 100% cotton fiber assemblies (JIS 1st class 100% cotton), 100% polyester (PET) fiber assemblies (Teijin Tetron) each alone and blended samples prepared as shown in Table 5-1 were used.

Table 5-1 Fiber assembly samples used for the experiment

Sample No.	Fiber assemblies	
	Cotton (%)	PET (%)
1	100	0
2	0	100
3	80	20
4	50	50

(2) As a cigarette sample, "Peace" with both cut edges was employed.

(b) Methods

The above mentioned fiber assemblies were conditioned at RH (humidity) 65% at 20°C for 72 h. Cotton fiber assemblies were further conditioned at additional RH 32% and 90% for 72 h to observe effects of RH on the propagation behavior.

According to the standard for flame retardance (1982) regulated by government for beddings and tents, stainless baskets, 10cm by 15 cm and 1, 1.5 and 2 cm in height, 2 baskets for each size with each height were made, in which conditioned fiber assemblies were filled with varied densities, 0.04 g/cm^3 - 0.093 g/cm^3.

A lighted cigarettes was placed at the center of a block of fiber assemblies prepared as mentioned above and covered with the other block of the same size as shown in Fig. 5-1. In this case, sensors (1.6 mm in external diameter and 200 mm in length) were set at 1, 1.5 or 2 cm apart from the lighted front, the center and the rear terminal of cigarette in the directions of upward, downward and horizontally as shown in Fig. 5-1. Temperature change at each position was recorded and accumulated heats were compared relatively by areas obtained from temperature-time curves.

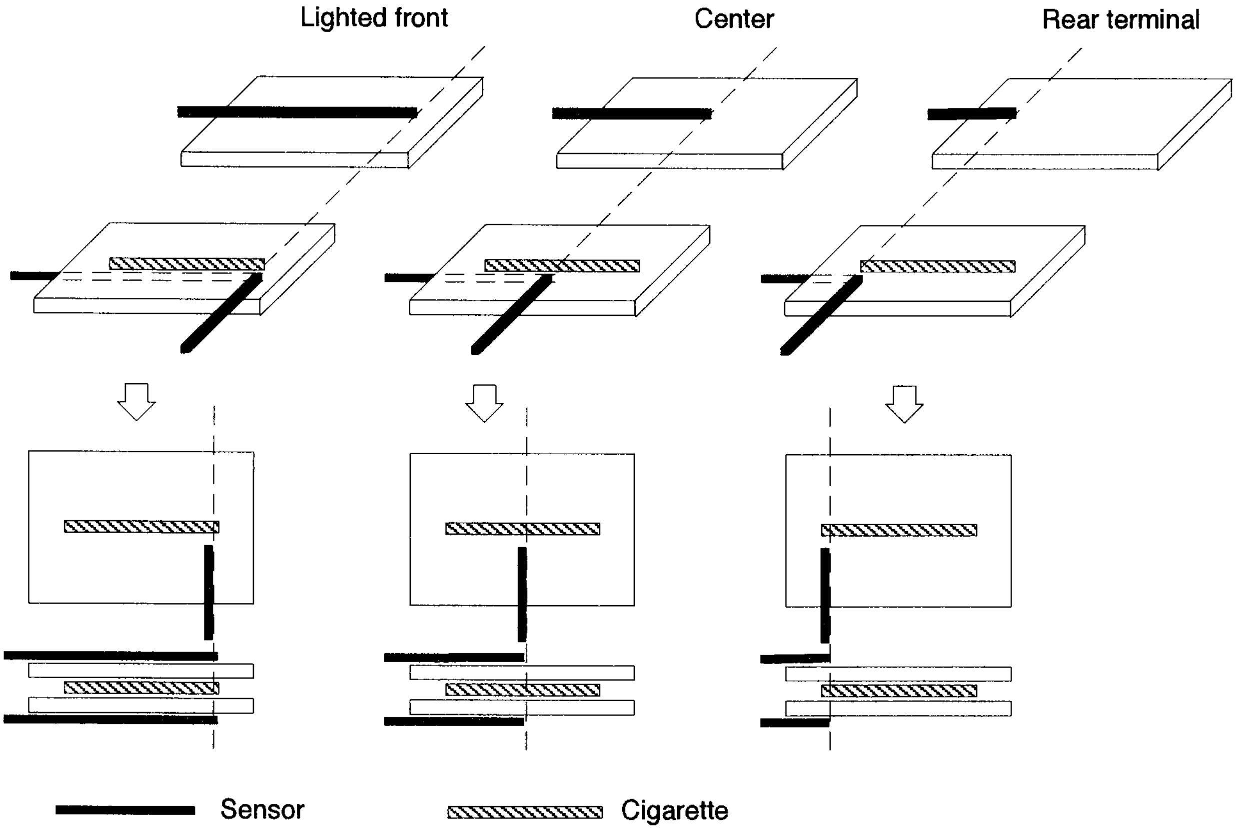


Fig. 5-1 Schematic illustration for positions of sensors and cigarette in fiber assemblies.

2) Results and Discussion

(a) Effects of covering

The combustion of fiber assemblies from burning cigarette associated with fire generally progresses by continuation of the self-sustained smoldering process from heat source, burning cigarette in this case, in a large amount of fiber assemblies. Taking practical conditions into consideration, such smoldering may progress in an open environment entirely exposed in air, alternatively in comparatively closed environment where the air supply is not sufficient. Therefore, the self-sustained smoldering behavior was observed with and without a asbestos cover. As shown in Fig. 5-2, both temperature and heat accumulation (area) increased with increase in the density of fiber assemblies, but temperatures were higher when smoldered without cover showing higher than 400°C in almost all cases and even over 500°C in the cases of densities more than 0.08 g/cm^3. But the density dependence is smaller and less difference was observed with change in density. On the other hand, larger areas for heat accumulation were observed when covered. Such results explain that the combustion proceeds actively in air rich atmosphere without cover to generate higher temperature, whereas accumulated heat is much more released resulting in heat loss showing smaller heat accumulation without cover. More detailed observation disclosed that since accumulated heat was released more largely upward and horizontally, downward accumulation was largest and the highest maximum temperature was shown by the downward propagation in the cases of smaller densities. But, in the cases of densities of 0.06 g/cm^3 or higher, the combustion became more active along the upward propagation in contact with air, which showed the highest temperature simultaneously with increase in the heat accumulation approaching that of the downward propagation. Temperature along the horizontal propagation showed gradual access to that of the upward propagation with increase in density to exceed the temperature along downward propagation, but heat accumulation always stayed at the lowest level because of the effect of heat release.

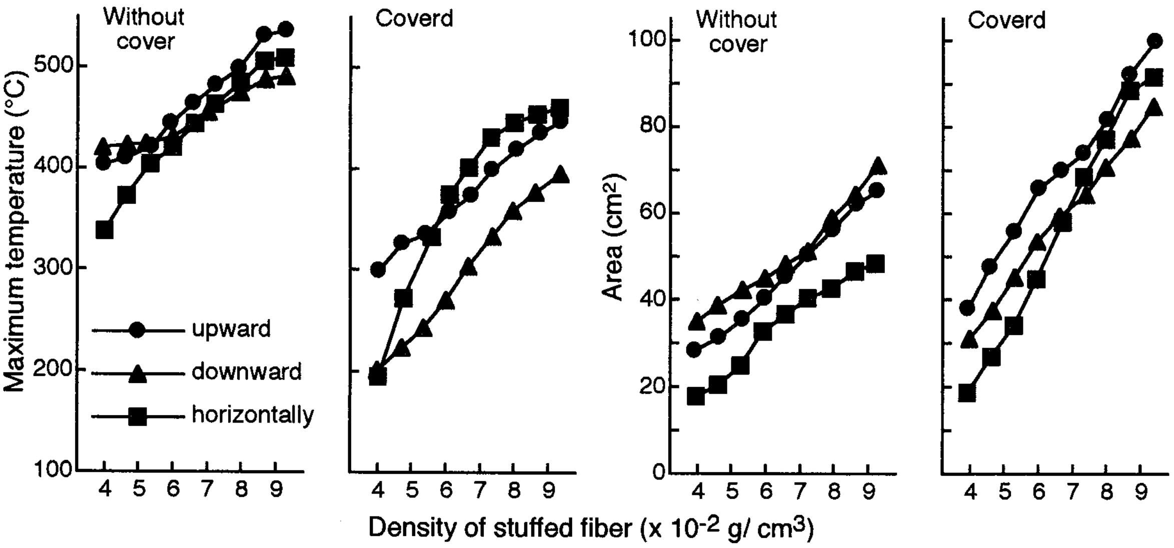


Fig. 5-2 Comparison beween heat propagating behavior in cotton fiber assemblies with and without a cover.

When covered on the other hand, the heat accumulation at upward direction became largest owing to the suppression of heat release by covering, and temperature was also highest at upward propagation region in the cases of lower densities, but both heat accumulation and temperature in the horizontal propagation area rapidly raised to reach the maximum temperature as well as to approach the accumulated heat observed for upward propagation. The downward propagation is always most inactive showing the lowest temperature in all density ranges as well as exhibiting the smaller heat accumulation in lower density ranges.

Overall observation suggests that larger temperature rise with much danger was found with fiber assemblies when exposed to the air during smoldering, but significant danger may be unavoidable when the heat accumulation grows by a long term continuous self-sustained smoldering. It was also found that smaller fiber assembly densities with the same volume showed lower temperature and smaller heat accumulation, which suggests that beddings, such as Futons, with low density fiber assemblies are more favorable to use practically for the viewpoint of safety.

As the results of the above investigations with and without a cover, including burning tests without cover carried out in a draft according to the Government Guidance, it was found that a number of repetition of experiments were required to obtain results with stable reproducibility since air was flowing all the time and significantly influenced the heat propagation in fiber assemblies when exposed to mobile air.

Therefore, in order to obtain reliable and constant results under the steady and stable conditions for the fundamental standpoint, the investigations were carried out with cover to confirm stabilized condition for the present study.

b) Comparison of heat propagation behavior at each position of cigarette

When a lighted cigarette is brought into contact with fiber assemblies, the heat of this cigarette propagates into fiber assemblies by burning itself from lighted front toward the rear terminal, so the propagation behavior of heat from a burning cigarette was observed at representative positions of cigarette, the lighted front, the center and the rear terminal in the directions of upward, downward and horizontal way, which showed that the horizontal propagation is the most rapid, followed by upward, and downward propagation was the slowest, specially the heat at lighted front propagated horizontally most rapidly showing a high peak, 600°C within 10 min and descended very rapidly again, therefore the heat accumulation was not so large at this time. However, it required 30 min from 150°C to reach room temperature. The upward propagation was little slower showing a peak 6-7 min later and descended comparatively slowly. The downward propagation was gradual showing a peak 25 min after and descending more slowly (Fig. 5-3).

The behavior at center was different from that observed for the front mentioned above, i.e., the horizontal propagation became slower and temperature rise was also retarded showing a peak 28-30 min later with slower descending. But, the heat accumulation showed a tendency of increasing. The upward propagation was also slower showing a peak 40 min after. Appearance of a peak from downward propagation was more retarded requiring 50 min to show a peak, but descending rate of temperature was comparatively fast. At rear terminal the onset of temperature rise was largely retarded by 25-30 min, but the horizontal propagation showed a peak 10 min after the onset of temperature rise and descending rate was rapid showing propagation behavior similar to that observed in the case of lighted front. However, the downward propagation is the slowest requiring 60 min for the appearance of a peak. Overall observation showed that the order of the propagation of heat from burning cigarette is the lighted front horizontally and followed by upward direction. The propagations downward at front and horizontal propagation at center almost similarly proceeded and the heat propagated almost similarly upward at center and horizontally at the rear terminal, and the maximum temperature appeared in the order of upward at rear terminal, downward center and downward at rear terminal. Thus, the heat propagation behavior in fiber assemblies are very complicated as described above. Of course, the maximum temperature and heat accumulation will differ with varied conditions depending on fiber density with or without cover etc. But it has been found that not much difference was observed for the heat propagation behavior.

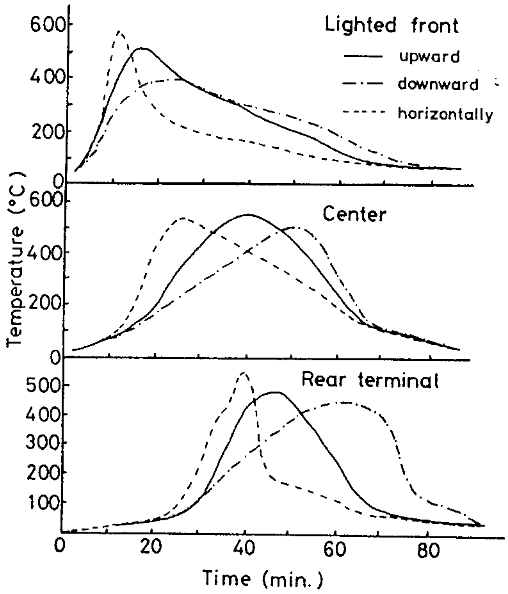


Fig. 5-3 Heat propagating behavior in cotton fiber assemblies in upward, downward and horizontal directions from burning cigarette at lighted front, center and rear terminal of cigarette.

(c) Effect of thickness

Effects of thickness of fiber assemblies in contact with a burning cigarette were observed by using 100% cotton fiber assemblies with varied thickness, 2, 3 and 4 cm. The results were, as shown in Fig. 5-4, that a large density dependence was observed for maximum temperature in the case of 2 cm thickness, whereas the difference observed among varied densities decreased with increase in thickness from 2 cm to 3 cm and 4 cm. In the cases of thickness 3 cm or thicker, the horizontal propagation showed the highest temperature irrespective of the fiber density. Temperatures exceeding 500°C were observed with 4 cm thickness showing leveling off tendency at 0.06 ~ 0.07g/cm^3 or larger fiber density. The downward propagation showed the lowest temperature in all cases, specially in the case of 4 cm thickness, temperature rise was largely depressed probably by lacking air because of too compact to contain enough air for sufficient combustion. The heat accumulation also showed considerable rise with fiber density as well as with thickness, and the horizontal propagation brought the largest heat accumulation and downward gave the least area, which correspond to what is shown in the case of the maximum temperature shown above. The thickness 3 cm exhibited an intermediate tendency between the two different behavior shown by thickness 2 cm and 4 cm, i.e., little difference was observed among 3 directions of propagation.

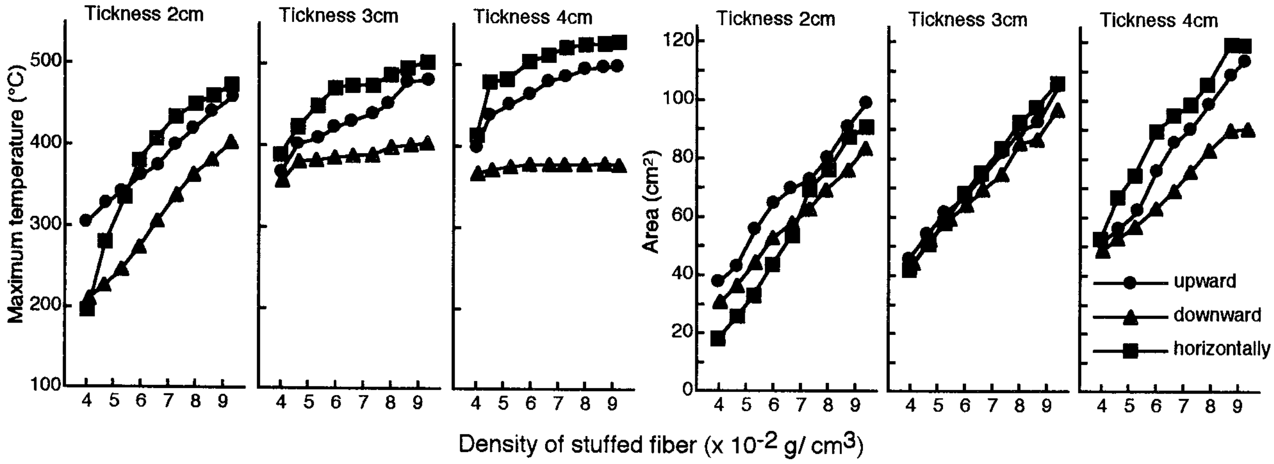


Fig. 5-4 Effect of thickness of fiber assemblies on heat propagating behavior from burning cigarette in cotton fiber assemblies.

From an angle of the safety, it can be concluded that the thinner and the less density, the safer. However, it has been recognized that in the case of combustion of flammable fiber materials by burning cigarettes, the self-sustained smoldering continuously proceeds followed by ignition when temperature reaches 400°C[15,16], which suggests a possibility of an instantaneous ignition when exposed to the atmospheric air. Taking the results obtained above into consideration, since almost all cases of the present investigations showed 400-500°C or higher, any practical case with much larger amount of fiber assemblies under air rich environment, surely involves very dangerous hazard. On the bases of our estimation from the results of the present investigations, 20 g or more of fiber assemblies, a medium of combustion, brings about temperature exceeding 400°C.

Sleeping Futons practically used by the general public made of a large amount of fiber assemblies are much more hazardous.

(d) Effect of water content

Effect of water content of fiber assemblies was investigated by using fiber assemblies with different water contents conditioned under RH 32, 65 and 60%. As shown in Fig. 5-5, both temperature and heat accumulation rose with increase in fiber density, the mutual relationship between the maximum temperature and the heat accumulation along the propagation direction showed a tendency similar to that observed in the case conditioned at RH 65%. Overall tendency was that the maximum temperature and heat accumulation were lowered with increase in water content to some extent. But, more detailed observation revealed that specially low density showed behavior irrespective of water content in some cases and effect of water content was less than expected, which is due to that water in fiber assemblies evaporates with propagation of heat, particularly since the evaporation is more rapid when the fiber density is lower, any effect of water content will diminish by evaporation of water with time though effect of water works immediately after the initiation of burning.

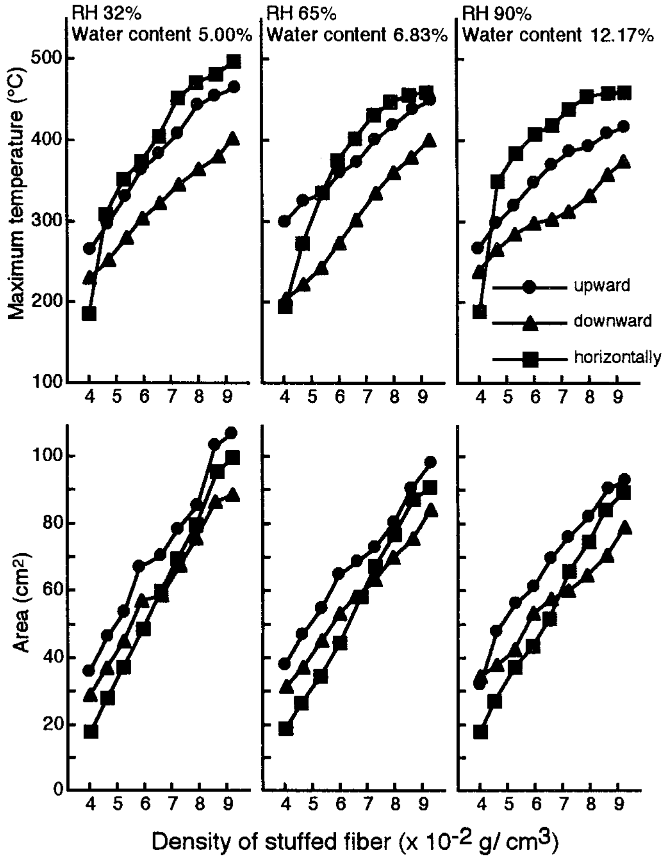


Fig. 5-5 Effect of water content of fiber on heat propagating behavior from burning cigarette in cotton fiber assemblies.

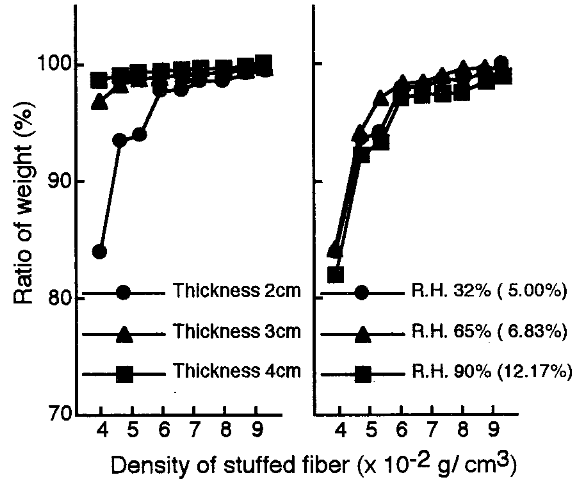


Fig. 5-6 Effect of thickness and water content of fiber on weight loss of fiber assemblies after smoldering combustion by burning cigarette.

(e) Effects of water content and thickness observed with weight loss

An investigation was subsequently carried out to compare weight loss obtained after burning under the different conditions, with different thickness and varied water contents. As shown in Fig. 5-6, 2 cm thickness showed a little lower weight losses in the cases of fiber densities of 0.05 g/cm^3 or lower. But, when the thickness increased to 3 cm or thicker nearly 100% loss was observed irrespective of the fiber thickness. As for the effect of water content, there found a tendency that weight loss was slightly lowered with increase in water content, but 0.06 g/cm^3 or higher fiber densities showed little dependence on water content showing weight losses 95% or higher nearly 100% except for densities lower than 0.06 g/cm^3. Such tendency that the thicker thickness and the higher density showed higher temperature and larger heat accumulation was also observed in this case.

(f) Effect of blending with PET

In contrast to 100% cotton fiber assemblies, effect of blending PET fiber was investigated by using cotton/PET blended fiber assemblies shown in Table 5-1. It was found from a preliminary experiment carried out with 100% PET fiber assemblies, the result of which showed that a burning cigarette was extinguished by PET molten by heat. Such phenomenon might be favorable from the standpoint of safety but a possibility for danger of molten PET can not be avoidable when it happens to touch the skin of the human body.

Recently, the demand for PET fiber assemblies in the market has been developed because of its merits. The investigations with blended fiber assemblies showed as shown in Fig. 5-7 that the maximum temperature and the heat accumulation showed reduction with increase in the ratio of PET, particularly, horizontal heat propagation was largely depressed.

(g) Effect of PET blending on weight loss

Finally, effect of PET blending on weight loss caused by combustion from burning cigarette was observed. As shown in Fig. 5-8, decrease in weight loss was observed by blending PET with 100% cotton, i.e., 100% cotton showed more than 85% weight loss, but the weight loss decreased to 50% by blending 20% PET and even further to 40% by blending 50% PET. When the fiber density increased to 0.07 g/cm^3, cotton 80%/PET 20% blended fiber assemblies showed increase in weight loss to 90% and approached the level for 100% cotton when the density exceeded 0.09 g/cm^3. But if ratio of PET increased to 50%, weight loss decreased in all cases, i.e., weight loss stayed at a level of 73% even density exceeded 0.09 g/cm^3. As mentioned above, PET blending were considerably effective also for the depression of combustion of fiber assemblies.

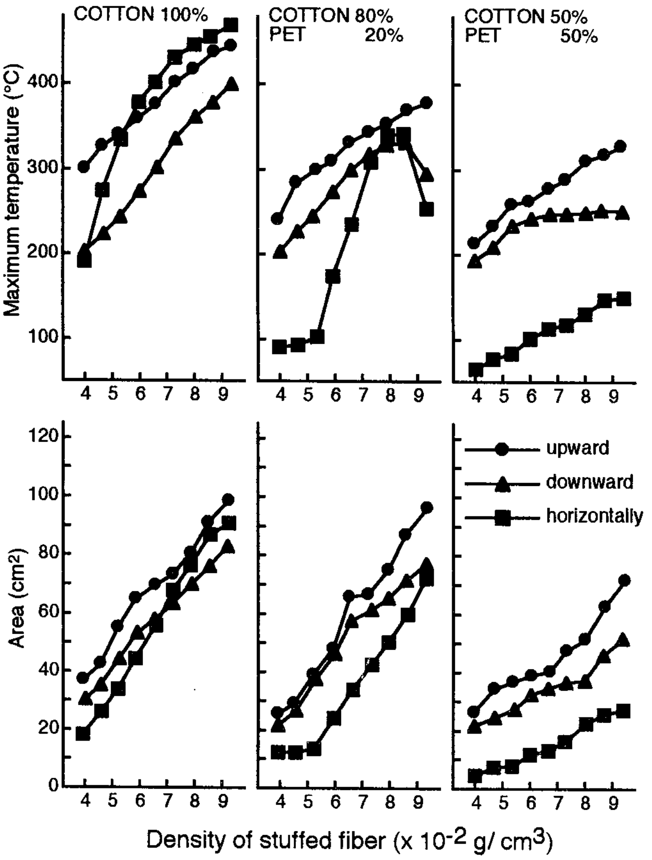


Fig. 5-7 Effect of blending polyester with cotton fiber assemblies on heat propagating behavior.

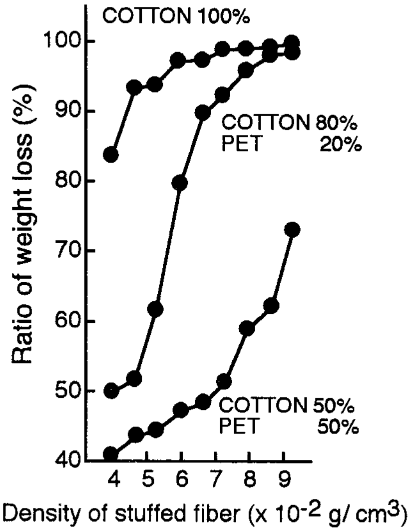


Fig. 5-8 Effect of blending polyester with cotton fiber assemblies on weight loss after smoldering combustion by burning cigarette.

3) Conclusion

It was thought to be not ignored that the fire often breaks out from a burning cigarette left on flammable fiber assemblies. Therefore, the heat propagation behavior in fiber assemblies from burning cigarettes was observed in the self-sustained smoldering processes under various conditions. The results are summarized as follows:

(a) The heat from a burning cigarette propagates in fiber assemblies with the highest rate horizontally and with the lowest rate downward.

(b) The temperature is higher when fiber assemblies are exposed to the air than when covered, especially in the upward direction, whereas the heat accumulation is more when covered, showing the largest accumulation in the upward direction.

(c) The maximum temperature and heat accumulation observed in the upward and horizontal heat propagation enhance with increase in density and thickness of stuffed fiber assemblies, but the downward propagation shows slightly decrease when the thickness is 4 cm or more.

(d) The effect of water content of fiber assemblies on temperature and heat accumulation is much less significant than we expected..

(e) The maximum temperature, heat accumulation and weight loss observed after the combustion of cotton fiber assemblies are considerably reduced by blending PET fiber.

5-1-2 Heat Propagation behavior Observed in Flame Retardant Finished Fiber Assemblies from Burning Cigarette

1) Experimental

(a) Materials

One hundred % cotton, 100% PET and cotton/PET blended fiber assemblies were the same as those used for the previous investigation described in 5-1-1.

One hundred % cotton fabric the same as that used for the previous investigations described in Chapter 2, 3 and 4 was also used as a ticking material for miniature Futons.

Cigarette was the same as that used for the previous investigation in 5-1-1, and matches and a cigarette lighter were used as additional heat sources this time.

Sodium hydroxide was used for the mercerization of cotton fiber assemblies.

As flame retardants and additives, boric acid, borax, diammonium hydrogen phosphate, ammonium sulfamate, ammonium chloride, ammonium sulfate, polyphosphoric carbamate, guanyl methylol phosphate, Pyrovatex CP, hexamethylolmelamine, phosphoric acid, sulfamic acid and urea were used.

(b) Methods

(1) Mercerization of cotton fiber assemblies

Since it was found that 100% cotton fiber assemblies required some kinds of pretreatment for sufficient penetration of flame retardants, the mercerization was attempted by impregnating cotton fiber assemblies with 10% sodium hydroxide solution for 30 min, wrapped with gauze for washing with water and dried at 105-110°C after centrifugation.

(2) Flame retardant finishes

As single solution, 10 and 20% solutions of diammonium hydrogen phosphate and ammonium sulfamate were prepared, and each mixed flame retardant solution was prepared by mixing as follows:

Boric acid and borax (3:7 weight ratio), diammonium hydrogen phosphate and ammonium sulfamate (1:1), polyphosphoric carbamate and guanyl methylol phosphate (1:1) and ammonium chloride, ammonium sulfate and diammonium hydrogen phosphate (1:1:1) respectively.

Mercerized 100% cotton fiber assemblies and 100% cotton fabric were immersed in the above mentioned flame retardant solutions, centrifuged (for fiber assemblies) or padded (for cotton fabric) to 90% pickup after 2 dip - 2 nip process and fiber assemblies were dried at 105-110°C and fabric was air dried. Boric acid and borax solution was used also for finishing cotton/PET blended fiber assemblies in the same manner as mentioned above.

For Pyrovatex finishes, in addition to a single solution, the following 6 kind of mixtures were prepared:

32% of Pyrovatex CP + 8% hexamethylolmelamine (M6)
+ 2% phosphoric acid
+ 2% phosphoric acid + 8% M6
+ 0.5% sulfamic acid + 8% M6
+ 1.5% phosphoric acid + 0.5% sulfamic acid + 8% M6
+ 8% M6 + 1% urea + 0.5% ammonium chloride

Mercerized cotton fiber assemblies were treated with each above solution, soaped and rinsed as described in 3-1-1, and every sample was conditioned at 20°C under RH 65% for 72 h.

(3) Water durability test for nondurable flame retardant finished fiber assemblies

According to JIS Z-2150B method, the above mentioned nondurable flame retardant finished fiber assemblies were immersed in water (bath ratio : 40) for 10 sec, wrapped with gauze for centrifugation and dried at 105-110°C.

(4) Treatment with organic solvents for evaluation of durability to dry cleaning

The above nondurable flame retardant finished fiber assemblies and fabric were treated with perchloroetylene alone as well as with perchloroethylene charged with 5 g/l of each anionic and nonionic surfactants for 30 sec at 40°C with a bath ratio of 20:1 in a Launder-O-meter according to JIS L 0860-1974.

(5) The heat propagation behavior was observed with the flame retardant finished fiber assemblies mentioned above by the method described in 5-1-1. Residual amounts of fiber assemblies were weighed at the completion of the combustion of cigarette and after extinguishing of fiber assemblies, by which residual ratios were calculated for the comparison with those of unfinished cases.

(6) Burning tests by matches and cigarette lighter

Burning tests were attempted according to the regulation 001-1967 of Japan Fire Protecting Association.

Two g of the above mentioned unfinished, flame retardant finished samples and those treated as mentioned in (c) and (d) above were made into balls 4 cm in diameter, hung with a wire hook, to which a match flame was contacted for 1 sec and combustion behavior was observed for each sample. After completion of combustion, each residual amount was weighed.

Residual portions were made into balls again, hung as mentioned above and contacted with lighter flame for 30 sec this time. The residual amount was weighed for each sample after self-extinguishing and ratio of residue was calculated to compare resistibilities before and after laundry and dry cleaning.

(7) Flame retardance of each sample mentioned above was evaluated by LOI method regulated by JIS K 7201-1976 described in 2-1-2.

(8) Preparation of miniature Futon

Unfinished and flame retardant 100% cotton fabric finished with 20% solution of boric acid and borax were used as the ticking for Futon. One hudred % cotton, cotton 80%/PET 20% and cotton 50%/PET 50% blended fiber assemblies, both unfinished and finished with the same solution were used as stuffings for Futon. Unfinished and above 3 kinds of finished fiber assemblies, and unfinished and finished cotton fabric (ticking) were used to prepare 4 kinds of combinations for each kind of fiber assemblies, i.e., unfinished ticking and unfinished stuffing, finished ticking and unfinished stuffing, unfinished ticking and finished stuffing and finished ticking and finished stuffing, 12 kinds of combinations in total were used for miniature Futons. Size and weight of miniature Futon were decided according to JIS L 4403-1974. The length and width were reduced to 1/10 for mattress and the length to 1/10 and the width to 1/5 for coverlet (the width required twice long to cover a mattress). The weight of fiber assemblies was 1/100 for mattress and 1/50 for coverlet. The thickness was approximately the same as the real Futon. A cigarette was placed at the center of this mattress and covered with the coverlet to observe the combustion behavior according to the method described in 5-1-1.

3) Results and Discussion

(a) Effects of various kinds of flame retardant fiber assemblies observed on maximum temperature and heat accumulation

The heat propagation behavior was observed with various kinds of flame retardant fiber assemblies prepared as mentioned above with a representative density 0.06 g/cm^3.

Maximum temperature at each direction was shown in Fig. 5-9 and areas from temperature - time curves in Fig. 5-10. As seen in these figures, the highest maximum temperature for unfinished fiber assemblies was observed in horizontal direction, 400°C followed by upward direction and the lowest was 300°C in downward direction. On the other hand, the upward propagation showed the highest temperature and the lowest temperature was shown in the horizontal direction in the cases of finished samples all showing remarkably lower temperatures compared with those of unfinished sample. In the case of heat accumulation, both unfinished and finished samples showed the largest areas in the upward direction and the smallest areas in the horizontal direction with marked reduction in every case. Overall tendency is that finished samples showed significant reductions of both maximum temperature and heat accumulation, particularly the heat propagation in the horizontal direction was mostly depressed. Comparison among effects of flame retardants revealed that nondurable flame retardants were more effective than durable flame retardants and a special attention was drawn to the fact that the best effect was shown by boric acid and borax, i.e., the maximum temperature was lowered down to 100-150°C (1/3-1/4) in upward and downward directions, and 70-100°C (1/5-1/6) in the horizontal direction. The heat accumulation was reduced to 1/4-1/5 in upward and downward directions and even down to 1/6-1/9 in the horizontal direction. Among nondurable flame retardants, organic substances gave less effect nearly the same as that shown by durable flame retardants, which is due to the combustibility of organic flame retardants themselves. In contrast, inorganic salts such as boric acid, borax or ammonium salts melt or generates ammonia endo-thermically, which results in considerable reduction of the heat accumulation. The exo-thermic reactions of organic flame retardants and endo-thermic reactions of inorganic flame retardants were confirmed by Nakanishi et al. by the thermal analysis, DSC. However, even a organic flame retardant Pyrovatex CP contributed to depress not only the maximum temperature down to 200°C (1/2) in the upward and downward directions and to 100°C (1/4) in the horizontal direction but also the heat accumulation to 1/2-1/3 in the upward and downward directions and even down to 1/6 in the horizontal direction. Such effects nearly correspond to those of inorganic ammonium salts.

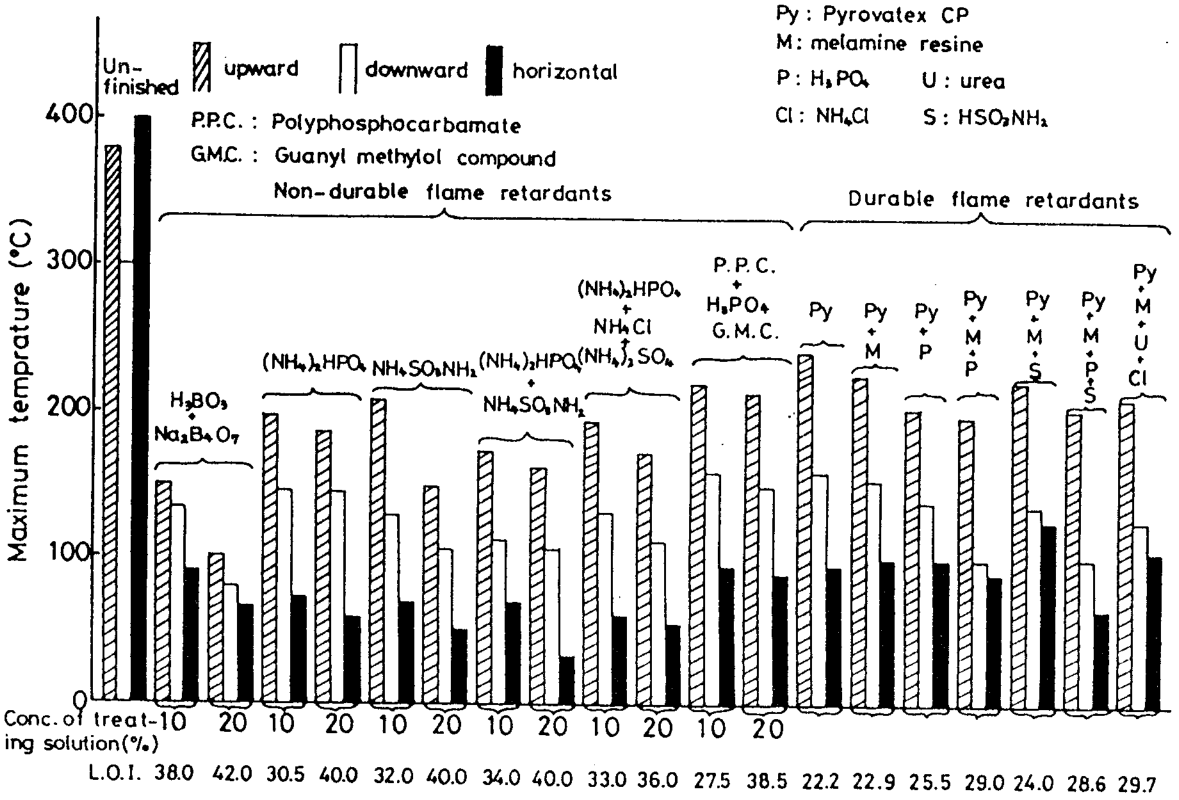


Fig. 5-9 Comparison of maximum temperatures of cotton fiber assemblies observed between unfinished and finished with various kinds of flame retardants.

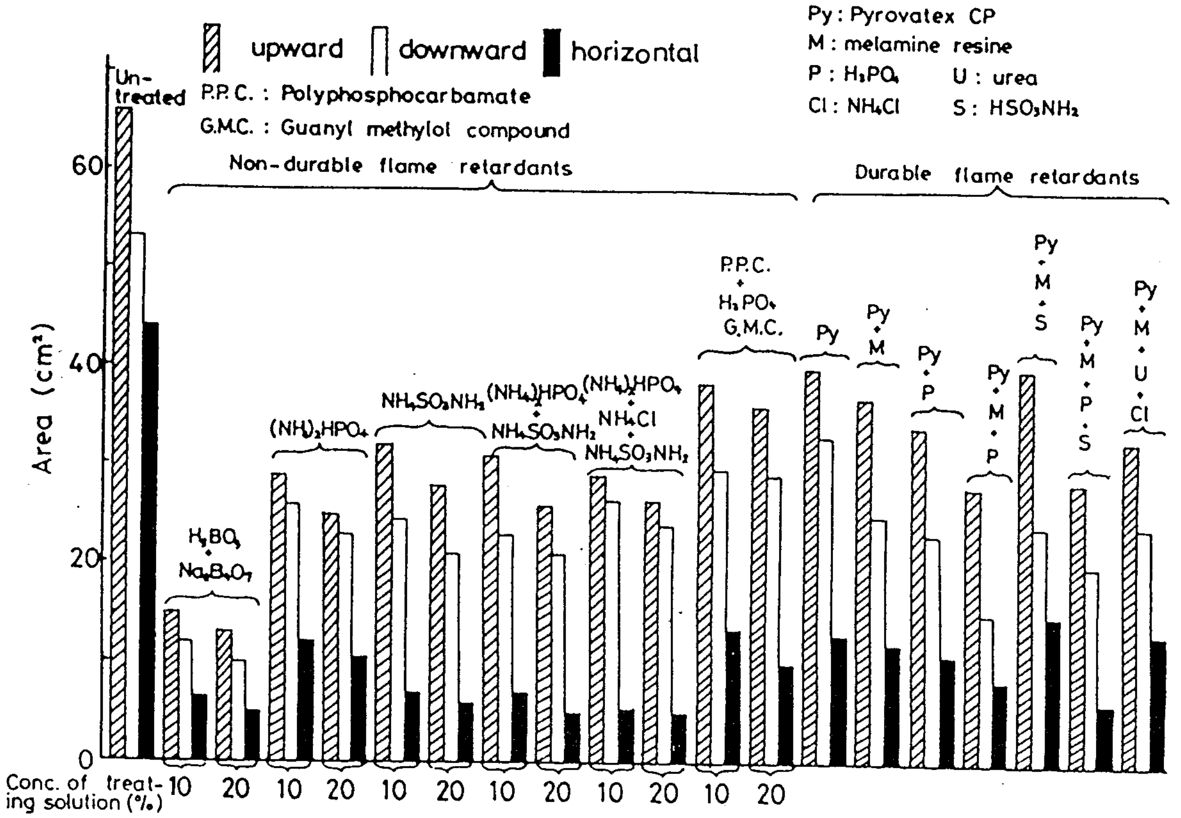


Fig. 5-10 Comparison of accumulated heat of cotton fiber assemblies observed between unfinished and finished with various kinds of flame retardants.

When another attention was paid to if the above depressing effect corresponds to LOI, a measure for the flame retardance. As shown in Fig. 5-9, the maximum temperature, and heat accumulation of each sample almost corresponds to the LOI value respectively, i. e., samples showing higher LOI values gave more depression of these values. Among a series of Pyrovatex finishes, Pyrovatex CP alone and Pyrovatex CP + M6 showed insufficient effects though effective to some extent compared with unfinished sample, but further addition of additives elevated LOI values, specially, increase in phosphorus and nitrogen by addition of phosphoric acid and urea brought a larger effect. This behavior was well reflected on the depressing effect on the burning behavior of fiber assemblies.

As described above, it has been clearly found that the heat propagation is largely suppressed by flame retardant finishes. Therefore, effects of fiber densities were observed with fiber assemblies together with blended fiber assemblies finished with 20% solution of boric acid and borax which showed the best effect among the flame retardants used this time.

(b) Effect of flame retardant finish on 100% cotton fiber assemblies with varied densities

Fig. 5-11-A shows that both maximum temperatures and areas, heat accumulation, steeply elevated with increase in fiber density in every direction in the case of unfinished 100% cotton fiber assemblies as indicated by open marks, whereas finished fiber assemblies showed entirely no density dependence in every direction keeping extremely lower level in both cases of temperature and area.

(c) Effect of flame retardant finish on cotton/PET blended fiber assemblies

As clearly shown in Figs.5-11-B and C, a tendency the same as shown in Fig. 5-11-A was observed with cotton/PET blended fiber assemblies, i.e., unfinished samples showed a rise of temperature and area in every direction though the slopes were more gentle and the levels were lower compared with those of 100% cotton samples, whereas finished samples showed little dependence at much lower level nearly the same as observed with 100% cotton fiber assemblies. But, the level became slightly higher with increase in ratio of PET probably because any flame retardant finish effective for 100% cotton is not sufficiently effective for any synthetic material, which suggests that it is better to finish 100% cotton and synthetic materials separately and blend after finishing. At any rate, finished blended samples kept a level of 90-150°C in the upward and downward directions and only 50-90°C in the horizontal direction.

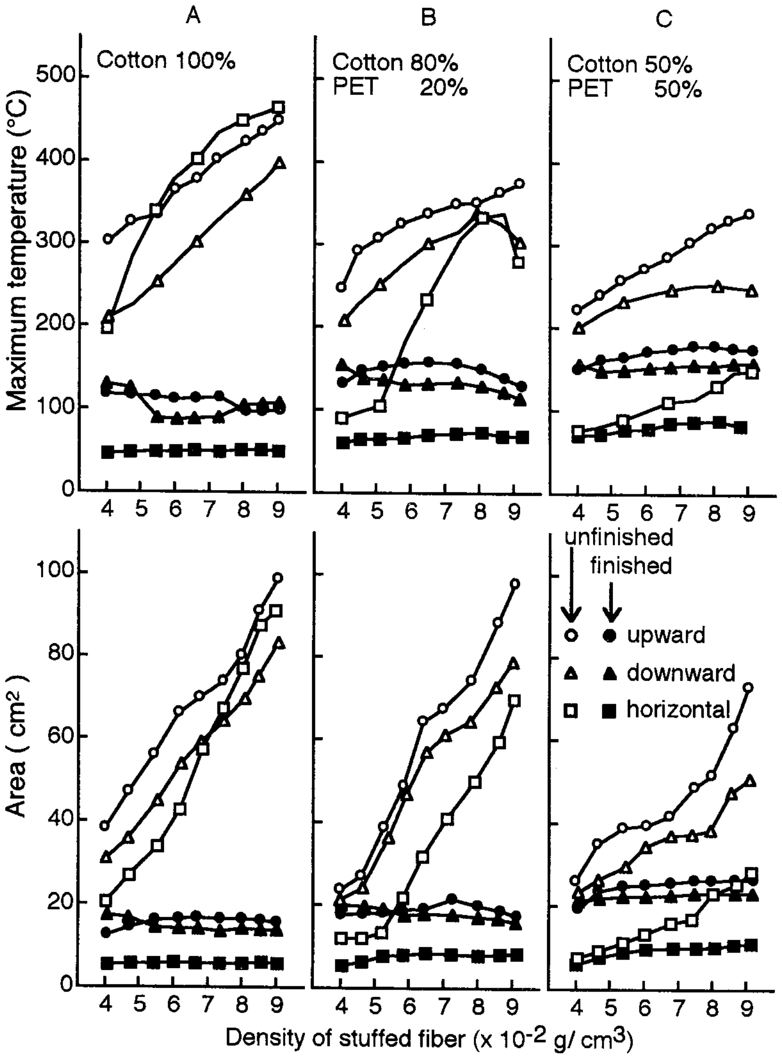


Fig. 5-11 Comparison of maximum temperatures and accumulated heat of Cotton/PET blended fiber assemblies observed between unfinished and finished with flame retardants.

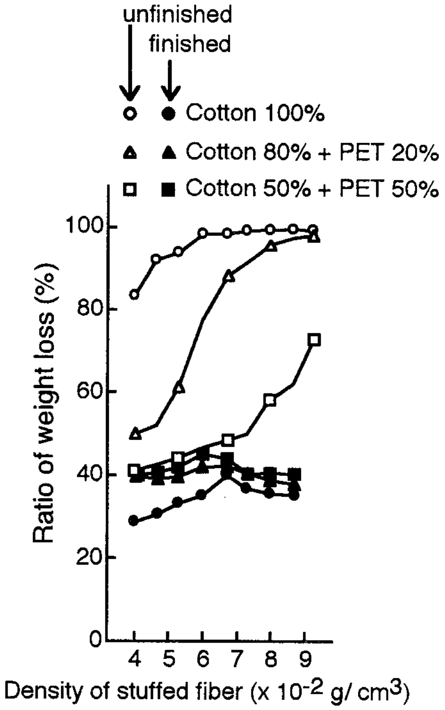


Fig. 5-12 Comparison of weight losses observed between unfinished and finished Cotton and Cotton/PET blended fiber assemblies.

(d) Effect of flame retardant finish observed from weight loss after self-extinguishing

As shown in Fig. 5-12, 100% cotton fiber assemblies almost completely burned up when the fiber density exceeded 0.06 g/cm^3, but weight loss considerably decreased with increase in ratio of PET exhibiting much difference among 3 different blending ratios in the case of unfinished fiber assemblies, whereas finished samples maintained at much lower level 30-40% with little density dependence and little difference among 3 kinds of fiber assemblies. However, in the case of finished fiber assemblies, a tendency opposite to that of unfinished samples was observed, i.e., weight loss of 100% cotton was lowest and it increased with increase in ratio of PET, which is due to the same reason mentioned above.

(e) Effect of flame retardant finish of ticking and stuffing fiber assemblies on combustion of Futon

In the practical cases, it is required to take ticking into consideration when Futon is dealt with. Therefore, the mutual relationship between effects of flame retardant finishes of both ticking and stuffing on the burning behavior of Futon was observed. Visual observation and ratios of weight losses are shown in Table 5-2, which is summarized as follows:

Only finished ticking with unfinished stuffing showed little effect.

Finished fiber assemblies in combination with unfinished ticking showed larger weight loss compared with that of finished fiber assemblies alone without ticking because combustion propagated along unfinished flammable ticking. The largest weight loss was observed with 100% cotton unfinished fiber assemblies and ticking.

Combination of finished ticking and finished stuffing only showed excellent effects, of which the least effect was observed with cotton 50%/PET 50% blended fiber assemblies.

Residue of cotton/PET blended fiber assemblies contained a large amount of white powdery product.

Table 5-2 Comparison of combusting behavior of Futons made of combinations of unfinished and finished fabric and fiber assemblies.

		unfinished fabric	Finished fabric
Unfinished fiber assemblies	100% cotton	Almost entirely burned up	Fabric remained as char fiber assemblies entirely burned up
	weight loss	99.9%	92.4%
	cotton 80% PET 20%	Almost entirely burned up	Fiber assemblies entirely burned up as 100% cotton
	weight loss	97.0%	90.0%
	cotton 50% PET 50%	Almost burned up with trace of residue	Fabric remained as char and white powdery pyrolyzed PET
	weight loss	92.1%	65.0%
Finished fiber assemblies	100% cotton	Fabric burned slightly left Fiber assemblies fairly remained	Entirely remained, only around cigarette slightly chared
	weight loss	73.2%	0%
	cotton 80% PET 20%	The same as 100% cotton white pouder slightly left	Almost remained, only around cigarette slightly chared
	weight loss	68.3%	0.2%
	cotton 50% PET 50%	Char and a powdery product left	Char and powdery product remained, but flame retardant finish not so effective as 100% or 80% cotton
	weight loss	59.4%	40.0%

(f) Evaluation of durabilities to water and dry cleaning

Nondurable flame retardant finishes only require much simpler finishing methods and have such merits as higher flame retardant effect and much less harm of pyrolytic gases and smoke. Therefore, it is of interest to see how nondurable flame retardant finished fiber assemblies resist to treatment with water as well as with organic solvents for dry cleaning. The durabilities were evaluated by the match test and the lighter test as mentioned above. Fig. 5-13 shows that little flame retardant effect was lost by water treatment and dry cleaning, specially, samples finished with 20% solutions showed almost no change in the flame retardance probably because samples finished with 20% solution still kept add-on enough to maintain the flame retardance even after the treatments, since these samples finished with a solutions of such high concentrations originally retained excess amounts of add-on. Such influence of dry cleaning was corresponded to changes in LOI values and very favorable agreement was observed as shown in Fig. 5-14. From the above results, it has been recognized that even nondurable flame retardant finished samples have durability against short time immersion in water or dry cleaning.

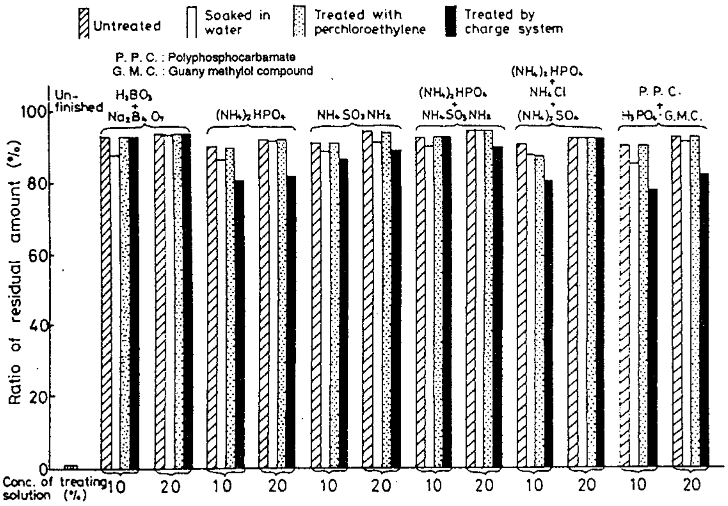


Fig. 5-13 Comparison of ratios of residual amounts after combustion of cotton fiber assemblies unfinished and finished with nondurable flame retardants observed before and after treating with water, perchloroethylene and charged perchloroethylene.

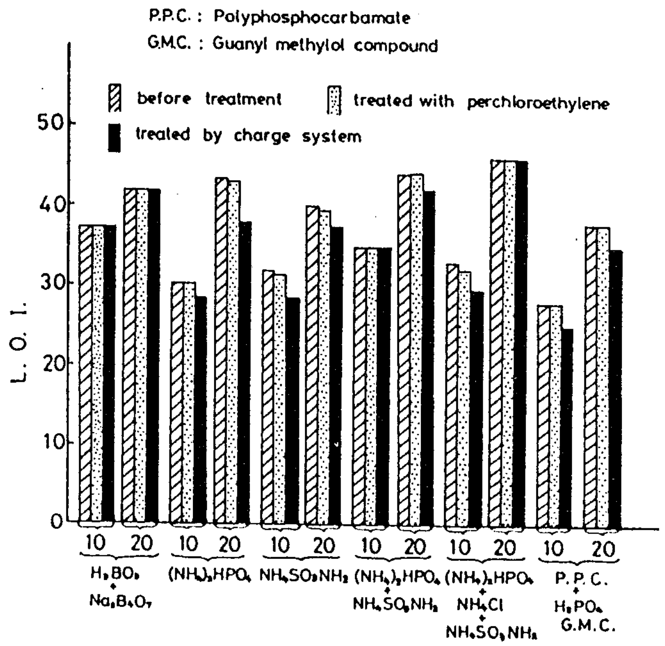


Fig. 5-14 Comparison of flame retardances of nondurable flame retardant finished cotton fabrics observed before and after treating with perchloroethylene or charged perchloroethylene.

3) Conclusion

Continued from the investigations on heat propagation behavior of unfinished fiber assemblies, this study deals with those of flame retardant finished fiber assemblies for comparison with behavior of unfinished sample. The results are summarized as follows:

Observations of heat propagation behavior in fiber assemblies finished with various kinds of flame retardants have revealed that both maximum temperatures and heat accumulation were remarkably depressed compared with those of unfinished fiber assemblies, especially, in the horizontal direction. The effects of inorganic flame retardants were larger than those of organic ones, particularly, a combination of boric acid and borax gave the largest effect.

As to the effects of flame retardant finish on cotton/PET blended fiber assemblies, depressing effect decreases with increase in ratio of PET because of ineffectiveness of flame retardant finish on PET fiber.

In the case of bedding, Futon, flame retardant finish is required for both ticking and fiber assemblies to attain any sufficient flame retardance.

It has been also confirmed that even inorganic nondurable flame retardants maintain sufficient flame retardant effect against a short time immersion in water and dry cleaning.

5-1-3 A Devised Simulated Cigarette as a Heat Source to Set up Variable Conditions for Observation of Heat Propagation in Fiber Assemblies from Any Heat Source

In addition to observations of heat propagation in fiber assemblies from real burning cigarettes, it seems more significantly interesting to observe heat propagation behavior under varied conditions of heat source, e.g., heat quantity and heating time. Therefore, we attempted to device a simulated cigarette with variable heating conditions so that the heat propagation is allowed to undergo from a heat source under any desired heating condition, which enabled us to obtain some findings not observable by any real cigarette.

1) Experimental

(a) Materials

Fiber assemblies and ticking fabric unfinished and finished with boric acid and borax were the same as those described in 5-1-1 and 5-1-2.

As real cigarette (R. C. below), the same cigarette used for the previous studies was employed also this time.

Nichrome wire (0.6 mmφ, 54 Ω/m), bobbin (a mullite made insulating tube 8 mm in external diameter, 5 mm in internal diameter and 100 mm long) on which nichrome wire is wound at one edge, nickel heater lead wire (0.5 mmφ, 350 mm long), a mullite made insulating tube for the above mentioned heater wire (1.5 mm in external diameter, 0.8 mm in internal diameter, 100 mm in length) and ceramic fibers for insulation were used for simulated cigarette (S. C. below).

(b) Methods

(1) A device for S. C.

S. C. was made as illustrated in Fig. 5-15, 600 mm of nichrome wire was wound at one edge of a bobbin with 0.8 mm pitch. The length of nichrome wire was varied to adjust the electric resistance of heater.

Heater lead wires (×2) covered with insulating tubes were inserted into the bobbin from the rear end and welded by spot welding to nichrome wire at the positions of A and B of the bobbin. These two heater lead wires were fixed at the rear end of the bobbin with silicon rubber.

The surface of nichrome wire wound on the bobbin was coated with very thin film of a ceramic bonding reagent.

An insulator, ceramic fiber, was inserted into the bobbin from both ends.

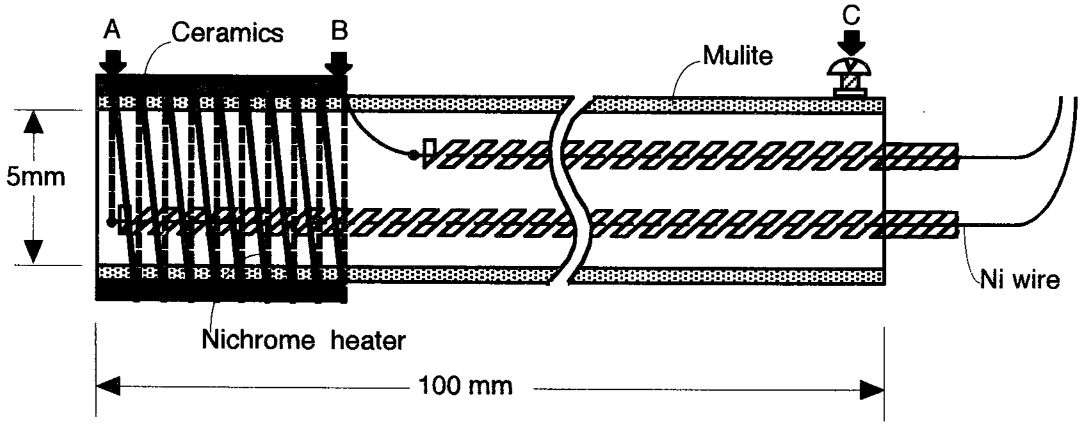


Fig. 5-15 Simulated cigarette.

(2) A device for S. C. sliding system

In order to simulate a cigarette in fiber assemblies burning from the lighted front toward the rear end, which required 60 min to burn 7 cm long. An equipment to slide a S. C. bobbin at a rate of 7 cm/h was made by winding a string fixed at C of S. C. shown in Fig. 5-15 at a pulley attached to a gear. The sliding rate was adjusted by the number of rpm of moter and gear ratio.

(3) Preparation of miniature Futon

Miniature Futons the sizes of which are (20×12.5×5) cm^3 were made according to JIS L 4403-1974. Ticking fabric and fiber assemblies (100% cotton) were conditioned at 20°C RH 65% (water content = 6.83%). The weight of fiber assemblies were 50 g for density 0.04 g/cm^3, 75 g for 0.06 g/cm^3 and 100 g for 0.08 g/cm^3. Various kinds of Futon were made by combining unfinished and finished ticking fabric and stuffing fiber assemblies as descried in 5-1-2.

(4) Setting of thermocouple sensors

As shown in Fig. 5-16, thermocouple sensors were set at 9 positions around a cigarette placed at the center of the above mentioned Furon, i.e., 5 cm (corresponding to the thickness of Futon) apart from the lighted front, center and the rear end in the upward direction {on the upper Futon covering the cigarette (①, ②, ③ in the figure), horizontal direction (④, ⑤, ⑥) and downward direction (at the bottom of the lower Futon, ⑦, ⑧, ⑨), from which temperature-time curves were recorded to compare heat propagation behavior, maximum temperatures and areas, as relative values of heat accumulation. As resistances of heat source, S. C. with 20, 27 and 32 Ω were prepared. Voltage was varied 8.0-16.5 V to establish many heating conditions. The measurement was repeated 6 times or more and averaged values and standard deviations were obtained.

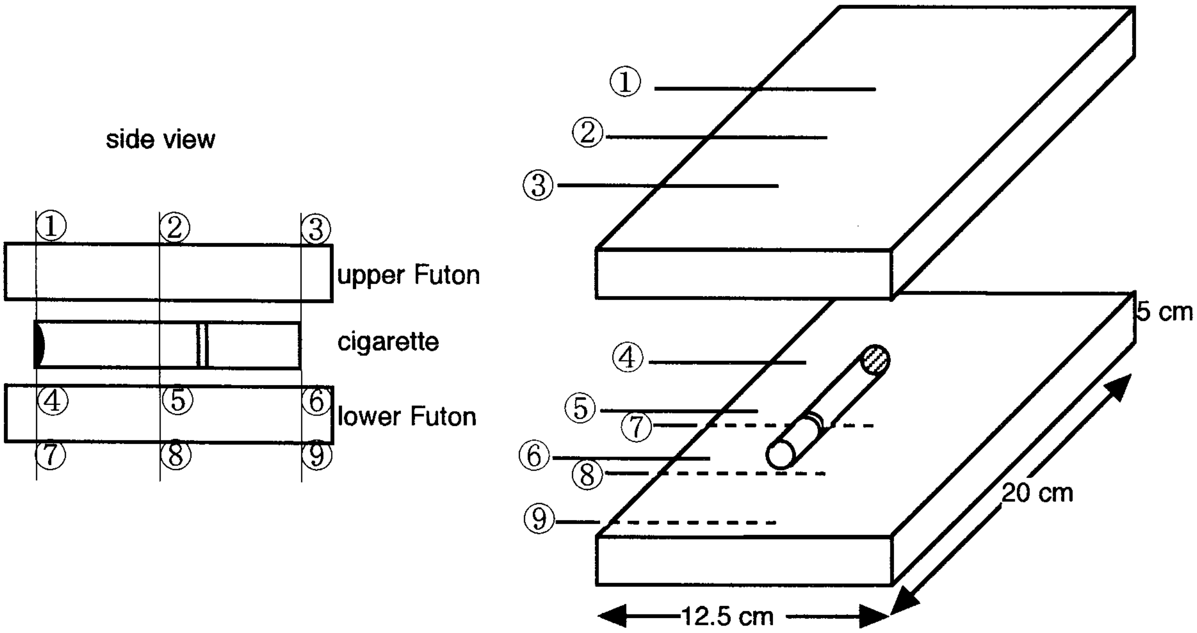


Fig. 5-16 Positions of temperture sensors

The numbers in circles show three directions (upward : 1, 2, 3 ; horizontal : 4, 5, 6 ; downward : 7, 8, 9) at three positions (ignited front, center, rear end) of a cigarette.

(5) Determination of heat of combustion of cigarette

The heat of combustion for a R. C. was measured by Shimadzu Automatic Bomb Calorimeter CA-4, with absolutely dried benzoic acid (26.45 kJ/g) as a standard sample.

2) Results and Discussion

(a) Comparison between heat propagation behavior from R. C. and S. C.

The heat quantity from S. C. was varied by changing voltage and time, by which heat propagation behavior from S. C. was compared with that from R. C. to find out a heating condition most similar to that of R. C.

(1) Comparison by take-off behavior and changes in temperature with time

Heat propagation behavior from R. C. and S. C. was first compared by how temperature-time curves take off. As a representative behavior, temperature-time curves obtained by sensors for 3 direction at the center of cigarette are shown in Fig. 5-17. Comparison between R. C. (indicated by open marks) and S. C. (solid marks) with change in the heat quantity and constant time for 60 min shows that the higher the voltage, the earlier the take-off, but the largest difference is observed in the horizontal direction (⑤) and the difference between R. C. and S. C. decreased in the order of upward direction (②) and downward (⑧) with little difference in the downward. As next trial, taking a possibility of varying heat quantity with time into consideration, heat quantity was altered from 8.0 V in the initial period 5-15 min to 10.0, 12.0 and 14.0 V instantaneously at different time intervals.

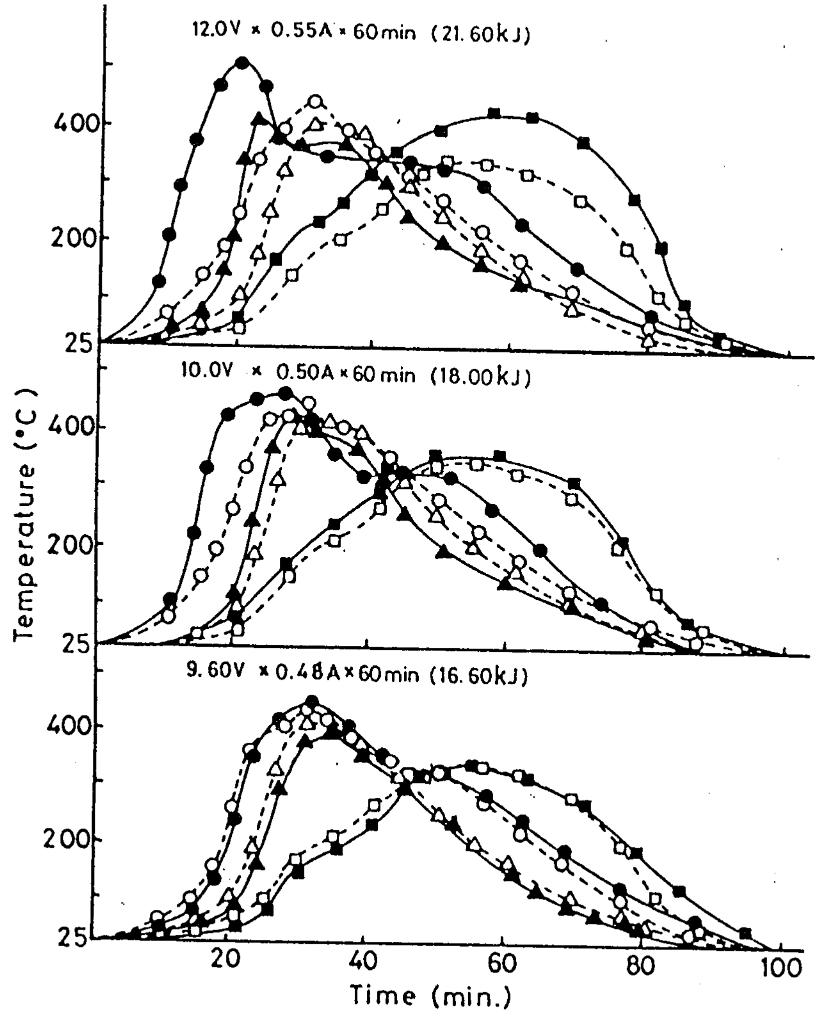


Fig. 5-17 The temperature changes at selected points of sleeping futon after installation of ignited real cigarette (RC, open symbols) or initiation of power-supply to installed-simulated cigarettes (SC, filled symbols) as a function of time.

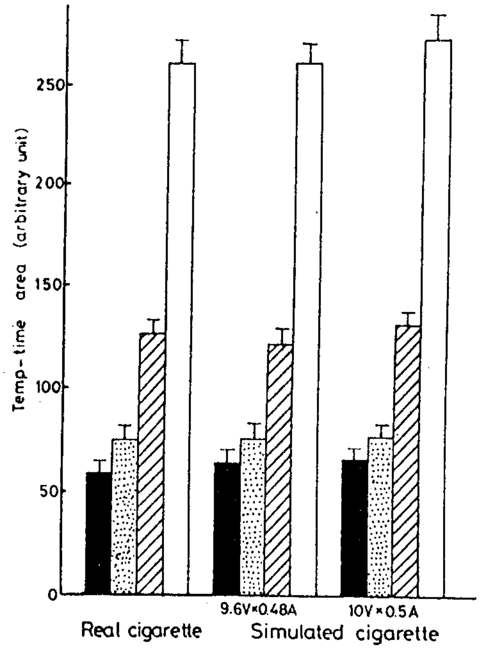
As the conclusion, the heat quantity which gives the heat propagation behavior most identical to that of R. C. is 16.6 kJ as shown at the bottom in Fig. 5-17, and it was also suggested that a R. C. would burn surrounding fiber assemblies with almost constant heat quantity without any change.

(2) Comparison of areas which express heat accumulation

Agreement of heat of combustion of R. C. and a selected heat quantity of S. C. was observed as follows :

As a measure for relative evaluation of the heat accumulation as the result of balancing between heat generation and heat release, areas surrounded by temperature-time curves obtained with supplied powers 9.6 V X 0.48 A and 10 V X 0.5 A of S. C. were compared with that of R. C. As shown in Fig. 5-18, S. C. with a heat quantity of 9.6 V X 0.48 A showed area value for each direction (upward, downward of horizontal) and the total area extremely similar to those of R. C., which means that 9.6 V X 0.48 A X 60 min, 16.60 kJ is almost identical with the heat quantity of R. C.

On the other hand, the heat of combustion of a cigarette was determined as mentioned above. The result has confirmed that an observed value of the heat of combustion of a cigarette is 16.64 kJ (S. D. = 0.31, n = 3), which is almost identical with 16.60 kJ observed by adjusting heat quantity of S. C. to 9.60 V X 0.48 A X 60 min. Therefore, it can be concluded that such heating condition as involving these voltage, current and time is the most adequate as a heat source which can simulate R. C.



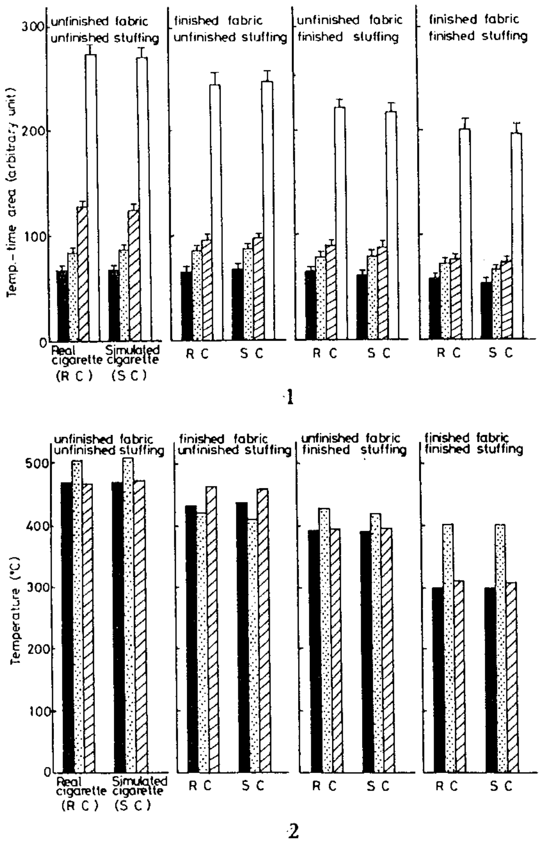


Fig. 5-18 Comparison of the accumulated heat estimated by the area for real and simulated cigarette.
The value in each case was the average and standard deviation with *n* = 6.

Fig. 5-19 Comparison of accumulated heats (1) and maximum temperature (2) between RC and SC observed with minuature Futons.
The composition of miniature Futons was shown above.

■, (A) upward ; ▦, (B) horizontal ; ▨, (C) downward ;
□, (A+B+C) total. Position of cigarette : center.

(3) Comparison by using miniature Futons

Four kinds of Futons made by combining unfinished and finished ticking and stuffing fiber assemblies (unfinished fiber assemblies + unfinished ticking, unfinished fiber assemblies + finished ticking , finished fiber assemblies + unfinished ticking, finished fiber assemblies + finished ticking) were used for comparing heat propagation behavior in Futon from S. C. with that from R. C. As a heat quantity, the above mentioned heating condition (9.60 V × 0.48 A × 60 min) was applied. As shown in Fig. 5-19, in both cases of temperature-time area and temperature, a combination of unfinished fabric and unfinished stuffing showed the highest values, followed by those of a combination of finished fabric and unfinished stuffing and the lowest values were shown by a combination of both finished fabric and stuffing (average of 6 repetitions, S. D. = 0.16). The attention should be paid to that the results shown by S. C. were almost identical with those by R. C. in every direction and the total areas of that in 3 directions were also very similar. Paying attention further to effects of flame retardant finish at each direction, reduction of area was most clearly shown in the downward direction and temperature was more largely lowered in the upward and downward directions but much less effect was observed in the horizontal direction.

(b) Effect of heating time

As mentioned above, it has been found that 60 min are required for complete combustion of one piece of cigarette in fiber assemblies. But, since it can be imagined that a cigarette might quench without burning out, it would be also meaningful to know what would happen to combustion or smoldering of fiber assemblies when its heat source, cigarette, quenches by itself before it burns out. However, it would be almost impossible to extinguish R. C. freely at desired time depending on the purpose of the experiment. In contrast S. C. enables us to adjust the heating time to simulate R. C. quenching at any time, to show the effect of heating time on smoldering or burning behavior in fiber assemblies from a heat source quenching at any desired time. Therefore, heat propagation behavior was observed by altering heating time for 15, 30 and 60 min in combination with increasing heat quantity of the heat source, which were measured at 9 positions shown in Fig. 5-16. Fig. 5-20 shows effects of heating time on maximum temperatures as well as on areas, heat accumulation, and those of heating quantity on maximum temperatures.

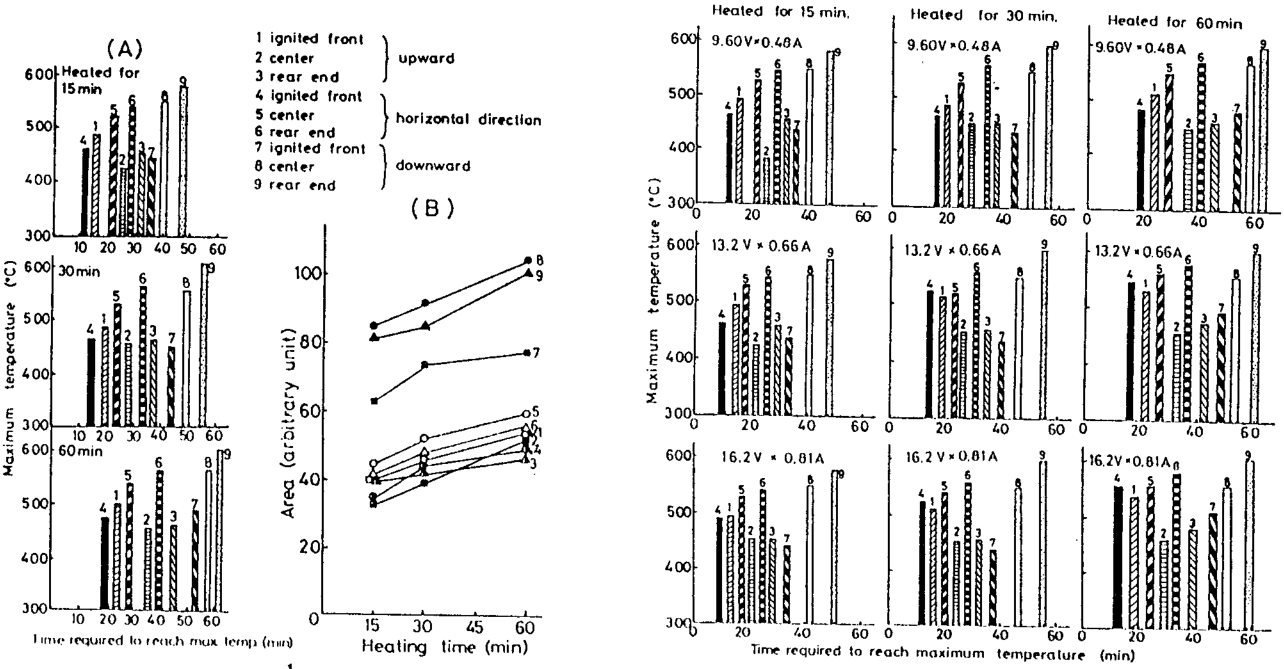


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Fig. 5-20 Effects of heating time on maximum temperature (20-1(A)) and accumulated heat (20-1(B)), and effects on heating quantity on maximum temperature (20-2).
The numbers and marks in the figures, corresponding to those in Fig. 5-20-1(A), 5-20-2 : The maximum temperature in ordinate was plotted for the time required to reach its maximum valus in abscissa. 5-20-1(B) : The accumulated heat estimated as the area of temperature-time curve was plotted as a function of heating time for the various positions of Futon. The rates of heating were constant for each test (20-1:276.5J/min; 20-2, upper : 276.5 ; middle 522.7 ; and lower : 787.3 J/min).

(1) A regularity in the order of position and direction where the temperature shows the peak

A kind of regularity was observed in the order of position of cigarette and the direction of heat propagation at which the peak temperature was shown irrespective of heating time and heat quantity (V × A), i.e., in the horizontal direction at the ignited front ④ → in the upward direction at the front ① → in the horizontal direction at the center ⑤ → in the upward direction at the center ② → in the horizontal direction at the rear end ⑥ → in the upward direction at the rear end ③ → in the downward direction at the front ⑦ → in the downward direction at the center ⑧ → in the downward direction at the rear end ⑨ as shown in Fig. 5-20. This order was decided with 100% reproducibility.

(2) Time required for reaching the peak temperature

As a general tendency, the time required to reach the peak temperature from the initiation of heating was the shortest in the horizontal direction and showed a large retardation in the downward direction. As for the effect of heating time, a tendency as shown in Fig. 5-20-1(A) was observed, i.e., the longer heating time required longer time to reach the peak temperature at every position in every direction.

(3) The maximum temperature

As shown in Fig. 5-20-2, comparison of the maximum temperatures observed among different positions and directions disclosed that the highest temperature was observed in the downward direction at the rear end ⑨ reaching 600°C followed by 550°C in the horizontal direction at the rear end ⑥ and in the downward direction at the center ⑧. The center in the horizontal direction was a little lower showing 530°C and followed by 470°C at the front in the both directions of upward direction ① and horizontal direction ④ and the lowest temperature was as low as 450°C in the upward direction at the center ②, in the downward direction at the front ⑦ and in the upward direction at the rear end ③. These temperatures showed little change with change in heating time except that 60 min heating only showed higher temperature with "Significant difference with 1% of danger ratio" in the downward direction at the ignited front and the rear end. Such a only slight effect of heating time on the maximum temperature will suggest that even with a short heating time, when fiber assemblies once ignited, the smoldering of fiber assemblies themselves is continued unquenched even after discontinuation of heating, e. g. even if burning cigarette happens to quench, which will bring about temperature rise though having the limitation by balancing between heat generation and loss by heat release. Anyway, it involves such hazard that the smoldering will turn to flaming at any time to cause a big fire.

(4) Areas expressing heat accumulation

It has been found that the heat accumulation is largest in the downward direction, especially at the center of cigarette. The upward and horizontal direction showed only 1/2 that in the downward direction. On the other hand, the effect of heating time on area was that areas increased with increase in heating time, particularly in the downward direction at the center and the rear end (8, 9) followed by in the horizontal direction at the center and the rear end (5, 6), and a smaller increases were observed in the upward direction (1, 2, 3) at the front positions (1, 4, 7) because of larger heat loss.

(c) Effect of heat quantity applied by heat source

Further investigations were carried out by changing heat quantity from (9,6 V× 0.48 A) the same as mentioned above to (13.2 V × 0.66 A) and (16.2 V × 0.81 A) and heating time from 15 min to 30 and 60 min respectively, and the maximum temperature and area were compared as shown in Figs. 5-20 (2) and 5-21.

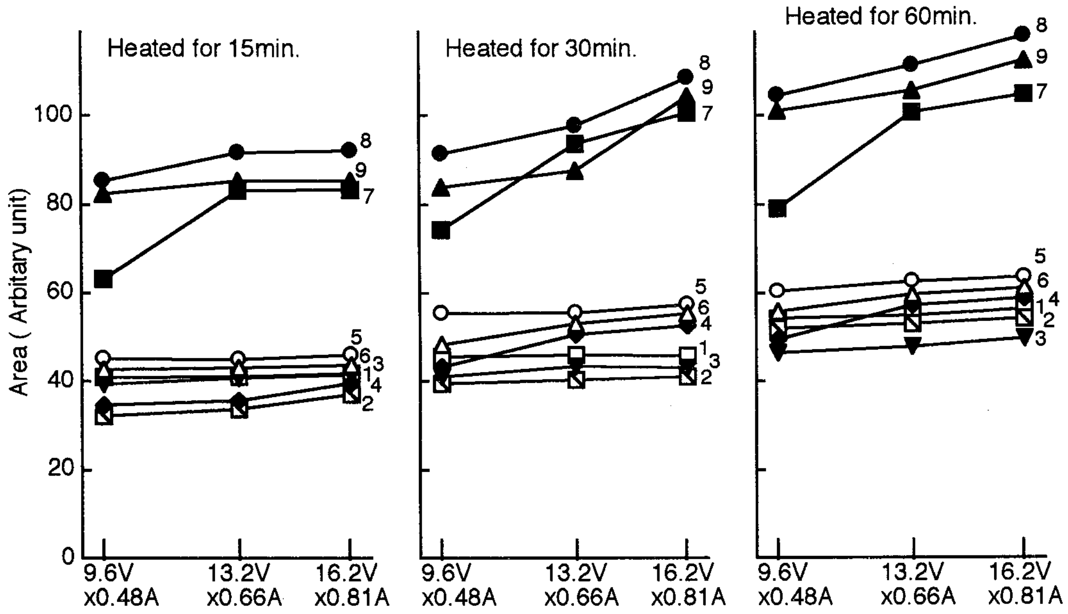

Fig. 5-21 Accumulated heat as a function of heating quantity for different heating time.

(1) The maximum temperature

As shown in Fig. 5-20 (2), little difference was observed with a few exception even with increase in heat quantity up to about ×2 and ×3. Such phenomenon means that, as described above, the heat propagation in fiber assemblies, combustion of fiber assemblies is mainly dominated by the heat combustion of medium fiber assemblies ignited by any heat source no matter how small it would be, consequently, it suggests a significant possibility of vigorous flaming combustion from a small heat source.

(2) Time required to reach the maximum temperature

Overall observation is that the rapidity of heat propagation in fiber assemblies from each position became faster with increase in the heat quantity from the heat source in the upward direction and horizontal direction. But, the propagation in the downward direction showed no change in every direction in the case of 15 min heating, whereas 30 min heating showed that the propagation in the upward and the horizontal directions at the ignited front became more rapid and that at the positions of center and rear end was found almost unchanged.

(3) Temperature vs time area, a measure for heat accumulation

Area recognized as a measure for the heat accumulation showed little change even with twice or three times of heat quantity except that areas in the downward direction increased with increase in the heat quantity of the heat source (Fig. 5-21). Thus, heat accumulation in the downward direction was significantly dominated by heat quantity as in the case of heating time, which suggests that the accumulated heat can be maintained at the similar level in the upward direction and the horizontal directions because the upper surface and sides are exposed to the air to allow the release of heat quantity, whereas the heat release is hindered in the downward direction at the bottom of fiber assemblies resulting in increase in the heat accumulation with increase in the heat quantity.

3) Conclusion

To investigate the burning behavior of fiber assemblies such as sleeping Futon, a smallest heat source was tested for the simulation of R. C. From the comparison of burning behavior of real cigarette and that of simulated cigarette, the heat quantity of R. C. was estimated to be 16.6 kJ. This value is corresponded to the heat of combustion of one piece of cigarette observed by using bomb calorimeter.

S. C. was inserted between two sheets of miniature Futons, heat propagation behavior was monitored by 9 pieces of thermocouple for many conditions of heat quantity to the extent of ×3 the above mentioned value and heating time of 15, 30 and 60 min respectively. The results are summarized as follows:

The temperature at the ignited front along the horizontal direction reached the maximum in the initial stage of heating. On the contrary, the downward direction retarded most remarkably to reach the maximum. Such order of position at which the time required for reaching the maximum temperature remained unchanged among 9 positions (3 directions and 3 positions of cigarette) even under the different conditions of heating, i. e., there found an obvious regularity as mentioned above. However, longer time was required to reach the maximum temperature with prolonged heating time

Heat accumulation expressed by temperature vs time area surrounded by that temperature-time curves and the baseline were also enlarged as the function of prolonged heating and increase in heat quantity, respectively and were specially enhanced in the downward direction at the center and rear ends.

On the other hand, either heating time or heat quantity both gave little effects on the level of maximum temperature. This suggests that once fiber assemblies are ignited, the rising level of temperature is dominantly depended on the progress of smoldering of fiber assemblies rather than the effect of heat source itself. The temperature at each position in each direction showed their inherent upper limit. The lowest temperature was 450°C and the highest 600°C, respectively. Accordingly, these temperatures both exceed the ignition point of cotton and much hazards are involved, which may occasionally turn to flaming combustion, causing outbreak of fire[4].

5-2 Heat of Combustion of Textiles and Fiber Assemblies and Effect of Flame Retardant Finishes

Introduction

Since materials surrounding our living environment are mainly flammable organic substances, the heat of combustion is an important problem from the standpoint of safety. The Fire Defense Agency has adopted "fire load" as a method to evaluate a degree of danger for buildings, houses and materials existing in the human living environment. The fire load method evaluates the degree of danger by the relative heat generation using the heat of combustion of 1 kg ceder lumber as the standard. In addition, since clothes and beddings closely or directly contact with the human body, the heat of combustion can be an important factor which directly dominates the safety of the human body. According to the investigation by Tokyo Fire Defense Agency, the ratio of deceased by burning clothes ignited from stoves, bonfire, cooking burners and flame of fire to the total number of deaths by disasters is 21.5%, which shows a significant danger of flammable materials in our environment[17,18].

From the above facts, a necessity for information about the heat of combustion can not be ignored and any minute information has been required by the authorities concerned.

Therefore, the evaluation of safety was tried from the viewpoint of the heat of combustion of fiber products such as clothing materials, beddings and interior materials for construction.

5-2-1 Experimental

1) Materials

One hundred % cotton fabric and fiber assemblies, 100% PET fiber assemblies and cotton/PET blended fiber assemblies were the same as used in the previous studies described above. In addition, various kinds of fabrics purchased in the market were used from the practical standpoint.

As nondurable compounds, urea, disodium hydrogen phosphate, sodium chloride, calcium chloride, sodium bromide, sodium sulfate, sufamic acid and boric acid and borax containing N, P, S, Br, Cl or B singly, and those containing 2 components, such as diammonium hydrogen phosphate, ammonium sulfate, ammonium chloride and ammonium bromide as well as urea + disodium hydrogen phosphate and phosphoric acid + ammonium hydroxide were employed.

As durable flame retardants, Pyrovatex CP, additives for Pyrovatex finishes, THPS monomer and additives for THPS finishes were used according to prescriptions listed in Table 5-3. Furthermore, THPS precondensate and NH_3 were used for PROBAN finish (see 3-1).

Table 5-3 Compositions of two series of durable retardant finishes with each main component Pyrovatex and THPS monomer

	Pyrovatex series (%)			THPS series (%)	
Py(1)	Py	32	THPS(1)	THPS monomer	25
Py(2)	Py	32		TEA	5
	M6 + catalyst	8			
Py(3)	Py	32	THPS(2)	THPS monomer	25
	H_3PO_4	2		TEA	5
Py(4)	Py	32		$CO(NH_2)_2$	10
	M6 + catalyst	8	THPS(3)	THPS monomer	25
	H_3PO_4	2		TEA	5
Py(5)	Py	32		M3	5
	$CO(NH_2)_2$	1		Catalyst	3
	NH_4Cl	0.5			
Py(6)	Py	32	THPS(4)	THPS monomer	25
	M6 + catalyst	8		TEA	5
	H_3PO_4	2		$CO(NH_2)_2$	10
	$CO(NH_2)_2$	1		M3	5
	NH_4Cl	0.5		Catalyst	3

Py, Pyrovatex ; TEA, triethanolamine ; M3, trimethylolmelamine ; M6, hexamethylolmelamine. The numbers without parenthesis correspond to the percentages of each component.

2) Methods

(a) Flame retardant finishes

As nondurable flame retardant finished samples, 100% cotton fabric was immersed in 5% and 20% solutions of the above mentioned nondurable compounds, padded to 90% pickup after 2 dip - 2 nip process and air dried.

One hundred % cotton fiber assemblies and 3 kinds of cotton/PET blended fiber assemblies were finished with 5% and 20% solutions of boric acid and borax by the method described in 5-1-2.

As durable flame retardant finished samples, the following three were prepared:

Pyrovatex finished 100% cotton fabric was prepared with Pyrovatex CP and additives according to the method mentioned in 3-1-1.

One hundred % cotton fabric was finished with THPS monomer and additives listed in Table 5-3 by the method described in 3-1-3.

Another durable flame retardant 100% cotton fabric was prepared with THPS precondensate by ammonia cure as described in 3-1-2.

(b) Preparation of Futons

Miniature Futons of 4 kind combinations of ticking and stuffing, i.e., unfinished ticking + unfinished stuffing, unfinished ticking + finished stuffing, finished ticking + unfinished stuffing and finished ticking + finished stuffing, were made according to the method mentioned in 5-1-2. In this case, size was decided as $(15 \times 15)\ \mathrm{cm}^2 \times 5$ cm (thickness) and fiber density was varied as 9 kinds of densities from 0.04 $\mathrm{g/cm}^3$ to 0.093 $\mathrm{g/cm}^3$. The weight of ticking was 9 g per Futon.

(c) Determination of heat combustion

A heat of combustion of each sample was determined by using Shimadzu Calorimeter CA-4 with absolutely dried benzoic acid as the standard. Weight of any sample was adjusted so that it is applicable for the calibration shown in Fig. 5-22.

(d) Burning method for Futon

Futons were combusted by sandwitching a lighted cigarette between 2 miniature Futons made as mentioned above. A weight loss of each sample was obtained by a difference between the weights of Futon before and after the combustion. Heat of combustion of each Futon was calculated by the product of a weight loss obtained above and a heat of combustion obtained by the calorimeter.

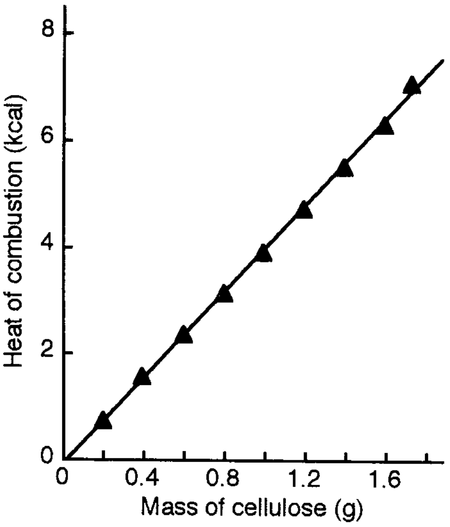

Fig. 5-22 Calibration for the heat of combustion observed as a function of the mass of cellulose fiber assemblies.

5-2-2 Results and Discussion

1) Effects of flame retardant finishes on the heat of combustion of cellulose fiber

An investigation was carried out to see how the heat of combustion of most flammable cellulose fiber changes by flame retardant finishes. As shown in Fig. 5-23, the heat of combustion of unfinished cellulose is in a range of 3.8-3.9 kcal/g. In contrast, samples treated with nondurable compounds showed reduction of the heat of combustion, particularly, those treated with 20% solutions exhibiting much higher LOI values showed larger reduction. Attention should be paid to the fact that a significant correlation is observed between reduction of heat of combustion and LOI value except for NaBr which showed much reduction though with LOI value lower than 28% probably because of generation of Br. Compounds which are capable for generating NH_3, SO_2 or hydrogen halides etc. by the thermal degradation showed favorable effects on reduction of the heat of combustion.

On the other hand, durable flame retardant finished samples showed the same level or rather a little higher level compared with the level of unfinished cellulose.

From the practical use, durable flame retardant finished materials are more convenient from the standpoint of durability, but nondurable flame retardant finish is more favorable from the viewpoint of safety.

2) Effects of shape and blending condition on heats of combustion of cotton and PET

A further investigation was thought to be necessary to see whether the heat of combustion is the same or different depending on shapes of the same material e.g., fabric, thread or fiber, as well as on blending conditions of cotton and PET when the overall heat of combustion of Futon is required. As shown in Fig. 5-24, entirely no change was observed among the above mentioned difference. In this case, values of the heat of combustion of cotton/PET blended samples obtained here were all identical with those calculated from the heat of combustion of each single sample and blending ratios.

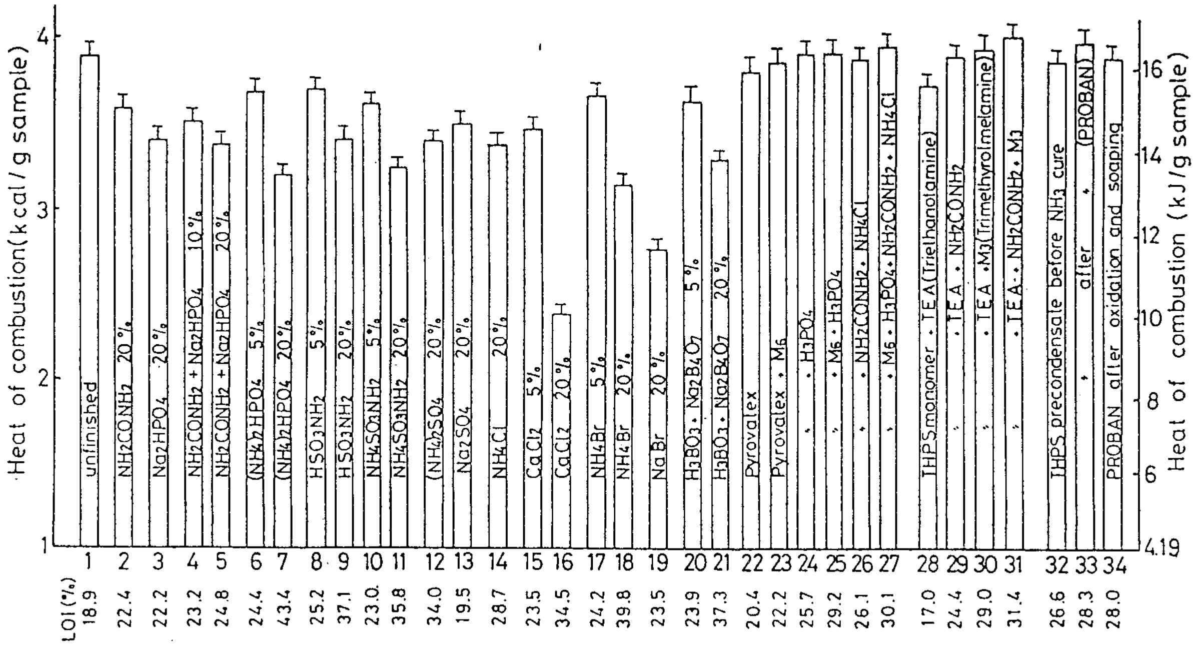

Fig. 5-23 Effects of different flame retardant finishes on the heat of combustion of cotton fabric. The treating materials are indicated within each bar. Numbers along abscissa show the sample numbers. LOI values are corresponded to the heat of combustion of individual samples. Abbreviations were referred to Table 5-3. The values were the mean ± S. D. with n=5.

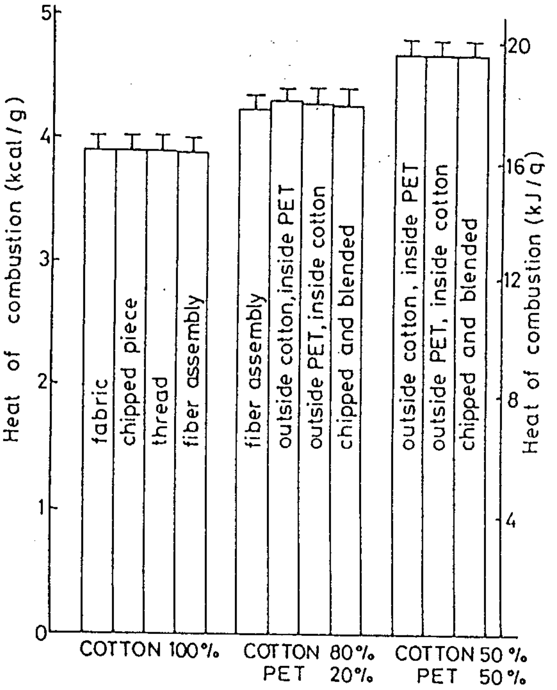

Fig. 5-24 Observed heat of combustion for the different shape and filling condition. Observed values of these blended materials are well agreed with those calculated from the heats of combustion and blended ratios of cotton and PET.

3) Comparison of heats of combustion observed with combustion of Futons

Combusting behavior of miniature Futons made by combining unfinished and finished fiber assemblies and unfinished and finished fabric was investigated previously and reported in 5-1-2, i. e., combination of both unfinished fabric and fiber assemblies gave entire combustion, on the contrary, that of both finished fabric and fiber assemblies showed 100% residue, combination of finished fiber assemblies with unfinished fabric gave 27% of residue, on the other hand, unfinished fiber assemblies combined with finished fabric showed a residue only less than 10%. Corresponding these results with values of the heat of combustion observed with the same Futons, the reasonable agreement was observed between combustion behavior and heats of combustion, i.e., as shown in Fig. 5-25 the highest values of heat of combustion were observed with unfinished ticking, unfinished fiber assemblies and combination of both unfinished ticking and fiber assemblies, in the cases of combination of unfinished and finished ticking or stuffing, combination of unfinished ticking and finished fiber assembles showed much more reduction compared with that of the other combination, on the other hand, in the case that both ticking and fiber assemblies were finished, ticking did not show any heat generation and overall heat of combustion was only 1/3 that of combination of both unfinished materials. The results shown in Fig. 5-25 were observed with Futons, fiber density of which was 0.04 g/cm^3, but it can be supposed that differences between unfinished samples and finished samples will enhance simultaneously with increase in the heat of combustion with increase in the fiber density.

Furthermore, another fact should be taken into consideration, i. e., the heat of combustion is generally obtained by a calorimeter under such condition that samples burn out completely in the atmospheric oxygen supply, whereas smoldering generally proceeds under the deficient oxygen supply passing through the charing state finally to reach ashing. Therefore, a further investigation was attempted to determine heats of combustion for chars in varied charing stage. As shown in Fig. 5-26, significant increase was observed with progress of charing, which suggests that values of heat of combustion obtained by calculating from values observed with samples without any chared portion will be lower than those in the practical case in which fiber assemblies undergo smoldering with simultaneous production of char. In another word, any Futon made of unfinished ticking and fiber assemblies produce heat of combustion much higher than the results shown here, consequently, differences in the heat of combustion between finished and unfinished materials will be further enhanced, which proves the effect of flame retardant finish more clearly.

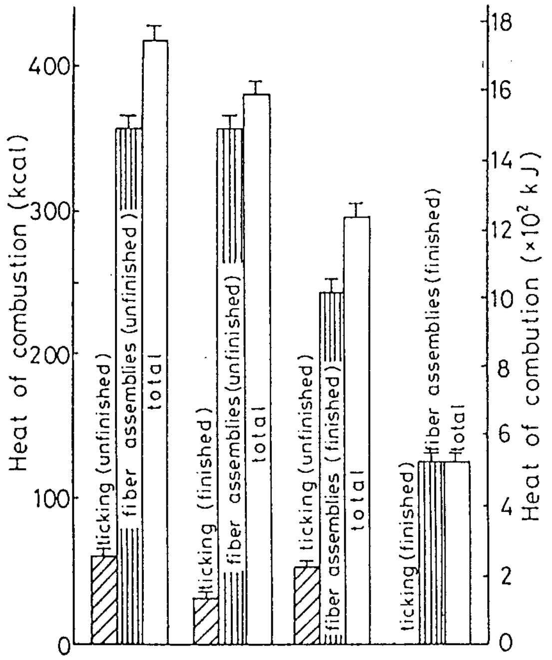

Fig. 5-25 The heats of combustion among miniature Futons composed of ticking and fiber assemblies with both or each of which finished or unfinished. The composition of miniature Futon was shown in the figure. Each mass of Futon was equal.

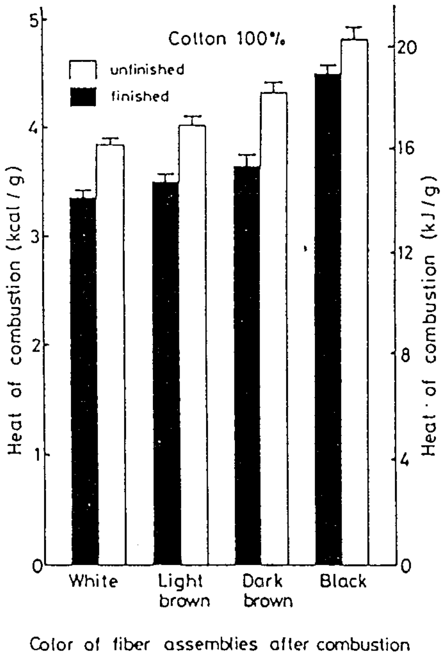

Fig. 5-26 Change in the heat of combustion of cotton fiber assemblies and fabric with progress of charing.

4) Heats of combustion of Cotton/PET blended fiber assemblies and effect of flame retardant finish

Since not only that the heat of combustion of PET is 5.45 kcal (22.84 kJ) extremely higher than that of cellulose but also that its molten portion sticks to the skin to cause serious burn, any ignited PET clothes on the body and smoldering PET fiber assemblies in Futon during sleeping are highly dangerous. The world-wide trend that PET has been most demanded for clothes, and PET fiber assemblies have been increasingly dealt in the market as a substute for cotton fiber assemblies can not be ignored. A problem of PET fiber assemblies with high heat of combustion can be moderated by blending cotton fiber assemblies with lower heat of combustion. In fact, we have also found that weight loss decreases by mixing PET fiber assemblies with cotton fiber assemblies as described in 5-1-2. Therefore, heats of combustion of blended fiber assemblies were observed with varied fiber densities, the results of which were, as shown in Fig. 5-27, that the heat of combustion exhibited a steep rise with enhancement of weight loss accompanied with increase in fiber assemblies in the case of unfinished fiber assemblies. When fiber density is lower, the result was that the higher the ratio of PET, the lower the heat of combustion, but a tendency such as an inversion of curve for 100% cotton and that for 80%cotton/20%PET blended was observed at or higher than 0.067 g/cm^3 fiber density (S.D.=0.33, n=6). In the case of 50%Cotton/50%PET blended fiber assemblies, overall heat of combustion was considerably reduced probably because of decrease in weight loss. On the other hand, finished fiber assemblies showed extremely large reduction in every fiber density, particularly 100% cotton maintained, the lowest level without any inversion because flame retardant finish used this time was effective for only cotton. 80% Cotton/20% PET blended fiber assemblies also showed a comparatively lower level 1/3 that of unfinished fiber assemblies.

Overall results suggest that the lower the fiber density, the more favorable from the standpoint of safety. In this sense, it has been proved that there is no problem when Futon is made according to what is regulated by JIS, since the fiber density regulated by JIS was 0.04 g/cm^3 which gave the lowest values in every case in the present study.

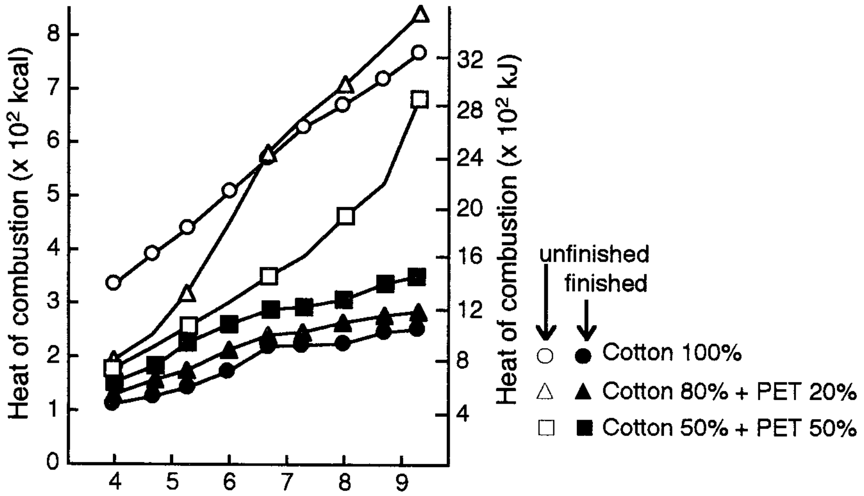

Fig. 5-27 Effects of blending PET with cotton fiber assemblies with and without flame retardant finish on the heat of combustion.
The curves for unfinished cotton 100% and cotton 80 / PET 20 blended fabric show an inversion each other (see text).

5) Heats of combustion of various kinds of commercial fabrics in the market and effects of flame retardant finishes

In order to understand the actual circumstance for the fiber products in the market which are usually purchased and utilized by consumers and extend to evaluate the safety of our daily life. The representative results are shown in Fig.5-28. In the cases of single fibers, unfinished 100% cotton showed the lowest value, all finished cotton showed a little higher probably owing to finishes with organic durable flame retardants, a value of unfinished wool was higher than cotton by about 1 kcal but finished wool showed reduction, unfinished PET exhibited a value further higher than that of wool by 0.5 kcal and no change was observed between unfinished and finished PET in both cases of aftertreatment and meltspinning, modacrylic and aromatic polyamide showed higher values by 0.5 kcal each and heat of combustion of nylon was the highest as high as 7.5 kcal almost twice that of cellulose. Widely used lingerie, negligee and stockings involve hazardous problem in this sense. Among blended fabrics, cotton blended fabrics showed lower values, and higher ratios of cotton gave lower values. Cotton fabric blended with modacrylic (No.17, 18) showed higher values than that of cotton fabric blended with PET (No.16) even with the same ratio of cotton, and aromatic polyamide gave further rise (comparison between No.15 and No.19). Blended fabric of unfinished and finished PET showed the same value compared with that of unfinished itself since heat of combustion of PET is not influenced by flame retardant finish (No.22). It has been also recognized that heat of combustion of flame retardant modacrylic fabric increased by blending with flammable acrylic fabric (No.24, 25).

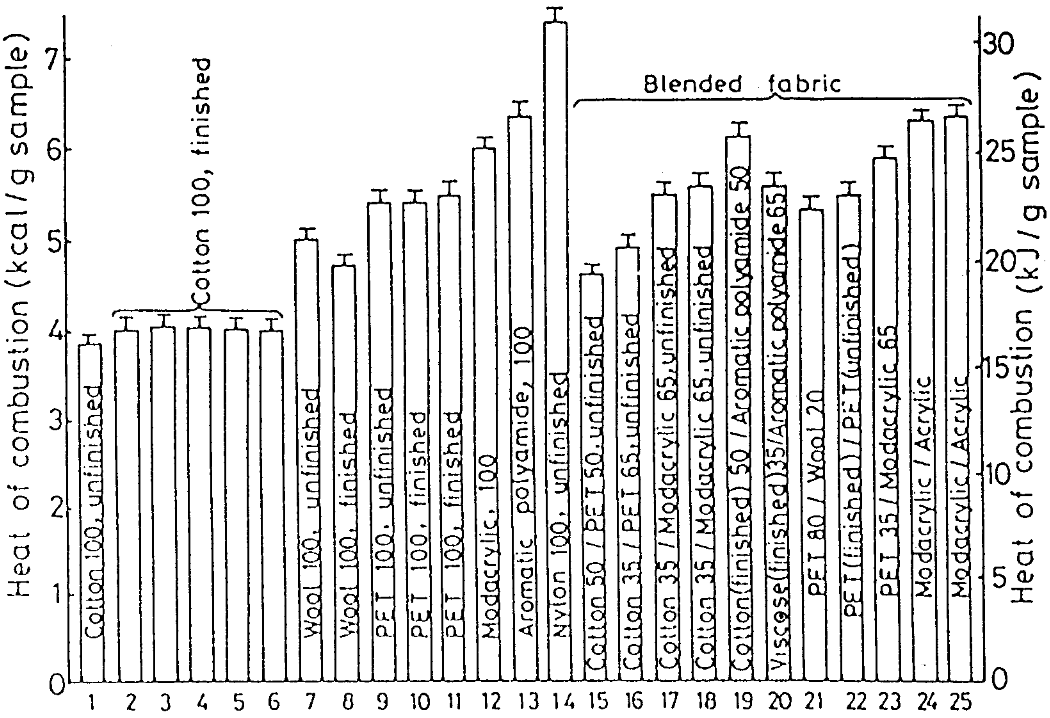

Fig. 5-28 Comparison of heats of combustion among different kinds of commercial fabrics and effects of flame retardant finishes on the heat of combustion.
Modacrylic material used here consists of acrylonitrile and vinyl (or vinylidene) chloride with the former weight fraction, 40% or more but less than 50%. Aromatic polyamide shown here is poly-metaphenylene iso-phthalamide. The numbers in each bar show the percentage of each constitutional fiber.

As mentioned above, heats of combustion of man-made fibers are higher than those of natural fibers. Considering from compositions of fibers, nitrogen-containing natural wool or synthetic modacrylic and polyamide (polymethaphenylene isophthalamide) show higher values compared respectively with natural fiber cotton and synthetic fiber PET constituted mainly with hydrocarbon. However, these nitrogen-containing fibers all showed a tendency of reduction of heat of combustion after characterized by flame retardance, by which effect and neccesity of flame retardant finish were clearly recognized. Cellulosic fibers are most favorable from safety because of the lowest heat of combustion, but weight loss by combustion is larger than those of other fibers due to its largest flammability. Since the heat of combustion depends on the weight loss resulted by combustion, depression of weight loss is required for any flammable material. The best way to secure the safety is to decrease weight loss by combustion of cellulose, since the heat of combustion of which is low.

The necessity for decreasing weight loss after combustion by the flame retardant finish of flammable fibers was clearly proved also in this sense.

5-2-3 Conclusion

The heats of combustion of fiber assemblies and fabrics used for clothing and bedding were investigated as the measure of safety required for the human daily life, in which the inorganic and organic flame retardant finishes were used. The results were as follows:

Inorganic undurable flame retardant finishes to both of fiber assemblies and fabrics reduced the heat of combustion. On the other hand, durable flame retardant finishes showed some increase.

A miniature Futon made of flame retardant finished ticking and fiber assemblies showed the heat of combustion much less than that made of both unfinished materials.

It was found that the higher the composition of cotton, the larger the effect of flame retardant finish on the reduction of the heat of combustion of cotton/PET blended fiber assemblies.

As to the widely used commercial fabrics, the heats of combustion of the man-made fibers were higher than those of the natural fibers, and also those of nitrogen containing fibers were higher than those of nitrogen-free fibers.

The safety will be more improved by reducing the heat of combustion of flammable textile products through the flame retardant finish.

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Chapter 6

Chapter 6 Thermal Analytical Observations of Fibers and Comparison Between Flame Retardant and Flammable Samples

Part 1 Observation of Solid Phase

6-1 Thermal Degradation Behavior Observed by Thermogravimetric Analysis

Introduction

We have studied the flame retardant finish of textile fibers from both basic and practical standpoints since textiles are generally highly flammable though indispensable for our daily life.

After our consecutive studies on the flame retardant finish carried out so far, the fact that the thermal degradation is the origin of combustion led us into temptation to extend our investigation over the thermal analytical observations. This time, therefore, attention was focused on the thermal degradation behavior of cotton to characterize the flame retardation from this aspect.

Tracing the history of pyrolytic degradation of cellulose, effects of the chemical modification of cellulose on the pyrolytic degradation were already investigated by McQuode[1], Pacsu and Schwender[2] and Madorsky et al.[3] 40 years ago. The mechanism of flame inhibition was reported by Rosser et al. also at nearly the same time[4]. Considerable numbers of studies on the thermal degradation of cellulose as well as on effects of flame retardants on the pyrolytic degradation were further published more recently[5-13]. Majority of these studies in the earlier period were achieved to obtain favorable carbon fibers.

The purpose of our present study is to observe thermal degradation behavior more minutely to find if there is any correlation between thermal degradation behavior and level of flame retardance for the characterization of flame retardant cellulose.

6-1-1 Evaluation of Flame Retardance by Characterized Thermal Degradation Behavior of Nondurable Flame Retardant Cotton Fiber

Cotton fabric was first treated with different compounds containing N, P, halogens (Cl, Br) and B in single or blended forms to observe thermal degradation behavior of nondurable flame retardant samples by the thermogravimetry.

1) Experimental

(a) Materials

The fabric used for this study was 100% cotton fabric described in 2-2-2

The treating reagents are listed in Table 6-1. These are compounds containing N, P, S, Cl, Br or B as flame retardant elements. Solutions of the desired concentrations were prepared as described also in Table 6-1. The cotton fabric was treated with these solutions as described in 3-1-4.

Table 6-1 Limiting oxygen index (LOI), flash point (FP), thermal degradation onset point (TDOP), maximum degradation rate point (MDRP) and ratio of residue obtained after heating up to FP of cotton fabric treated with compounds containing nitrogen (N), phosphorus (P), sulfur (S), chlorine (Cl), bromine (Br) or boron (B) in comparison with untreated sample.

Group	No.	Treating reagent	Conc. (%)	LOI (%)	FP (°C)	TDOP (°C)	MDRP (°C)	FP-TDOP (°C)	FP-MDRP (°C)	Residue after heating up to FP (%)
		UT (untreated)	-	18.9	353	350	374	3	-21	12.0
N	1	NH_2CONH_2	20	22.2	350	347	369	3	-19	21.0
P	2	Na_2HPO_4	20	22.2	319	314	346	5	-27	29.0
	3	1 + 2	20	23.5	320	315	347	5	-27	25.3
	4	1 + 2	30	24.8	319	300	348	19	-29	27.4
	5	$(NH_4)_2HPO_4$	20	43.4	283	238	251	45	32	48.0
	6	$NH_4OH + H_3PO_4$	20	43.4	273	226	251	47	22	55.0
S	7	Na_2SO_4	20	20.0	365	340	368	25	-3	30.0
	8	$(NH_4)_2SO_4$	20	34.0	337	236	245	101	92	43.0
	9	HSO_3NH_2	20	37.1	264	214	238	50	26	55.0
	10	$NH_4SO_3NH_2$	20	35.8	270	228	232	42	38	43.0
Cl	11	$CaCl_2$	20	34.5	310	245	249	65	61	51.0
	12	NH_4Cl	20	28.0	290	198	208	92	82	36.0
	13	$NH_4OH + HCl$	20	28.0	296	195	206	101	90	37.0
Br	14	NaBr	20	23.5	276	265	312	11	-36	33.7
	15	NH_4Br	20	40.0	267	194	218	73	48	45.0
	16	$NH_4OH + HBr$	20	39.0	284	196	216	88	68	44.0
B	17	$H_3BO_3 + Na_2B_4O_7$	5	23.9	354	322	342	32	12	32.7
	18	$H_3BO_3 + Na_2B_4O_7$	20	38.0	368	318	335	50	32	48.0

(b) Methods

(1) Determination of flame retardance

The flame retardance of each sample was determined by the burning test method for the polymer materials regulated by the limiting oxygen index (LOI) method described in 2-1-2.

(2) Thermal analyses

Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained at a heating rate of 10 °C/min in air using Shimadzu thermal analysis equipment, DT. TGA-40. The maximum degradation rate point (MDRP) was determined for each sample as the temperature at which the differential thermogravimetric (DTG) curve showed a peak (B) as illustrated in Fig. 6-1.

The thermal degradation onset point (TDOP) was determined for each sample as the point of intersection of a line extrapolated from the initial stage of each TG curve and a line from point B tangent to a curve formed just above B as also shown in Fig. 6-1.

Flash point (FP) was estimated on Shimadzu FPC-30 equipped with DT-30 heating controller at a heating rate of 10°C/min as the temperature at which a sharp peak appeared instantaneously on each DT curve as also illustrated in Fig. 6-1.

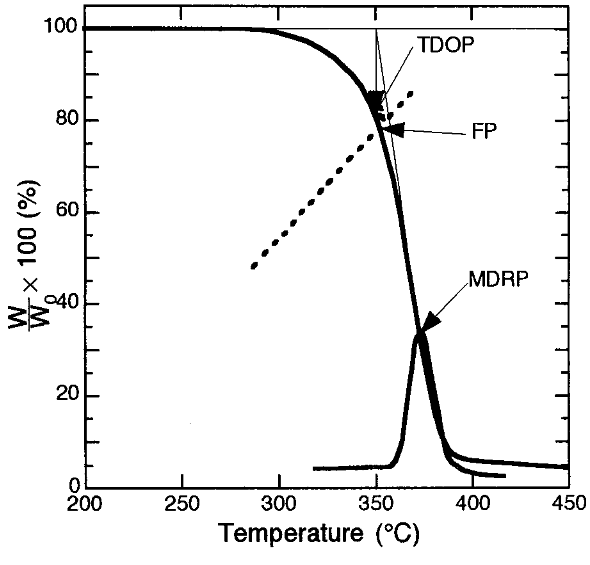


Fig. 6-1 Illustration to explain how to determine MDRP, TDOP and FP on TG curve in combination with DTG curve and DT curve.

(3) Evaluation for self-extinguishability

The residual amount of char obtained after ignition is taken as a measure to evaluate inflammability or extinguishability since flame retardant samples probably quench by themselves after ignition, whereas flammable samples never quench by themselves and almost burn completely when ignited.

Therefore, during the thermogravimetric analysis, heating was stopped at the flash point, and the ratio of residual amount was obtained from the weight loss on TG curve for each sample.

2) Results and Discussion

(a) Evaluation of flame retardance by determination of LOI

Prior to the observation of the thermal degradation behavior, the flame retardance of each sample was evaluated by the LOI value as shown in Table 6-1. Nakanishi et al. have already confirmed that LOI values correlate well with char lengths and char areas which are recognized to be practical measures for evaluating flame retardance[14]. Samples with LOI values 27-28% or higher are designated as flame retardant which show short char lengths and small char areas indicating that they quench by themselves after piloted ignition.

As for the elements which contribute to the flame retardation, any single element gives LOI lower than 28% except for boron, whereas combinations of two elements contribute to flame retardance raising LOI values up to 40% or higher. But even with two components, LOI remains low when the concentration of treating reagent is not sufficient as seen in the case of sample No. 17 in Table 6-1.

Several researchers have also recognized that insufficient add-on of a flame retardant, for example P content, may reduce the flame retardance[15-18]. In general, the synergistic effect of two components, e.g. N and P, N and S or N and halogens, and appropriate concentrations of treating reagents are required for flame retardation.

(b) Relationship between flame retardance and TDOP

As shown in Table 6-1, samples having LOI values lower than 28% show higher TDOP, while those with LOI values 28% or higher show lower TDOP. As shown in Fig. 6-2, TG curves of almost all treated samples indicate mass loss starting at lower temperatures compared with the untreated sample, that is TDOP shifts to lower temperatures. Moreover, as shown in Fig. 6-2(a)-(d), the samples with the flame retardance indicated by the circled numbers, show larger shift than those without flame retardance having LOI values lower than 28%. Such shift of TG curves has already been observed with flame retardant samples by some researchers[1,3,7], but any detailed information, particularly in comparison with LOI values, has not been reported so far.

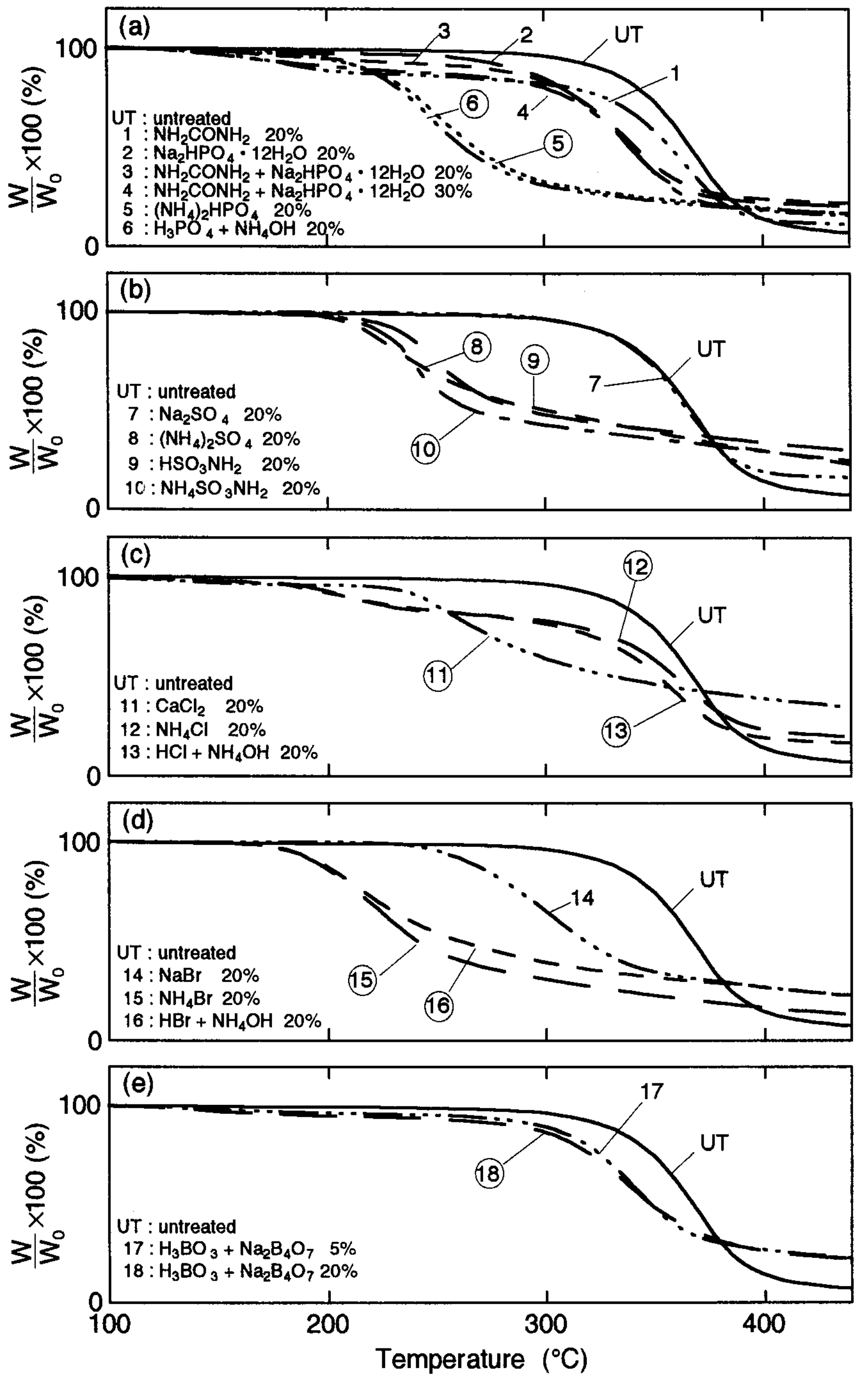


Fig. 6-2 Comparison of TG curves showing difference in TDOP observed between flame retardant samples and samples without flame retardance. TG curves are shown separately (a)-(e) to avoid confusion. (a) : sample containing N, P or N + P, (b) : samples containing S or S + N, (c) : samples containing Cl or Cl + N, (d) : samples containing Br or Br + N, (e) : samples containing B in different concentrations.

The above result probably means that the flame retardant samples thermally decompose at lower temperatures followed by pyrolytic gas formation, which results in the production of radical scavenger such as acetonitrile[19] or halogens blocking the formation of flammable gases, and also non-combustible gases such as SO_2, CO_2, NH_3 or acid vapors which dilute any flammable gases.

As to the effect of Br alone, as well as in combination with P, several publications have indicated[3,4,20-23] and Nakanishi et al. have confirmed not only on cellulosic fibers[24] but also on polyester (PET) fibers[25,26], that these gases contribute to inhibit combustion in the gas phase and P simultaneously acts to dehydrate the sample to produce char for the self-extingushability in the solid phase[27,28].

Thus, the flame retardant samples, even though ignited, extinguish by themselves at an early stage of the thermal treatment with the aid of the formation of radical scavengers, non-combustible gases and char.

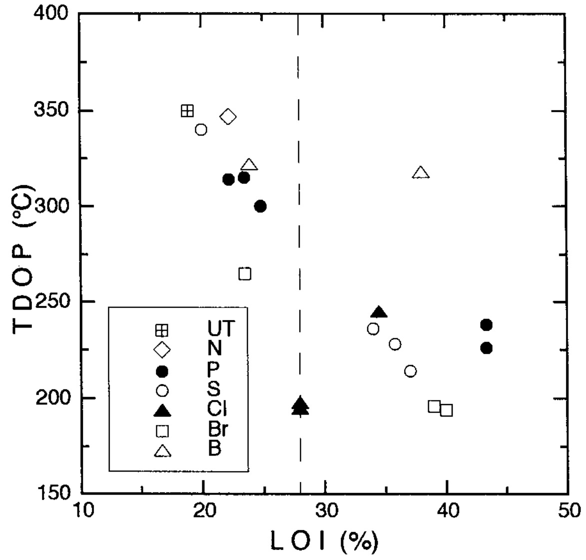
The flame retardation mechanism of borax, however, is entirely different from that of other reagents. Borate melts to form an enamel like film to cover the surface of the substrate which protects it from the flame as well as shutting off the supply of oxygen required for burning. Moreover, since borax acts endo-thermically when exposed to heat because of its water of crystallization, the temperature around the borax film is lowered, which contributes to quenching. In such case, there is no need for early thermal decomposition as with other flame retardants which depend on pyrolytic gas formation. Therefore, it is not unreasonable that TDOP of the sample treated with 20% $H_3BO_3 + Na_2B_4O_7$ is much higher than that of other flame retardant samples. Fig. 6-2(e) clarifies that a shift to lower temperature shown by TG curve No.18 of the sample treated with 20% $H_3BO_3 + Na_2B_4O_7$ is much less than those of other flame retardant samples.

Fig. 6-3 shows the relationship between TDOP and LOI values, which indicates that TDOP correlates well with LOI. Samples with LOI values lower than 28% have little flame retardance and show much higher TDOP, almost between 300-350°C, whereas TDOP values of samples with higher LOI are much lower, except the sample treated with 20% $H_3BO_3 + Na_2B_4O_7$. This deviation is clearly due to the different flame retardation mechanism.

(c) Relationship between flame retardance and MDRP or FP

The relationship between LOI values and MDRP shows a tendency similar to that seen between LOI and TDOP as shown in Fig. 6-4. Samples with LOI values below 28% show higher MDRP, while the flame retardant samples with LOI values 28% or higher have lower MDRP, though MDRP is higher than TDOP in every case.

The relationship between LOI value and FP was also considered, but less correlation was found when compared with those observed in the cases of TDOP and MDRP.



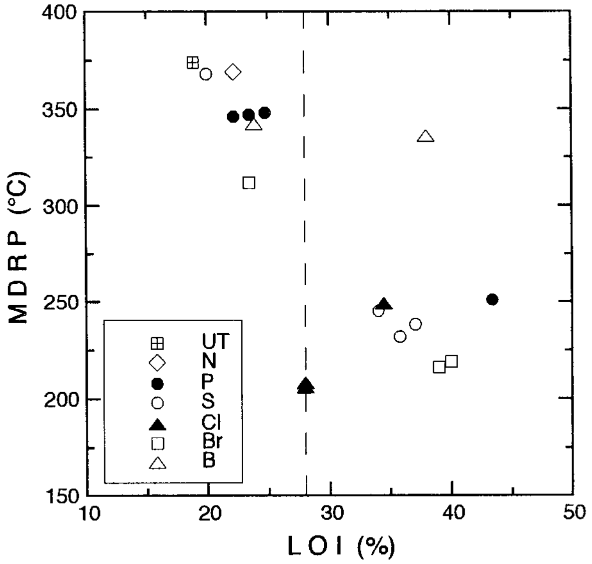


Fig. 6-3 Correlation between LOI and TDOP observed with cotton fabric untreated and treated with reagents containing P, S, Cl, Br or B singly or in combination with N.

Fig. 6-4 Correlation between LOI and MDRP observed with cotton fabric untreated and treated with reagents containing P, S, Cl, Br or B singly or in combination with N.

(d) Relationship among TDOP, FP and MDRP

It was thought to be important to consider how TDOP, FP and MDRP relate to one another, or if different tendencies are observable between flame retardant and flammable samples.

Fig. 6-5 indicates the positions of these three points on TG curves of representative samples, which clearly reveals that the samples with LOI values lower than 28% (Fig. 6-5a) are already ignited immediately or soon after TDOP before the thermal degradation rate reaches its maximum, whereas the flame retardant samples are hardly ignited after the maximum point of pyrolytic gas production as seen in Fig. 6-5b.

Such relationships are graphically illustrated in Fig. 6-6 and 6-7 as a correlation between LOI and difference between FP and TDOP (Fig.6-6) or between FP and MDRP (Fig. 6-7). Samples with LOI values lower than 28% show lower values of difference (FP-TDOP), less than 30°C, and even negative values in the case of difference (FP-MDRP).

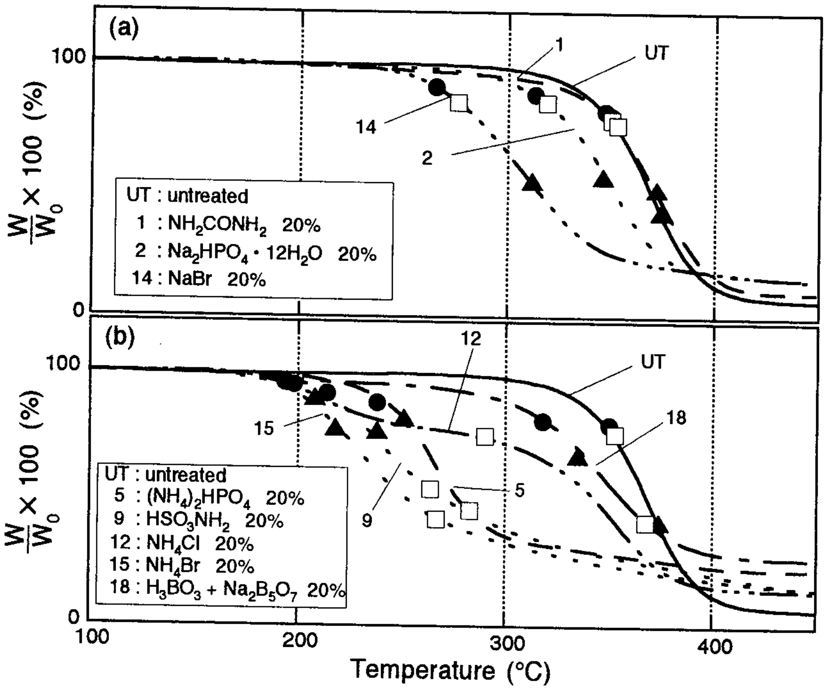


Fig. 6-5 Mutual relationship among TDOP (solid circle), MDRP (solid triangle) and FP (cpen square) on TG curves and difference in mutual position observed between the flame retardant samples (b) and the samples without flame retardance (a).

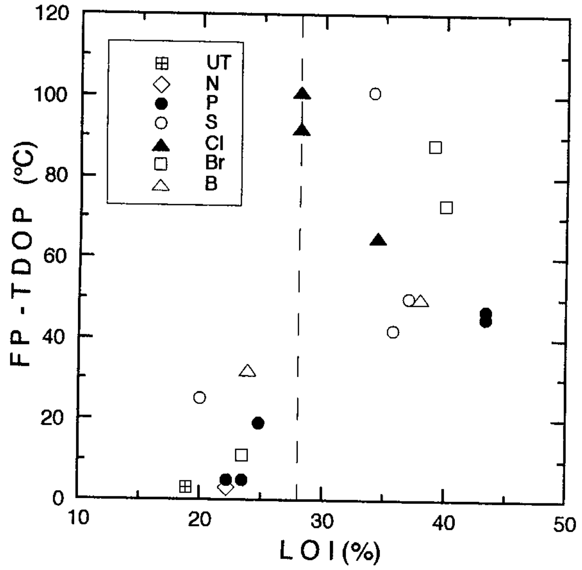


Fig. 6-6 Correlativity of LOI with difference between TDOP and FP.

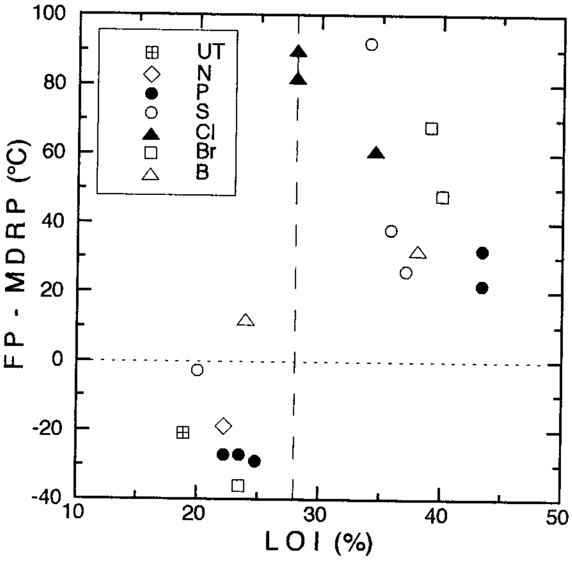


Fig. 6-7 Correlativity of LOI with difference between MDRP and FP.

(e) Relationship between LOI values and residual amounts of char obtained after ignition

One of the most important factors for flame retardation is self-extinguishability which is reflected in the amount of char residue after ignition. Fig. 6-8 indicates that the residual amounts char obtained after discontinuation of heating at FP correlate strongly with the corresponding LOI values, suggesting that flame retardant samples can self-extinguish.

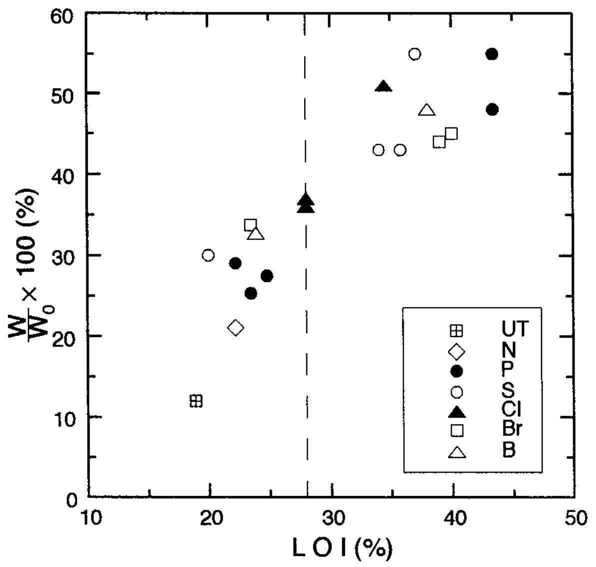


Fig. 6-8 Correlation between LOI values and ratios of residual amounts obtained after heating up to FP.

3) Conclusion

By means of thermogravimetric observations we have shown significant differences in thermal degradation behavior of flame retardant samples and of samples without flame retardance.

In general, with very few exceptions, the thermal degradation of flame retardant samples is initiated at lower temperatures compared with flammable samples to generate incombustible gases and radical scavengers in the early stage of the thermal degradation, which inhibits the combustion and results in self-extinguishment.

Flammable samples were ignited immediately or soon after the onset of the thermal degradation before the degradation rate reaches the maximum point, whereas flame retardant samples were ignited considerably above the thermal degradation onset point after the thermal degradation rate reaches the maximum.

The residual amounts of char obtained after heating to flash points correlated well with the flame retardance, which can be a measure for the evaluation of self-extinguishability.

6-1-2 Evaluation of Flame Retardance Characterized by Apparent Activation Energy of Thermal Degradation observed for Nondurable Flame Retardant Cotton Fiber

The flame retardance of finished materials has been evaluated commercially by burning tests at vertical or 45° angle, as well as by the limiting oxygen index (LOI). Flame retardant materials have also been studied from the fundamental aspect by thermal analyses, e.g., the thermogravimetry or pyrolytic gas analysis, to observe thermal degradation behavior. Since thermal degradation is a chemical reaction involving decomposition and oxidation in a complicated system which depends on the shape of sample, activation energy (Ea) with its variation is thought to be an important factor for the study of thermal degradation.

Studies on Ea from thermogravimetric traces have been reported since 1950s. We have found that the majority of papers have dealt, in general, with synthetic polymers represented by polystyrene and polyethylene [29], nylon 4 and Nylon 4 copolymer [30], teflon [31-37] and aromatic polyether [38,39], or low molecular materials such as calcium oxalate [40]. No information has been reported so far concerning Ea of flame retardant samples containing different kinds of flame retardant elements.

Therefore, we focused our investigation on Ea, specially on its variation, at different steps of the thermal degradation process, since the overall or average Ea seems to be less meaningful. Samples used for the present investigation were the same as those employed for the previous study,i.e.,cotton fabric treated with various compounds containing not only N and P, but also sulfur(S), chlorine(Cl), bromine(Br) or boron (B).

Ozawa's method [41] was adopted for the thermogravimetric analysis, and Ea values of flame retardant samples were compared with those of flammable samples. The results indicate that the thermal degradation behavior observed in the previous investigation is reflected as well in Ea values.

1) Experimental

(a) Materials

The fabric material and the treating reagents used for the present investigation were all the same as those employed for the previous study. The treating reagents were compounds containing flame retardant elements, N, P, S, Cl, Br or B as listed in Table 6-2.

(b) Treating method

The cotton fabric was impregnated with 5% or 20% solutions of these compounds as shown in Table 6-2, padded and air dried. The final contents of the compounds in the treated samples were gravimetrically analyzed and found to be about 4% add-on from 5% solutions, and approximately 16% add-on from 20% solutions.

(c) Determination of flame retardance

The flame retardance was determined as described in the previous studies.

(d) Thermogravimetry

Thermogravimetric (TG) curves were obtained as mentioned in 6-1-1.

Table 6-2 List of LOI, TDOP, MDRP, FP, Ea at these three temperatures and ratios of residue obtained after heating upto 600°C observed with samples treated with 5% or 20% solutions of compounds containing P, S, Cl, Br or / and N in comparison with untreated cotton fabric.

	LOI	TDOP		MDRP		FP		Residue after heating up to 600°C
		Ea (kJ / mol)	temp. (°C)	Ea (kJ / mol)	temp. (°C)	Ea (kJ / mol)	temp. (°C)	
untreated	18.9	17.6	350	190	374	186	353	0.2
1 NH_2CONH_2	22.2	*	347	193	369	120	350	2.0.
2 Na_2HPO_4	22.2	253	314	220	346	250	319	5.3
3 $(NH_4)_2HPO_4$ 5%	24.4	146	275	155	280	162	296	10.0
4 $(NH_4)_2HPO_4$ 20%	43.4	83	238	115	251	201	283	27.0
5 $NH_4OH + H_3PO_4$ 20%	43.4	75	226	120	251	147	273	25.0
6 Na_2SO_4	20.0	257	340	210	368	210	365	7.9
7 $(NH_4)_2SO_4$ 20%	34.0	63	236	92	245	20	337	7.4
8 HSO_3NH_2 5%	25.3	210	225	222	240	197	280	3.0
9 HSO_3NH_2 20%	37.1	33	214	138	238	55	264	5.3
10 $NH_4SO_3NH_2$ 5%	23.0	124	238	198	245	>350	271	4.0
11 $NH_4SO_3NH_2$ 20%	35.8	5	228	79	232	30	270	6.2
12 $CaCl_2$ 5%	23.5	155	245	163	250	225	300	8.0
13 $CaCl_2$ 20%	34.5	92	245	110	249	130	310	23.2
14 NH_4Cl 20%	28.0	24	198	32	208	57	290	4.2
15 $NH_4OH + HCl$ 20%	28.0	53	195	67	206	91	296	5.3
16 NaBr 20%	23.5	118	265	250	312	188	276	4.2
17 NH_4Br 20%	40.0	90	194	113	219	50	267	5.0
18 $NH_4OH + HBr$ 20%	39.0	29	196	71	216	12.5	284	4.0
19 $H_3BO_3 + NaB_4O_7$ 5%	23.9	237	322	199	342	196	354	7.0
20 $H_3BO_3 + NaB_4O_7$ 20%	38.0	140	318	165	336	90	368	28.0

(e) Determination of TDOP and MDRP and FP

TDOP, MDRP and FP were determined as described in 6-1-1 (Fig. 6-1).

(f) Determination of Ea

Considerable number of methods for the determination of Ea from thermogravimetric data have been reported by many researchers [29,32,37,40-48]. Every method has both merits and demerits as a matter of course. We adopted Ozawa's method [41] since this method is an integral method which is simpler and more applicable than the differential methods. Moreover, the integral method enables us to easily obtain Ea even without knowing the nature of degradation mechanism.

According to the Ozawa's method, the following equation is finally derived assuming that the kinetic equation of thermal degradation is represented by the Arrhenius equation.

$$-\log\beta_1 - \frac{0.4567E}{RT_1} = -\log\beta_2 - \frac{0.4567E}{RT_2} = \cdots\cdots\cdots$$

where β is the heating rate, E the activation energy, R the gas constant and T the absolute temperature.

Ea can be obtained from the slope of a line given by plots of log β versus reciprocal absolute temperatures for given values of the fractional residual weights of the sample.

2) Results and Discussion

(a) Application of the Ozawa's method to obtain Ea of thermal degradation of cotton fiber

Fig. 6-9 shows TG curves for untreated cotton fabric at heating rates of 3, 6, 8 and 10°C/min. On these TG curves, temperatures at various residual weight ratios were read and reciprocal absolute temperatures were plotted against the logarithmic heating rates. The plots were approximately linear for each residual weight as exhibited in Fig. 6-10. Ea was calculated from the slopes. Ea values of the treated samples were obtained by the same procedure.

(b) Effects of flame retardant elements on Ea of the thermal degradation

Attention was first paid to find how the addition of each flame retardant element affects Ea for the thermal degradation of cellulose, as well as to see how Ea changes with the progress of the thermal degradation. Therefore, Ea values of each sample were plotted against the residual weights obtained at various stages in the process of thermal degradation as shown in Fig. 6-11. This reveals that Ea values of all treated samples change extensively with decrease in residual weight, but that of the untreated sample remains unchanged except for a slight increase in Ea in the initial stage of thermal degradation. The effects of the treating reagents on Ea are either to elevate or reduce Ea at each stage of thermal degradation. But, as seen in Fig. 6-11, the Ea versus weight curves for the treated samples are clearly separated into two groups. One group(upper) indicated by open marks, includes the untreated sample and treated samples with Ea values higher than that of the untreated sample. The other group(lower), indicated by solid marks, consists of treated samples with lower Ea values.

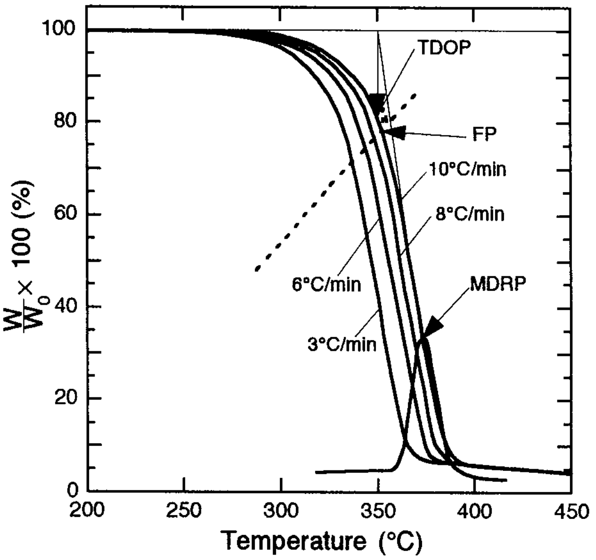


Fig. 6-9 TG curves of cotton fiber observed at various heating rates with an illustration to explain how to determine TDOP, MDRP, FP.

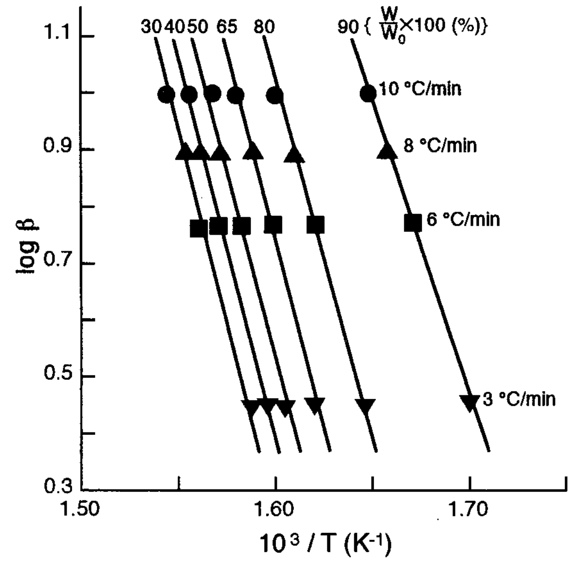


Fig. 6-10 Plots of logarithmic heating rate versus reciprocal T at each indicated weight value.

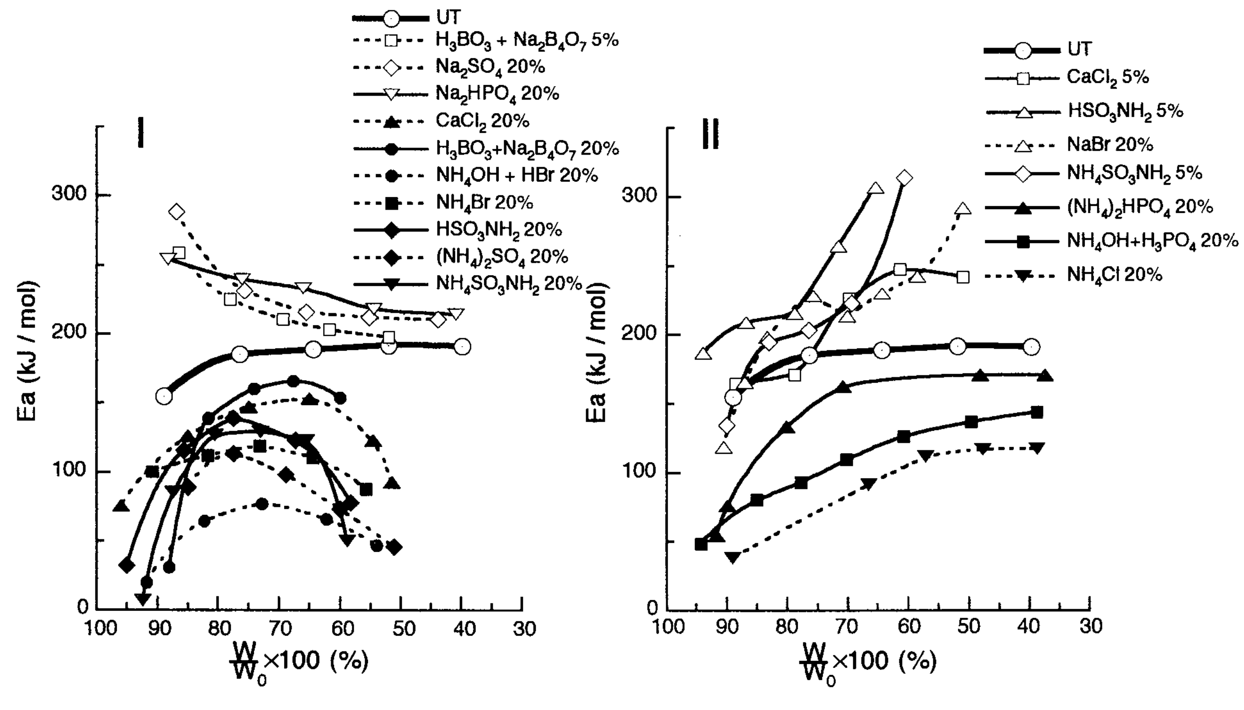


Fig. 6-11 Ea value versus ratios of residues showing Ea distribution in the process of thermal degradation of cotton fiber untreated and treated with various kinds of compounds containing flame retardant elements (5% and 20% mean concentrations of solutions of these compounds used for treating cotton fabric to prepare the samples used for the present study).

It is noticeable that the curves with solid marks are all from the samples treated with 20% solutions of compounds containing N and one other flame retardant element (P, S, halogens) except for B which works alone without combination with N. The curves with open marks are for the samples treated with 5% solutions of the above mentioned compounds and 20% solutions of the compounds containing only one element, P, S or Br which does not act as flame retardant without combining with N.

Considering the variation of Ea with decrease in residual weight in greater detail, we note the followings: The curves in the higher Ea region show two types of behavior, descending or ascending type reaching 300kJ/mol or higher. These results are very reasonable since the samples of the descending type in upper group (I) contain nonvolatile inorganic sodium salts which require higher Ea for the thermal decomposition particularly in the initial stage, whereas the ascending behavior starting from lower Ea (II) were shown by samples containing volatile halides, ammonium salts or sulfamine, which are readily decomposable by thermal treatment.

On the other hand, Ea versus weight curves with solid marks in the lower region start from considerably low Ea values, which agrees well with the results reported in the previous section that the thermal degradation of the flame retardant samples is initiated at lower temperatures by the aid of easily decomposable flame retardant compounds. Ea increases with enhancement of the generation of pyrolytic gases from the compounds as well as from cellulosic fiber, and decreases after the degradation rate reaches maximum probably because of facilitated decomposition of cellulosic fiber in combination with effective flame retardant elements. Such tendency is applicable to almost all the samples, but a few exception can be noted, i, e., the samples treated with 20% solutions of compounds containing N and P showed increasing tendency during the heat treatment (in lower group). Since P having dehydrating property works effectively in combination with N to produce char, as Nakanishi et al. already proved by the pyrolytic gas formation [64] and as evidenced by the residual amounts observed after heating up to 600°C listed in Table 6-2, the existence of more char in the above samples might require higher Ea for the degradation.

Only NH_4Cl showed typical behavior of increasing almost linearly and leveling off later without any decrease within the region as observed in the lower group.

Ea values at TDOP, MDRP and FP of each sample were obtained also according to Ozawa' s method by determining residual ratios at these temperatures on TG curve obtained at heating rate of 10°C/min, reading temperatures at these ratios on other TG curves obtained at 8°C/min, 6°C/min and 3°C/min, followed by plotting these reciprocal absolute temperatures against the logarithmic heating rate. Ea values were obtained from the slopes and listed in Table 6-2.

(c) Ea at TDOP, MDRP and FP

To express more comprehensibly the difference in Ea observed between flame retardant and flammable samples, Ea values at TDOP, MDRP and FP are plotted against each of these three temperatures. As shown in Fig. 6-16 the plots of TDOP versus Ea at TDOP (Fig.6-12-I) and those of MDRP versus Ea at MDRP (Fig.6-12-II) disclose that the solid circles for flame retardant samples are assembled in a small area near the origin, 245°C by 90 kJ/mol area for TDOP, and 250°C by 140kJ/mol area for MDRP .

On the other hand, the open points for the flammable samples with LOI < 28% are located in the higher temperature region. But we can not ignore the deviation of one solid circle of the sample treated with 20% solution of boric acid and borax. This sample always showed behavior different from those of other flame retardant samples because of the different flame retardation mechanism of borate as described in the previous section.

Compared with the clearly separated patterns of the above two cases, the plots of FP versus Ea at FP (Fig.6-12-III) show more deviations. This is probably due to the fact that the flame retardant samples which produce more char or calcium oxide in the process of thermal degradation (indicated by symbol ◉) require higher Ea and are located at positions higher than those for other flame retardant samples.

As mentioned above, the positions of the plots illustrated in Fig. 6-12 clearly confirm that the flame retardant samples start decomposing and reach the maximum rate of thermal degradation at lower temperatures with lower Ea compared with the flammable samples.

(d) Relationship between LOI values and Ea at TDOP, MDRP or FP

Fig. 6-13 shows plots of LOI versus Ea at TDOP, MDRP and FP. The solid points for the flame retardant samples with LOI ≧ 28% occupy the lower region of Ea in every case with three exceptions indicated by a different symbol. Since these plots are from the samples containing N and P or calcium as observed in the case shown in Fig.6-12-III, such deviations are due to the same reason as that given above. The above relationship finally confirms the typical behavior observed with the flame retardant samples also from the kinetic view point of the thermal degradation.

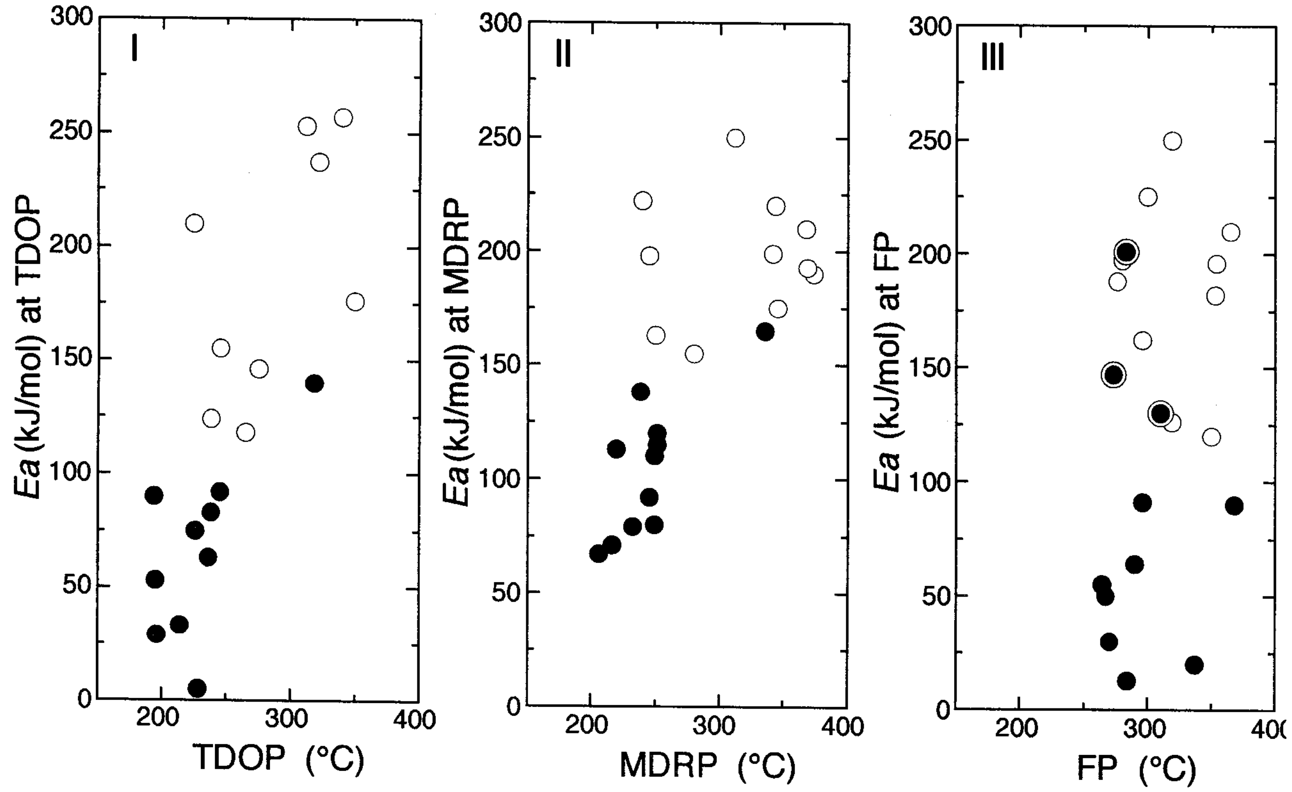


Fig. 6-12 Plots of TDOP, MDRP or FP versus Ea at these temperatures to confirm different tendencies observed between Ea of samples with LOI value ≧ 28% and those with LOI value < 28%. Samples with LOI value ≧ 28% are indicated by solid circles and those with LOI < 28% by open circles, ◉ indicates the samples containing N and P or Ca.

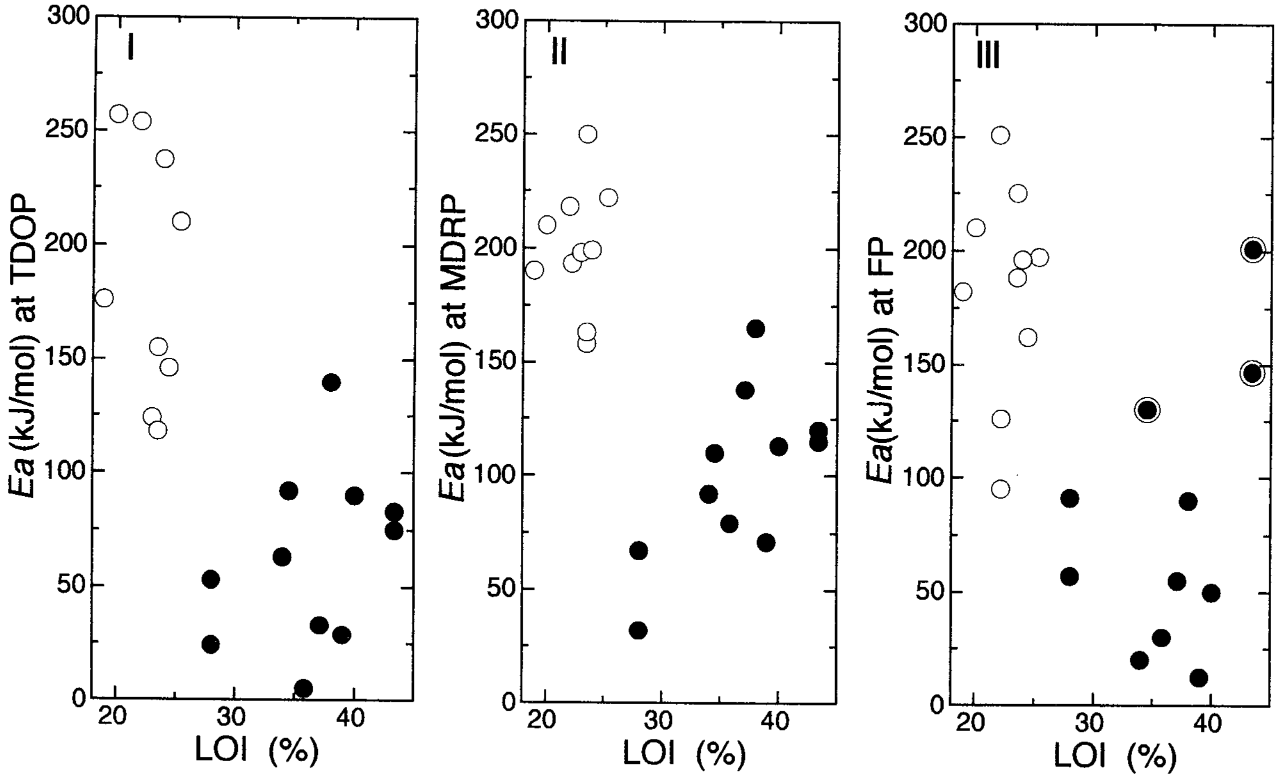


Fig. 6-13 Relationship between LOI values and Ea at TDOP, MDRP and FP. (samples with LOI ≧ 28% are indicated by solid marks and those with LOI < 28% by open marks, ◉ indicates the samples containing N and P or Ca.

3) Conclusion

In conclusion, flame retardation is characterized by comparing Ea of the flame retardant samples with that of flammable samples. Ea values of flame retardant samples are generally lower than those of flammable samples, which is confirmed by observing the relationships between TDOP, MDRP or FP and Ea at each of these temperatures, as well as between LOI values and Ea at TDOP, MDRP and FP. Thus, the flame retardants affect Ea throughout the process of thermal degradation. The thermal degradation behavior observed in the previous investigation is evidently reflected on Ea and supported well by the results obtained in the present investigation.

6-1-3 Thermal Degradation Behavior of Durable Flame Retardant Cotton Fiber

Since more attention has been paid to durable flame retardant finishes because of the practical importance from the general public commnsense, we have studied the finishing conditions to obtain the best flame retardance and favorable physical properties for the end-uses from the practical viewpoints. But it was thought to be still important to investigate durable flame retardant finished samples from the aspect of thermal degradation.

The studies on durable flame retardant finishes have been attempted widely in the world so far[49-56]. But, as for studies on the thermal analysis of durable flame retardant samples, little information has been available up to present.

Therefore, we have extended our previous investigations on the three kinds of durable flame retardant finishes as mentioned in 3-1 above over the thermogravimetric analysis to observe the thermal degradation behavior for the thermal degradation reaction to compare the results with those observed with nondurable flame retardant samples described above. The samples used for the investigation were the most flammable cellulosic (cotton in this case) fabric treated with the most worldwide famous durable flame retardants, Pyrovatex CP, THPS in the forms of monomer and a condensate with urea (THPS precondensate) with or without additives mentioned in 3-1. The results obtained from these samples were compared with those from nondurable flame retardant fiinished samples and discussed.

Furthermore, we paid attention to the residual amount remaining after the thermal treatment. Since the self-extingushability is one of the important factors to evaluate quenching ability which will act after the onset of combustion, and the residual amount of char can be a measure for the self - extinguishability, we attempted to evaluate the flame retardance also from the residual ratio shown by each TG curve after the termination of heating at FP or at 600°C.

1) Experimental

(a) Materials

(1) Fabric

The fabric used for this investigation was 100% cotton described in 2-2-2.

(2) Treating reagents

(i)Flame retardants

① Pyrovatex CP was offered by Ciba Geigy Co. (Switzerland)

② THPS was a product of Nihonkayaku Co.

③ THPS precondensate with urea was offered by Albright and Wilson Co. (England)

(ii) Additives for each flame retardant

① Hexamethylolmelamine (M6) (offered by Mitsuitoatsu Kagaku Co.), ortho-phosphoric acid, urea and ammonium chloride (products of Wako Chem. Co.) were used with Pyrovatex CP for thermo-fixed Pyrovatex finish.

② Sodium acetate and polyoxyethylene nonylphenyl ether were used with THPS precondensate for Proban finish (THPS with ammonia cure).

③ Trimethylolmelamine (M3), aminomethylpropanol (catalyst P, offered by Mitsuitoatsu Co.) triethanolamine (TEA, pH adjuster, a product of Wako Chem. Co.) were used for thermo-fixed THPS.

(b) Methods

(1) Flame retardant finishes

(i) Finishing with Pyrovatex CP

This finish was carried out on the basis of process and results already described in 3-1-1.

The following 5 kinds of treating baths were prepared.

① 32% (V/V%) of Pyrovatex CP solution alone (Py 1).

② A solution consisting of 32% of Pyrovatex CP and 8% of M6 (Py 2)

③ A solution consisting of 32% of Pyrovatex CP and 2% of ortho-phosphoric acid (Py 3).

④ A solution consisting of 32% of Pyrovatex CP, 8% of M6 and 2% of ortho-phosphoric acid

(Py 4)

⑤ A solution containing 32% of Pyrovatex CP, 8% of M6, 2% of ortho-phosphoric acid, 1% of urea and 0.5% ammonium chloride (Py 5).

The cotton fabric was immersed in the above each solution separately to treat in the same manner described in 3-1-1.

(ii) Finishing with THPS-urea precondensate by ammonia cure (Proban finish)

This finish was performed according to the method established by Nakanishi et al. described in 3-1-2. The cotton fabric was treated under the following 5 conditions.

① The fabric was immersed in 40% (V/V%) of THPS precondensate solution for 10 min, padded to 90% pickup and air dried until the water content reached down to 25% (Pb 1). This water content should be strictly controlled for the following ammonia cure.

② The fabric treated as described above was further treated by the ammonia cure as mentioned in 3-1-2 (Pb 2).

③ The sample thus treated was further treated by oxidation with 10% of H_2O_2 for 10 min at 60°C followed by soaping with a solution containing 0.2% of sodium carbonate and 0.08% of a nonionic surfactant for 10 min at 60°C to remove formaldehyde formed in the finishing process (Pb 3).

④ The fabric was treated with 40% of THPS precondensate containing 2.6% of sodium acetate and 0.2% of the above mentioned nonionic surfactant and predried to adjust the water content of sample to 25% to which NH_3 gas was introduced for ammonia cure as mentioned above (Pb 4).

⑤ Sample Pb 4 was further treated by oxidation and soaping as described above two) (Pb 5).

(iii) Finishing with THPS by heat cure.

The cotton fabric was finished according to the method described in 3-1-3.

Cotton fabric was treated with the following 4 kinds of solutions by 2dip-2nip method adjusting its pickup to 90%.

① A solution containing 32% (V/V%) of THPS and 5% TEA to adjust pH at around 7±0.2 (Ts 1).

② A solution containing 32% of THPS, 5% of TEA and 1% of urea as a nitrogen donor (Ts 2).

③ A solution consisting of 32% of THPS, 5% of TEA, 12% of M3 and 1% of Catalyst P (Ts 3).

④ A solution consisting of 32% of THPS, 5% of TEA, 1% of urea, 12% of M3 and 1% of Catalyst P (Ts 4).

These treated samples were heated for 20 min at 140°C followed by oxidation and soaping to minimize contents of formaldehyde and any excess of reagents by the same procedure described above.

(2) Evaluation of flame retardance

The flame retardance of the above mentioned each sample was determined as mentioned in 2-1.

(3) Thermal Analysis

TG curves and DTG curves were obtained as mentioned in 6-1-1 above.

TDOP, MDRP and FP were determined as described also in 6-1-1.

Every sample to be used for the thermal analysis was cut into powdery fine particles to minimize any effect of air diffusion.

(4) Evaluation for self-extingushability

It was thought, as in the case of nondurable flame retardant finishes, that residual amounts of char remaining after ignition could be a measure for the evaluation of flammability or extinguishability. Therefore, heating was stopped during the thermogravimetric analysis at FP of each sample determined as mentioned above and the ratio of residual amount was obtained from each TG curve at the points of FP and 600°C.

2) Results and Discussion

(a) Evaluation of flame retardance and effects of finishes

The flame retardance was evaluated by LOI value determined for each sample and listed in Table 6-3.

Samples with LOI values of 27-28% or higher are recognized to be flame retardant showing short char lengths or small char areas[14], which proves that they could quench by themselves before long after ignition.

The effects of the treatment with the above flame retardants are as follows.

Table. 6-3 List of LOI, TDOP, MDRP, FP and residual ratios obtained after heating up to FP and 600°C, samples are cotton fabric untreated and treated with Pyrovatex CP, THPS monomer and precondensate under various conditions.

Symbol for sample	Treating conditions	LOI (%)	TDOP	FP	MDRP	Residue (%)	
			(°C)	(°C)	(°C)	up to FP	up to 600°C
UT	untreated	18.9	350	353	374	12.0	0.2
Py1	Pyrovatex CP (Py)	20.4	328	335	354	40.0	6.0
Py2	Py + M6	22.2	302	320	321	41.0	7.0
Py3	Py + H_3PO_4	25.5	310	326	330	43.0	13.0
Py4	Py + M6 + H_3PO_4	29.5	312	328	333	51.0	20.0
Py5	Py + M6 + H_3PO_4 + urea + NH_4Cl	30.0	316	326	336	60.0	25.0
Pb1	THPS precondensate before NH_3 cure	26.5	213	270	245	43.0	17.0
Pb2	THPS precondensate after NH_3 cure	28.5	284	292	300	71.0	20.0
Pb3	Pb2 → oxidation → soaping	29.0	298	306	310	53.0	23.0
Pb4	THPS precond. + NaOAC + nonionic surfactant after NH_3 cure	30.0	284	294	297	76.0	25.0
Pb5	Pb4 → oxidation → soaping	29.5	298	304	308	53.0	24.0
Ts1	THPS + TEA	20.0	314	327	337	40.0	7.0
Ts2	THPS + TEA + urea	24.4	314	328	336	42.0	10.0
Ts3	THPS + TEA + M3 + Catalyst P	29.0	312	320	329	50.0	20.0
Ts4	THPS + TEA + urea + M3 + Catalyst P	30.0	318	325	330	55.0	22.0

(1) Finish with Pyrovatex (Py)

Among 5 kinds of conditions, the finish with Pyrovatex CP alone (Py 1) gave the lowest LOI not much different from that of untreated sample, which means that some additives are required. Resin and ortho-phosphoric acid did not give enough effect when added singly, but the samples treated with both resin and ortho-phosphoric acid in combination with Pyrovatex CP showed sufficient flame retardance and further addition of urea and ammonium chloride elevated LOI value. The above results will suggests that the resin and phosphoric acid showed a synergistic effect and additional nitrogen and a halogen from urea and ammonium chloride enhanced the effect.

(2) Finish with THPS precondensate with ammonia cure (Pb).

Comparing the flame retardance before and after the ammonia cure, LOI value is lower than 28% (in the case of Pb1) before ammonia cure but becomes higher after curing irrespective of with / without additives and the after treatment.

(3) Finish with THPS by heat cure (Ts)

Addition of a pH adjuster, TEA, and nitrogen donor, urea, failed to give the flame retardance, but further addition of resin and a catalyst showed an efficiency for flame retardance.

(b) TG curves of treated samples in comparison with that of untreated sample

As shown in Fig. 6-14, TG curve of every treated sample showed a shift to lower temperature, which was the same tendency already observed by other researchers with samples containing nitrogen and phosphorus[10,14,57-61] as well as with other flame retardant elements. Proban finish gave the largest shift and Pyrovatex finish apparently the smallest shift.

In the case of Proban finish, the sample treated with THPS precondensate alone before ammonia cure exhibited an extremely large shift showing the onset of weight loss at around 165°C. After curing, TG curves shifted back to higher temperatures starting weight loss at about 270-280°C. Not much difference was observed among TG curves of the cured samples. The above results probably explained as follows : THPS precondensate with urea, a comparatively decomposable THPS dimer with an amide bond as shown in Fig. 6-15, is easily decomposed at much lower temperature, which gave a large effect on TG curve of the sample treated with this dimer before curing. After ammonia cure, THPS precondensate absorbed in the amorphous regions of fiber structure polymerizes to form Proban polymer by the mechanism shown in Fig. 6-15. It can be deduced that such flame retardant polymer is much less decomposable, moreover, char formation from cellulosic fiber by the dehydrating action of the heated polymer (probably P_2O_5)retarded the decomposition of the cured samples.

The thermogravimetric behavior of samples finished with THPS monomer by thermal treatment (Ts1-Ts4) is similar to that of the samples obtained by Proban finish after ammonia cure (Pb2, Pb3, Pb4, Pb5) except that shift of TG curves of Ts samples was less than that of Proban samples by approximately 20°C.

TG curves of Pyrovatex-finished samples showed somewhat a different behavior, curving and descending with a comparatively gentle slope from 290°C to 370-390°C, whereas the slope of TG curves shown by the samples finished with Proban polymer and those finished with thermo-fixed THPS was steeper, descending from 300 ~ 310°C to 340 ~ 350°C. This means that Pyrovatex finish gives more gradual thermal degradation.

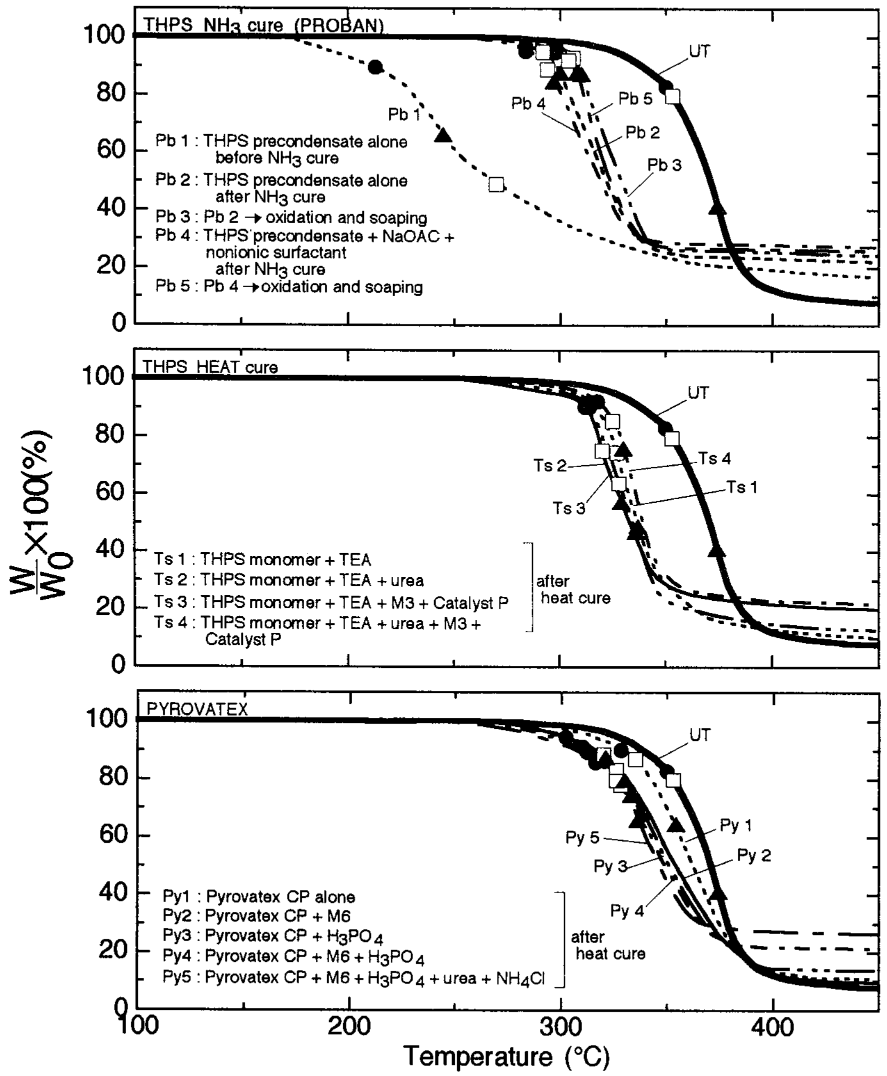
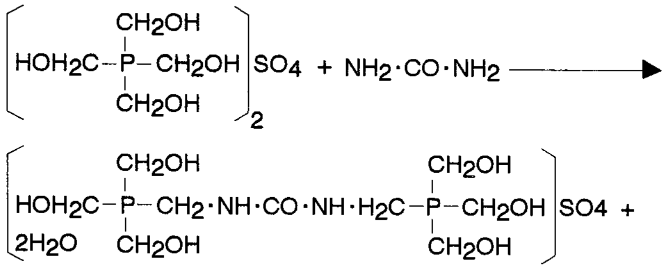


Fig. 6-14 TG curves for cotton cellulose treated with three types of durable flame retardants under various conditions and TDOP, FP and MDRP on these TG curves in comparison with those of untreated cotton cellulose.

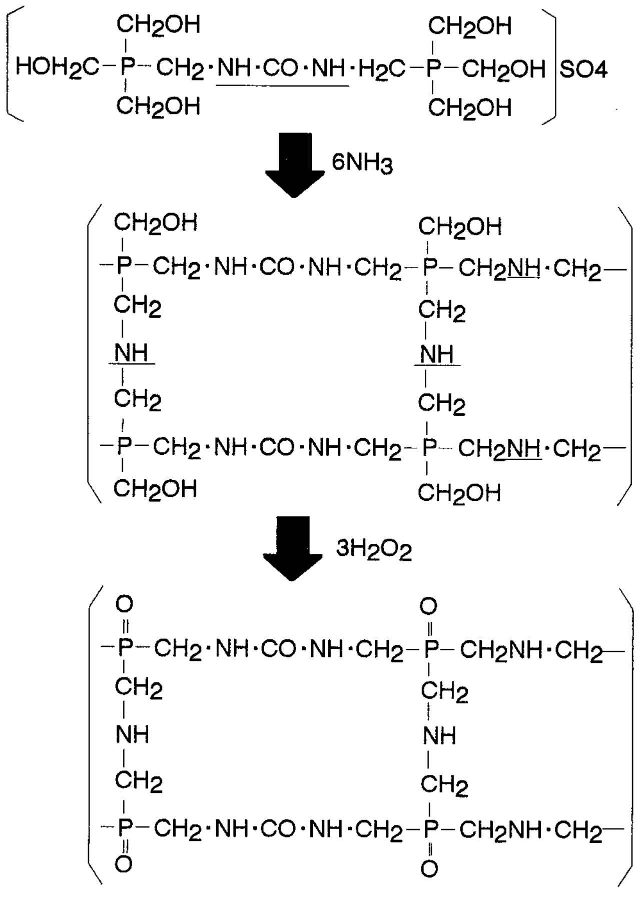
· Precondensate



$$\left[HOH_2C-\overset{CH_2OH}{\underset{CH_2OH}{P}}-CH_2OH\right]_2 SO_4 + NH_2\cdot CO\cdot NH_2 \longrightarrow$$

$$\left[HOH_2C-\overset{CH_2OH}{\underset{CH_2OH}{P}}-CH_2\cdot NH\cdot CO\cdot NH\cdot H_2C-\overset{CH_2OH}{\underset{CH_2OH}{P}}-CH_2OH\right] SO_4 + 2H_2O$$

· THPS — amide Finish — Ammonia Cure



$$\left[HOH_2C-\overset{CH_2OH}{\underset{CH_2OH}{P}}-CH_2\cdot \underline{NH\cdot CO\cdot NH}\cdot H_2C-\overset{CH_2OH}{\underset{CH_2OH}{P}}-CH_2OH\right] SO_4$$

PROBAN Polymer

$+ 4CH_2O + (NH_4)_2SO_4 + 10H_2O$

Fig. 6-15 Formation of THPS precondensate and mechanism of ammonia cure.

(c) Relationships among TDOP, FP and MDRP on TG curves

The attention was further paid to the mutual relationship among the three temperatures at which the thermal degradation and piloted ignition start and thermal degradation rate reaches the maximum. These three points (TDOP indicated by ●, FP by □, MDRP by ▲) are marked on TG curve of each sample (Fig. 6-14). The order of the position of these three points on TG curve is TDOP, FP and MDRP the same as that of the untreated sample except for sample treated with THPS precondensate without ammonia cure (Pb 1) which showed much retarded FP. Such tendency is contrary to what was observed in the case of nondurable flame retardant samples which have shown that flammable samples are ignited soon after TDOP similarly to untreated sample and flame retardant samples are ignited after MDRP. A characteristic difference from untreated sample observed with all the samples but Pb 1 without curing is that the interval between TDOP and FP is longer. This means prolonged ignition after the onset of thermal degradation. In addition, every MDRP locates at an upper position with a shorter interval from FP, which implicates self-extinguishing at a lower temperature to leave more residual amount of char. Particularly, Proban finished-samples with ammonia cure draw attention to that these three points fall in close positions one another on each TG curve.

(d) Relationship between LOI and TDOP, FP and MDRP for each finished sample

It is thought to be important to see if there is any difference between flame retardant samples and flammable samples in TDOP, FP and MDRP as well as to mutually compare these three types of finished samples. Fig. 6-16 shows plots of LOI values vs TDOP, FP or MDRP for Proban-finished samples, thermo-fixed THPS monomer-finished and Pyrovatex-finished samples. The plots for flame retardant samples with LOI values of ≥ 28% are indicated by solid marks and those for the samples with LOI values of < 28% by open marks.

The ammonia cured Proban finished-samples with LOI values of > 28% occupied a temperature region higher than that of the samples with LOI values of < 28% without ammonia cure. This is probably because polymer formed by ammonia cure required higher temperature for the thermal decomposition than dimer without curing.

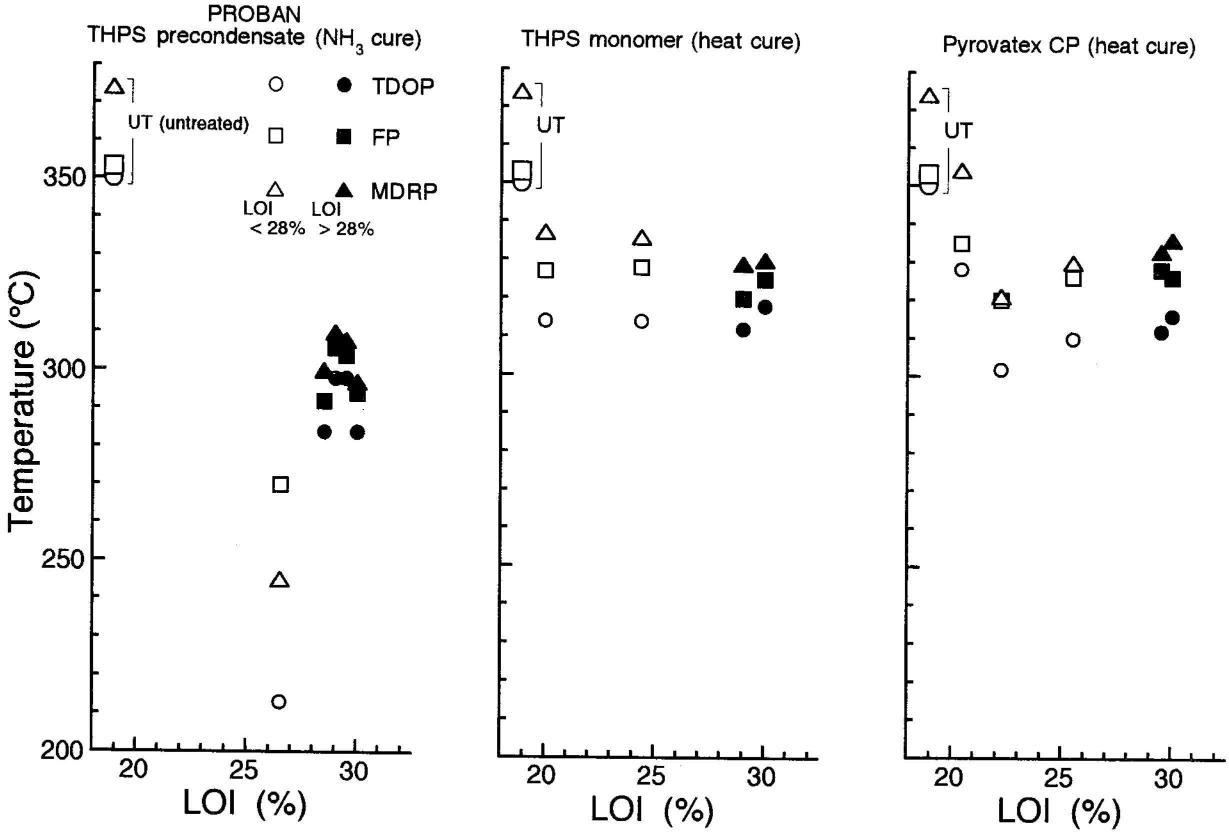


Fig. 6-16 Relationship between LOI values and TDOP, FP or MDRP to compare these temperatures between samples with and without flame retardance as well as among Proban finish, thermo-fixed THPS monomer and Pyrovatex finishes.

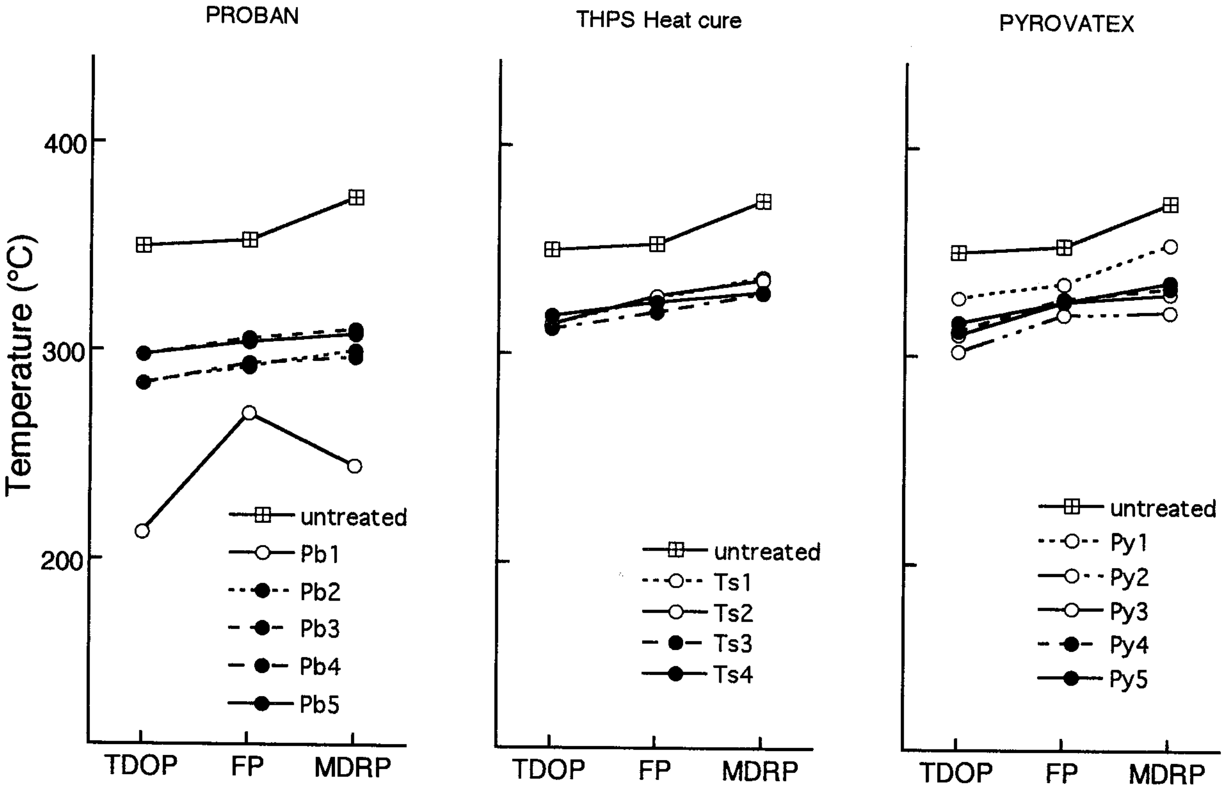


Fig. 6-17 More comprehensible illustration for comparison of TDOP, FP and MDRP between flame retardant samples and flammable samples as well as among the three types of finishes.

On the other hand, little difference was shown in temperature ranges between flame retardant samples with LOI values of > 28% and flammable samples with LOI values of < 28% in both cases of the thermo-fixed samples, which seems to be irreconcilable to the results observed with samples treated with nondurable inorganic flame retardants that flame retardant samples with LOI values of 28% or higher showed lower temperature ranges than flammable samples with LOI values lower than 28%. Such difference is probably attributed to the difference in the retardation mechanisms between nondurable flame retardant finished samples and durable flame retardant finished samples.

Thus, as far as TDOP, FP and MDRP in the process of thermal degradation are concerned, there found little difference between samples with and without flame retardance in the case of samples finished with organic durable flame retardants after curing. Such tendency is more clearly illustrated by plotting TDOP, FP and MDRP for Proban, THPS monomer and Pyrovatex-finished samples respectively as shown in Fig. 6-17. Solid and open circles fall in almost the same temperature region in the cases of THPS monomer or Pyrovatex-finished samples with curing, whereas Proban-finished samples show that open marks for the sample without curing are located at lower positions than those of solid marks for the samples with curing. Therefore, these results led us to consider that the difference in temperature region observed between solid and open marks is probably attributed not to with / without flame retardance but to with / without curing in the case of durable flame retardant-finished samples.

(e) Evaluation of self - extinguishability by observing residual ratios

As described above, since the residual amount of char remaining after the thermal treatment can be a measure to evaluate the self-extinguishability, residual ratios were obtained from TG curves after heating up to FP as well as to 600°C and listed in Table 6-2. It is obviously shown that residual ratios of all the samples are comparatively proportional to LOI values. Moreover, such tendency is evidenced by comparing the end of TG curves shown in Fig. 6-2, though these curves are terminated at 450°C in this figure.

3) Conclusion

TG curves of all treated samples shifted to lower temperature than that of untreated cotton cellulose, Proban treated samples showed the largest shift and the other two thermo-fixed samples less shift, and a steeper slop of TG curves was observed with samples treated with both THPS oligomer and monomer, and more gradual slope with Pyrovatex-finished samples. Such thermal degradation behavior suggests that Pyrovatex-finished samples decompose comparatively slowly and samples treated with two types of THPS-treated samples more rapidly.

It should be noted that thermal degradation behavior shown by durable flame retardant cotton fiber is largely different from that observed in the nondurable flame retardant cotton fiber described in the previous section, which is probably because the thermal degradation of durable flame retardants occurs simultaneously with cellulose molecule itself since their molecules are closely bound chemically with cellulose molecule to achieve durable flame retardation, whereas nondurable flame retardants and cellulose degrade separately each other without any chemical bonding.

Residual ratios obtained after heating up to FP and 600°C are comparatively proportional to LOI values, which can be a measure for the self-extinguishability after ignition. A little difference is observed among the levels of self extinguishability of the three kinds of finished samples.

6-1-4 Apparent Activation Energy of Thermal Degradation observed for Durable Flame Retardant Cotton Fiber

Subsequently from the observation of thermal degradation behavior of durable flame retardant cotton fiber described above in 6-1-2, Ea values of the same samples were obtained.

Ea was determined by the Ozawa's method [41], and Ea distribution, not overall, was observed in the process of thermal degradation as in the case of nondurable flame retardant finishes. Ea values at these three points were obtained to observe Ea change with the rise of temperature in each case, which was compared with that observed in the case of nondurable flame retardant cotton fiber.

1) Experimental

(a) Materials

(1) Fabric

The fabric used for this investigation was the same as that used for the investigation on thermal degradation behavior described in 2-2-2.

(2) Treating reagents

Treating reagents and additives were also the same as those described in 6-1-2.

(b) Methods

(1) Flame retardant finishes

The three kinds of durable flame retardant finishes, Pyrovatex finish, Proban finish and THPS heat cure finish, were carried out by the methods mentioned also in 6-1-2.

(2) Determination of flame retardance

Flame retardance of each sample was evaluated by LOI method as described in the previous section.

(3) Determination of Ea

Ea was determined according to the Ozawa's method [41] for each sample as mentioned in the previous section 6-1-3.

2) Results and Discussion

(a) Ea distribution in the process of thermal degradation

Ea for the thermal degradation is important as one of the kinetic parameters for the thermal degradation reaction. Also in this case, Ea distribution changing with the progress of thermal degradation was observed since the overall Ea value seems to be less significant. The residual ratios at various stage of thermal degradation were plotted against correspondent Ea values for all treated samples in comparison with those of unfinished sample as shown in Fig. 6-18. An obvious difference is found between Proban-finished samples and other two thermo-fixed samples, i. e., Proban-finished samples required higher Ea throughout the thermal degradation process, particularly the samples treated with THPS precondensate alone (Pb2, Pb3) showed steep rise of Ea curves after ammonia cure which implicates a rapid reaction of thermal decomposition requiring high Ea within the initial short stage of thermal degradation reaction. In the case of Proban finish, the flame retardation mechanism is that Proban polymer is converted to phosphorus pentoxide by heat which strongly dehydrates cotton fiber to convert it to carbon by changing itself to polyphosphoric acid. Once carbon is formed effectively with the simultaneous formation of polyphosphoric acid, the thermal reaction turns gradual followed by leveling off requiring 300kJ/mol or higher Ea. But addition of a nonionic surfactant brought Ea down to that of unfinished sample. This is supposedly due to that since the nonionic surfactant is a strong penetrant, THPS precondensate permeated much more deeply into the fiber structure to get closer contact with fiber, which results in approaching to the degradation of fiber itself showing a considerable access to Ea curve of unfinished cotton fiber. Whereas sample without ammonia cure exhibited a different behavior showing a peak. Since THPS precondensate, dimer, is easily decomposable, the sample treated with this compound requires only lower Ea for degradation before ammonia cure and at the completion of degradation of this dimer, it approaches to Ea curve of cotton fiber itself.

In the case of samples treated with THPS monomer followed by thermo-fixation, samples with LOI values of < 28% containing TEA (Ts1 , Ts2) showed unusually high Ea values around 250kJ/mol even at the initial stage of the thermal degradation and a little change in Ea throughout the degradation process, though higher Ea was required in the presence of urea as shown by Ts2. On the other hand, samples with LOI values > 28% (Ts3, Ts4) gave normal Ea curves ascending in the initial stage and leveling off later. In this case, samples treated with THPS monomer and additives, TEA (pH adjuster), aminomethylpropanol (catalyst) and M3, resin for cross linkage with cellulose by thermo-fixation, required fairly lower Ea compared with untreated cotton fiber throughout the degradation process, which means that addition of the catalyst probably facilitated the thermal degradation to reduce Ea for decomposition. This can be one of merits of this flame retardant finish. But further addition of urea to this mixture (Ts4) extremely raised Ea as observed in the case of Ts2 which suggests that nitrogen donor, urea, decomposes separately requiring extra Ea.

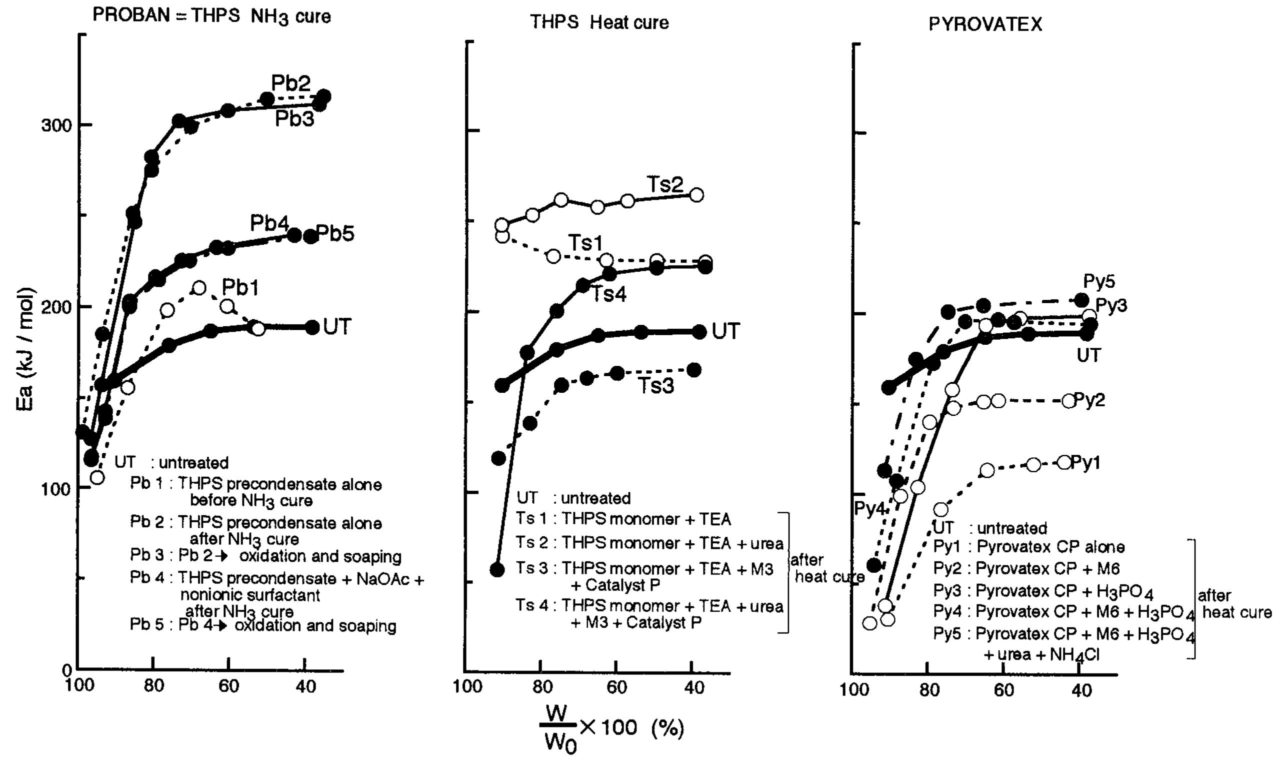


Fig. 6-18 Ea vs residual ratio curves to demonstrate Ea distribution in the process of thermal degradation for samples treated with the three types of durable flame retardants.

In contrast with Proban finish, Pyrovatex-finished sample gave Ea curves with gentle slops which implicates a gradual thermal reaction. Such phenomenon is coincident with the tendency observed in TG curves shown above. In addition, Ea curves showed characteristic change with additives, i. e., Pyrovatex CP alone or together with a resin required lower Ea, especially in the case of sample treated with Pyrovatex alone without flame retardance (Py 1) gave an extremely low Ea curve only about 1/2 that of a flame retardant sample (Py 5) and addition of M6 (Py 2) showed some rise by 26-27%. Another addition of phosphoric acid exhibited much more rise by 90% (Py3). LOI values of these samples are all below 28%. But addition of both resin and phosphoric acid (Py 4, Py 5) gave the flame retardance showing LOI values > 28%, Ea level of which is a little higher than that of unfinished sample showing the same level as that of Py3 after leveling off. Addition of urea showed a little higher curve also as in the case of THPS heat cure.

(b) Relationship between LOI and Ea values at TDOP, FP and MDRP

Finally, Ea values at TDOP, FP and MDRP vs LOI values are shown in Fig. 6-19 to see if another characteristic difference can be found between flame retardant samples with LOI value > 28% and those with LOI values < 28%. The flame retardant samples (closed marks) showed higher Ea values at all three temperature than those of the flammable samples (open marks) with LOI values < 28% in the case of Pyrovatex finish, whereas THPS thermo-fixed samples showed just a contrary result, i. e., the samples with LOI values < 28% required higher Ea. This result seems to reveal the fact that since the flame retardant molecules are much more efficiently fixed to cotton fiber for higher flame retardance in the case of flame retardant samples, the thermal degradation reaction of flame retardant sample is much influenced by cotton fiber itself, which results in changing Ea to approach to Ea of untreated sample. In the case of Proban finish, Ea values at TDOP and at FP are lower and those at MDRP become higher after ammonia cure when compared with those observed before curing, but plots locate in a Ea range the same as that of untreated sample though scattering over a wider range. Such tendency can be also expressed by another illustration as shown in Fig. 6-20, which shows Ea values at TDOP, FP or MDRP observed for Proban, THPS monomer and Pyrovatex-finished samples in comparison with those of untreated sample. Solid marks indicate Ea values of samples with LOI values > 28% and open marks those of samples with LOI < 28%. The overall tendency is that in the cases of thermo-fixed THPS monomer and Pyrovatex-finished samples, Ea values of samples with LOI < 28% are considerably higher (THPS) or lower (Pyrovatex) than those of untreated sample but Ea values of flame retardant samples with LOI > 28% get closer to those of untreated sample as indicated by solid marks. On the other hand, Proban-finished samples show such different tendency that Ea values of all flame retardant samples fall into the vicinity of those of untreated sample, e. g., locality of Ea at FP for flame retardant samples is almost the same as that of untreated sample though Ea values of TDOP are lower and those of MDRP are higher than that of untreated sample.

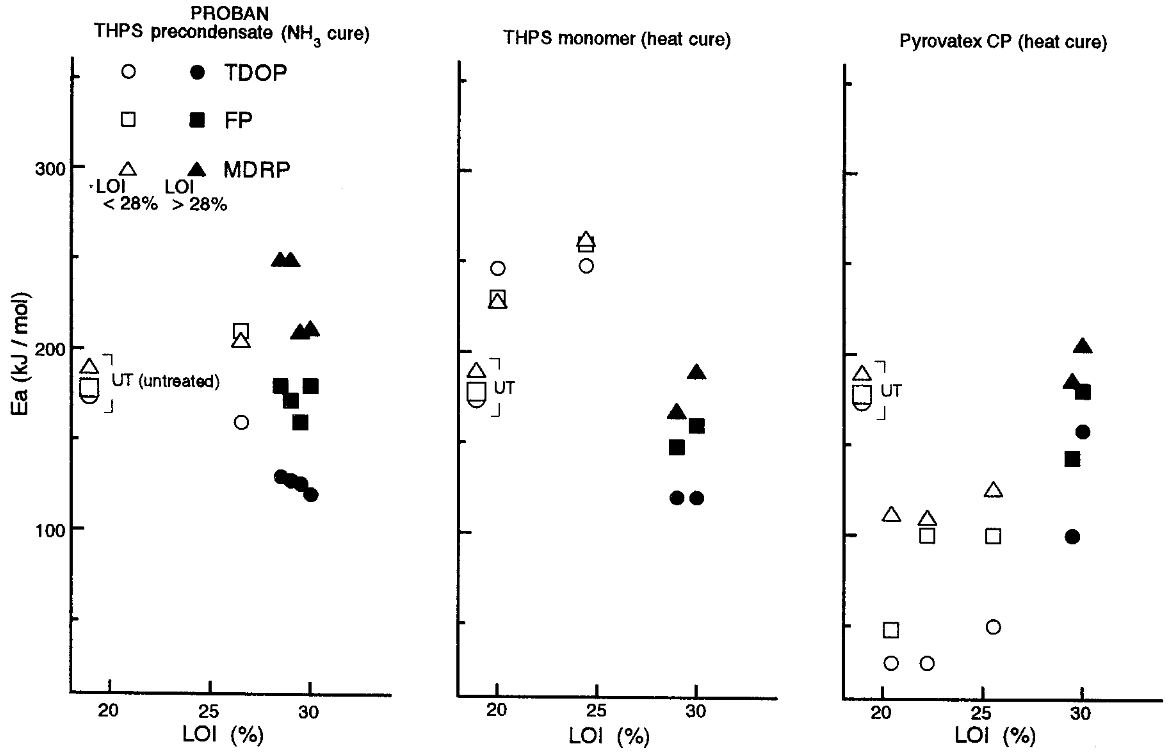


Fig. 6-19 Relationship between LOI values and Ea showing difference between samples with and without flame retardance and that among the three types of finishes.

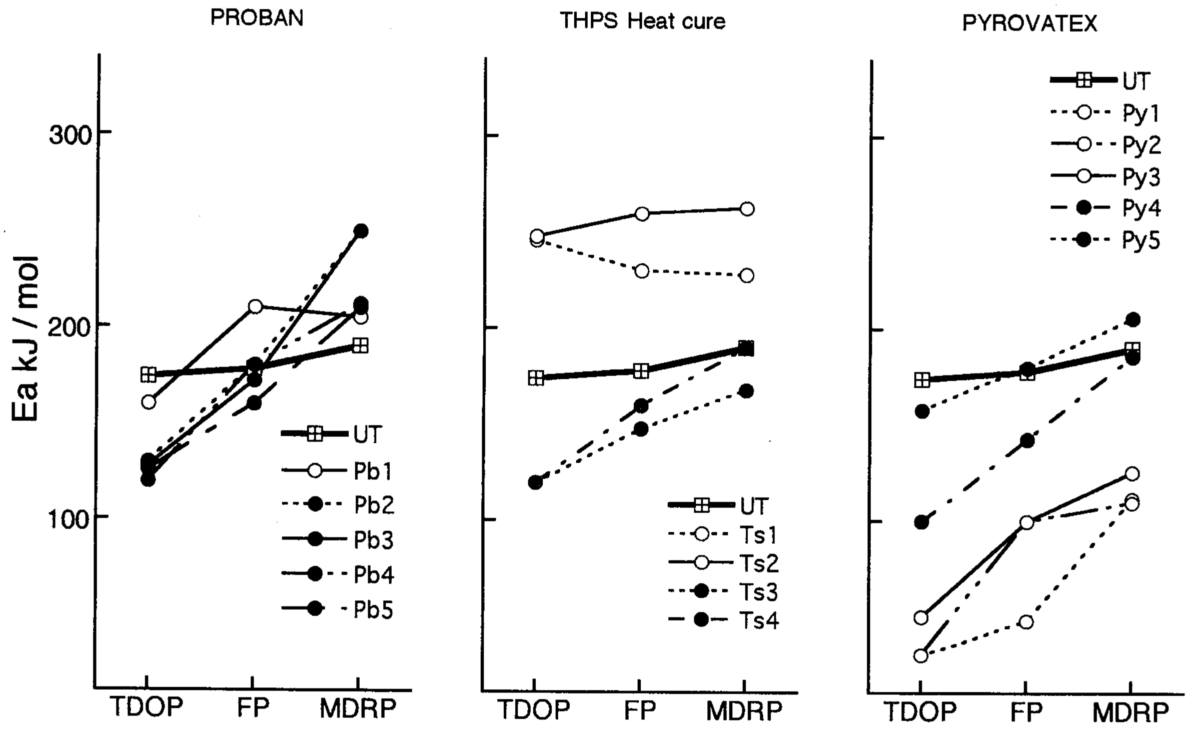


Fig. 6-20 Ea at TDOP, FP and MDRP for comparison of Ea region between samples with and without flame retardance showing difference among the types of finishes.

3) Conclusion

Ea vs residual ratios curves showed that Proban-finished samples are located in the highest region and Pyrovatex-treated samples at the lowest position. Comparing the slopes of these curves, Provatex-treated samples show the slowest curves and the other two exhibit steeper curves. The above results suggest that Pyrovatex polymer thermally decomposes gradually with comparatively lower Ea, whereas THPS polymer more rapidly requiring higher Ea, particularly Ea for the thermal decomposition of ammonia cured Proban polymer is the highest.

6-1-5 Structural Modification of Cotton Fiber in Connection with Thermal Degradation Behavior Observed by Infrared Absorption Spectroscopy

As a part of a series of studies concerning flame retardation of flammable fibers, the previous studies described in 6-1 were dealt with the thermal degradation observed with proceeding of thermal degradation of cellulose.

The next attention was subsequently paid to how the structures of these fibers would change with proceeding of thermal degradation, e.g., at the thermal degradation onset point, flash point and the maximum degradation rate point and the final point (500°C for cellulose, 600°C for PET) which was further extended to effects of flame retardant finishes on the structural changes mentioned above as well as to how such structural changes would be reflected on infrared (IR) absorption spectra.

As for the IR absorption spectral analysis for the recognition of molecular structures of organic substances, the contribution of a series of studies by Shimanouchi et al. has been world wide [62-100].

The authors have attempted to apply the IR absorption spectral observation to textile fibers for practical use and obtained significant and advantageous results [101-103].

1) Experimental

(a) Materials

Sample fabric was 100% cotton the same as used for the previous studies.

As nondurable flame retardants, ammonium and sodium salts of P, S and Br as well as boric acid and borax were used with urea as listed in Table 6-4. On the other hand, THPS precondensate for ammonia cure for PROBAN finish and Pyrovatex CP and additives for Pyrovatex finish were used as durable flame retardant finishes shown also in Table 6-4.

(b) Methods

(1) Flame retardant finishes

Each flame retardant finish was carried out as described in 3-1

(2) Evaluation of flame retardance

Flame retardance of each sample was evaluated by LOI method described in 2-1-2.

(3) Thermal analysis

Thermogravimetric observation and determinations of TDOP, MDRP and FP were performed as described in 6-1.

Table 6-4 List of compounds used to treat cotton fabric for IR absorption spectral observations.

		Compounds used for treatment	
	1	Unfinished cotton	
Nondurable	2	NH2CONH2	20%
	3	Na2HPO4 · 12H2O	20%
	4	(NH4)2HPO4	5%
	5	(NH4)2HPO4	20%
	6	Na2SO4	20%
	7	(NH4)2SO4	20%
	8	NH4SO3NH2	5%
	9	NH4SO3NH2	20%
	10	NaBr	20%
	11	NH4Br	20%
	12	H3BO3 + Na2B4O7	5%
	13	H3BO3 + Na2B4O7	20%
Durable	14	THPS-urea precondensate (before Ammonia cure)	40%
	15	THPS precondensate (after Ammonia cure)	40%
	16	Pyrovatex CP	32%
	17	Pyrovatex CP +	32%
		Hexamethylolmelamine (M6) +	8%
		H3PO4	2%

(4) IR absorption spectral observation

IR absorption spectrum of each sample was observed by using a FTIR absorption spectrophotometer Perkin Elmer Type 1800 (Perkin Elmer Co.) under the following conditions;

Mode: DTGS

Range of wavelength: 4000-400cm^{-1}

Number of scanning: 100 times

N_2 was used for purging

Heating was stopped at each point of TDOP, FP, MDRP and 500°C respectively, and each residue was subjected to IR absorption spectral observations.

Each sample was cut with scissors into powdery pieces, and chared portion of any residue was pulverized in a mortar.

Each sample was mixed with moisture-free KBr (about 80 mg) fine powder uniformly and pressed into a pellet by using Barnes QWIK Handi-Press and set on a holder for the spectroscopic observation.

2) Results and Discussion

(a) Evaluation of flame retardance

Flame retardance of each sample, untreated and treated sample was evaluated by LOI method. Samples treated with 20% solutions of compounds containing N, P, S or Br alone such as urea, Na_2HPO_4, Na_2SO_4 or NaBr showed LOI values lower than the critical level of flame retardance 27-28%, whereas those treated with compounds containing both N and P, S or Br such as $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$, $NH_4SO_3NH_2$ and NH_4Br gave LOI values higher than 27-28% showing flame retardant samples, but samples treated with 5% solutions of the same compounds failed to possess flame retardance even though treated with compounds containing 2 elements because of insufficient add-on of these flame retardant element. Furthermore, boric acid and borax gave LOI value higher than the critical level only with 20% solution but 5% solution did not reach the critical level by the same reason. As to durable flame retardant finished, PROBAN finish without ammonia cure and Pyrovatex alone failed to give flame retardance, whereas PROBAN finish after ammonia cure and Pyrovatex CP with additives, resin and H_3PO_4 succeeded to give flame retardance.

(b) Decision of TDOP. MDRP and FP

TDOP, MDRP and FP of each sample determined as described in 6-1 are shown in Table 6-1 and 6-3. Samples treated with compounds containing single element, each of N, P and S, i. e., urea,

Na_2HPO_4 and Na_2SO_4, and boric acid and borax showed these 3 points comparatively close to those of unfinished cotton sample higher than 300°C . In contrast, samples treated with compounds containing P, S and Br in combination with N, i.e., $(NH_4)_2HPO_4$, $(NH_4)_2SO_4$ and NH_4Br, exhibit much lower temperatures, especially NH_4Br showed the lowest temperatures. Comparison of 2 kinds of durable flame retardant finished samples disclosed that Pyrovatex finished samples gave much higher temperatures than PROBAN finished samples. When PROBAN finished samples are compared between before and after ammonia cure, TDOP and MDRP are considerably elevated after ammonia cure though FP shows little difference.

Another attention was paid to how late samples are ignited after onset of thermal degradation. Untreated sample and those treated with compounds containing N, P alone ignited immediately after TDOP, whereas those treated with compounds containing P and S in combination with N as well as containing Br or B ignited significantly behind TDOP, particularly $(NH_4)_2SO_4$ and Br salts gave large retardation. Such results well agreed with flame retardance, i. e., flammable samples showed a little difference between TDOP and FP, whereas flame retardant sample showed significantly retarded ignition, which confirmed effects of flame retardant finishes.

Structural change in each sample with proceeding of thermal degradation was observed on the bases of these transitional temperatures through IR absorption spectral observation.

(c) IR absorption spectral observations

Each sample heated upto above mentioned TDOP, MDRP, FP and end point 500°C respectively was subjected to the IR absorption spectral observation as described above.

Absorption spectral changes with rising temperature are shown in Fig. 6-21~6-32.

(1) Untreated cotton cellulose

Fig. 6-21 exhibits IR absorption spectral changes of untreated cotton cellulose, which showed little change after heating upto TDOP (348.6°C) except that absorbance at $1700cm^{-1}$ (1710 ± 15 cm^{-1}) assigned to carbonyl group, C=O stretching vibration, enhanced disclosing that the structure of cellulose is not damaged at TDOP. This peak kept increasing upto MDRP and little change was shown after ignition at FP, but considerably decrease was observed at 500°C . On the other hand, cellulose typical absorption at $2950cm^{-1}$ due to C-H stretching, a large band at $3400cm^{-1}$ assigned to O-H stretching, several small peaks in a range from 1450 to $1200cm^{-1}$ due to -CH-bending vibration and those in a range from 800 to $400cm^{-1}$ probably due to out-of-plane bending of -OH showed considerable reduction at MDRP (375.6°C) during 27°C rise of temperature but maintaining absorption bands undamaged in a range of 1200-1000cm^{-1} assigned to C-O stretching and -OH bending of secondary alcohol as well as to -OH stretching. But these bands due to stretching and bending of hydrocarbons typical of the structure of cellulose all disappeared at FP (353.0°C) simultaneously with ignition and also at end point 500°C leaving 2 peaks at 1700cm^{-1} for carbonyl group and at 1600cm^{-1} due to in-plane skeletal vibration of a benzene derivative as a char precursor, and another broad trace of absorption at 1200cm^{-1} assigned to C-H in-plane bending of a benzene like ring with conjugated double bonds also as a precursor of char.

(2) Cotton cellulose treated with urea

As shown in Fig. 9-22, untreated and urea-treated samples showed strong absorption bands at 1670cm^{-1} and 1620cm^{-1} due to C=O stretching of amine II of primary acid amide, -CONH$_2$ and amine I of secondary acid amide -CONH- respectively, from urea itself, but these peaks were reduced at TDOP (343.7°C) showing a spectrum similar to that of untreated sample shown above maintaining peaks at 2950cm^{-1} and 1430-1200cm^{-1} unchanged, which interpreted that the skeletal structure of cellulose remained undamaged at this temperature where the thermal degradation just started but urea considerably decomposed at this point producing NH$_3$, CO or CO$_2$. Spectra observed at MDRP (372.9°C), FP (350.0°C) and 500°C were all very similar to those obtained in the case of untreated cotton sample shown above.

(3) Sample treated with Na$_2$HPO$_4$

As shown in Fig. 6-23, Na$_2$HPO$_4$-treated sample showed a tendency of change in spectrum similar to that of unfinished or urea-finished cotton though each temperature of TDOP, MDRP and FP is 30-40°C lower than that of unfinished samples except that residue obtained after heating upto FP and 500°C showed spectra with peaks at 1140, 930 and 560cm^{-1} probably due to -P- stretching in phosphoric compounds strongly influenced by treating reagent Na$_2$HPO$_4$, possibly heat resistant compound, remaining after cellulosic component was converted to char.

(4) Sample treated with (NH$_4$)$_2$HPO$_4$

Absorption spectrum of sample treated with 20% solution of (NH$_4$)$_2$HPO$_4$ is shown in Fig. 6-24 but that of sample treated with 5% solution was omitted. This compound gives flame retardance to cellulosic product because of the synergistic effect of N and P, but it has been found by our study that insufficient add-on, e. g., when treated with 5% solution, fails to contribute to flame retardation. Therefore, highly flame retardant sample with sufficient add-on LOI value of which is extremely high, 43.3% and flammable sample with insufficient add-on were used to see if there might be any difference in structural change between these two with and without flame retardance.

Comparison between spectrum of each unheated sample showed that spectrum of 5%-treated flammable sample was almost identical with that of untreated sample, whereas 20%-treated flame retardant sample was significantly influenced by a sharp band with strong intensity at around 1400cm^{-1} assigned to N-H stretching vibration of ammonium ion, NH_4^+. At TDOP. 5%-treated sample showed an almost similar change with appearance of peak at 1700cm^{-1} as observed with the above mentioned samples, whereas 20%-treated sample showed no apparent peak at 1700cm^{-1} which means that any carbonyl group had not been produced at TDOP (240.8°C) in this sample suggesting that 240°C might be too low to produce carbonyl group, no wonder 5%-treated sample showed a peak at 1700cm^{-1} at TDOP which is 267.0°C higher than that of 20%-treated sample by about 27°C . Both samples were not ignited before MDRP unlike the above 3 samples. At MDRP, 5%-treated sample exhibited a considerably different behavior compared with those shown above, i.e., absorption bands in a range of 1500cm^{-1} or lower frequencies almost disappeared at 290°C unlike unfinished and above mentioned finished samples MDRP of which are much higher, e. g., 344.1°C or even 375.6°C for unfinished cotton. On the other hand, 20%-treated sample showed a peak of carbonyl group at MDRP, 254.5°C , this time, but in contrast to 5%-treated sample, many small peaks observed in a range of 1450-400cm^{-1} still remained at this temperature. At further higher temperatures, FP and 500°C , 5%-treated sample gave spectra very similar to those of untreated and finished samples mentioned above with clear peaks at 1700, 1600 and 1200cm^{-1} assigned to carbonyl group and C=C stretching of conjugated double bonds as well as to C-H in-plane bending vibration of ring with conjugated double bonding as a precursor of char product respectively as mentioned above. However, 20%-treated sample left another clear peak at 1000cm^{-1} at FP (284.0°C) probably assigned to C-H out-of-plane bending of CH_2=CH-, terminal vinyl group. Another typical difference in spectrum of this sample heated up to 500°C is almost flat showing that this residue was entirely charred. Such phenomenon that cellulosic sample with sufficient add-on of $(NH_4)_2HPO_4$ is much more easily charred compared with other samples, i. e., $(NH_4)_2HPO_4$ facilitates charing cellulosic materials.

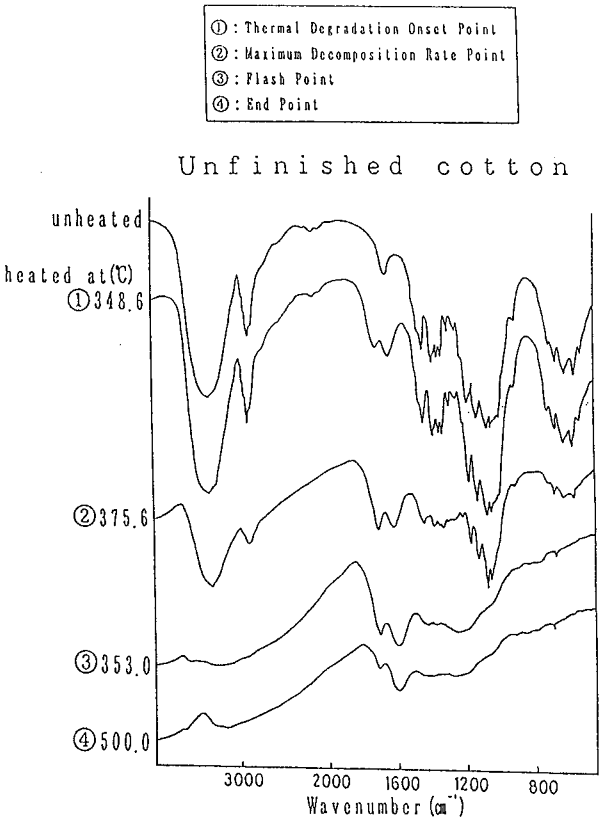


Fig. 6-21 Change in IR absorption spectrum of untreated cotton fiber observed with proceeding of thermal degradation.

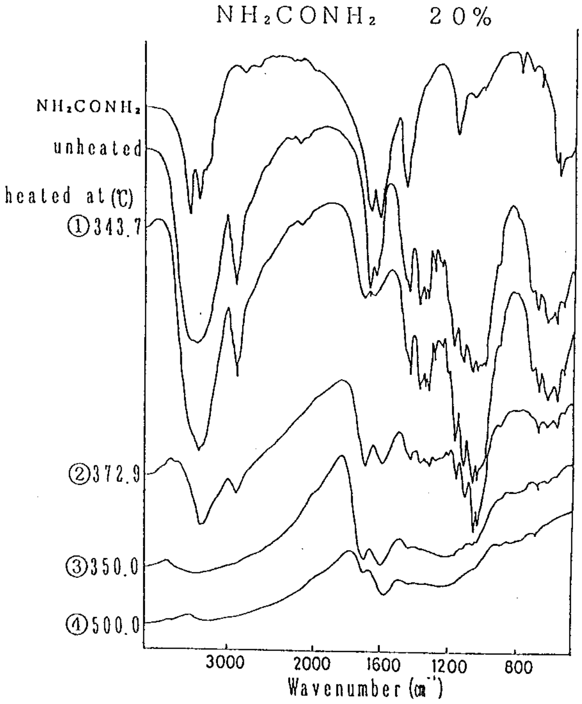


Fig. 6-22 IR spectral change in cotton fiber treated with urea.

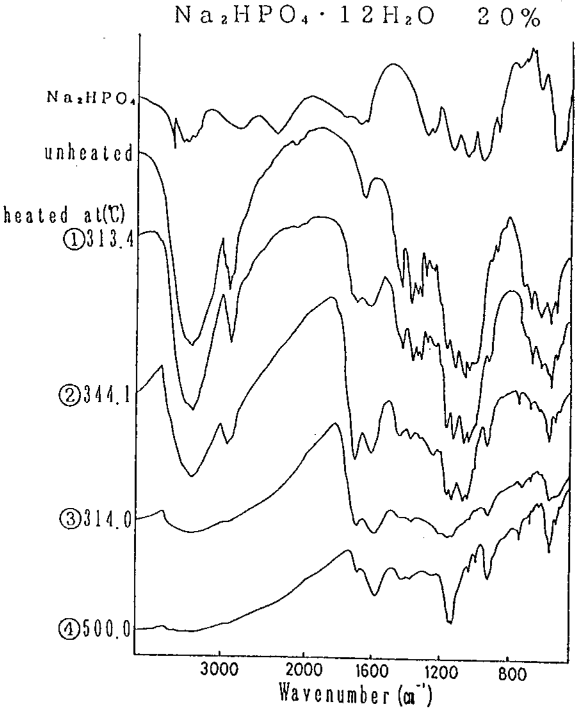


Fig. 6-23 IR spectral change in cotton fiber treated with 20% of Na_2HPO_4.

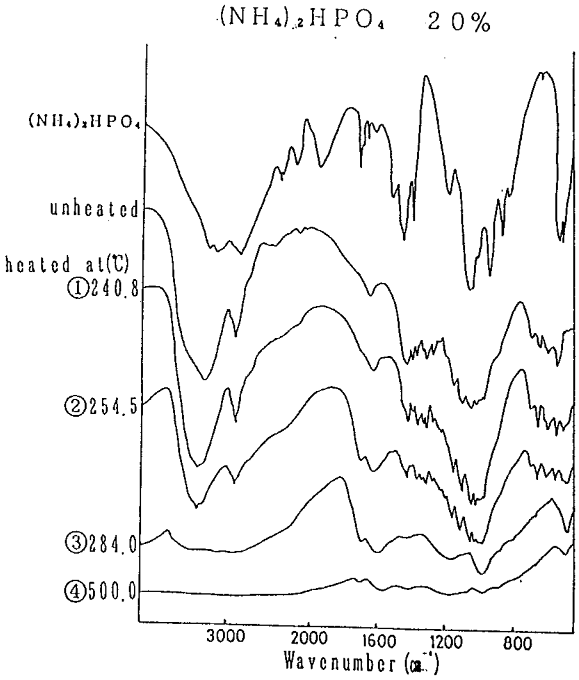


Fig. 6-24 IR spectral change in cotton fiber treated with 20% of $(NH_4)_2HPO_4$.

(5) Sample treated with Na_2SO_4

Spectra of Na_2SO_4-treated cotton cellulose are all strongly influenced by absorption at 620cm^{-1} due to S-O stretching of sulfate, but change in spectrum with temperature rise was similar to that of unfinished sample, which is reasonable since this sample is flammable with LOI value as low as that of untreated sample. Therefore, figure is not shown for this sample.

(6) Sample treated with $(NH_4)_2SO_4$

This treating reagent showed 4 large peaks, at 3200cm^{-1} for N-H stretching of ammonium ion NH_4^+, at 1400cm^{-1} for S=O stretching of neutral sulfuric ester $-O-SO_2-O-$, at 1105 and 620cm^{-1} due to inorganic sulfate ion, SO_4^{2-}, which gave an influence to the spectrum of cellulose similar to that observed with sample treated with 20% $(NH_4)_2HPO_4$ shown above except for effects of SO_4^{2-} ion at 1105 and 620cm^{-1} (Fig. 6-25). At TDOP, absorption at 1700cm^{-1} showed a little increase appearing as a shoulder, not peak, probably because TDOP of this sample is lower (242.2°C) though a little higher than that of 20% $(NH_4)_2HPO_4$-treated sample which did not show any increase at this point. It seemed that the essential spectrum of cellulose skeletal structure was not damaged at this stage also in this case. During 10°C rise of temperature, absorption due to carbonyl group showed further increase at MDRP (251.8°C), whereas a peak at 2950cm^{-1} and small peaks in a range from 1400 to 1300cm^{-1} decreased showing cleavage of the structure of cellulose to some extent. Ignition of this sample at FP was occurred at 336.0°C , 100°C higher than MDRP, broad spectrum with traces of a few absorption at 1700, 1600 and 1200cm^{-1} similar to that of 5% $(NH_4)_2HPO_4$-treated sample except for less absorption at 1700 and 1200cm^{-1} and also a trace of S=O stretching at 800cm^{-1}. Spectrum obtained after heating up to 500°C was also very alike to that obtained at FP showing little change during a rise of temperature from 336-500°C . When compared with Na_2SO_4-treated sample containing with S alone without flame retardance, this sample containing both N and S with high LOI value showed that thermal degradation and charing were initiated in earlier stages at lower temperatures as observed with 20% $(NH_4)_2HPO_4$-treated sample highly flame retardant with the highest LOI value.

(7) Sample treated with $NH_4SO_3NH_2$

$NH_4SO_3NH_2$ has 6-7 sharp peaks assigned to acid amide, ammonium ion, sulfamic acid, sulfonyl group etc., but those which apparently influenced the absorption spectrum of cellulose were peaks at 1410, 1260 and 1210 and also at 800cm^{-1} only in the case of 20%-treated samples due to ammonium ion, -NH_2 bending vibration of amide II of secondary acid amide, S=O stretching of sulfonyl group and CH_2-NH_2 respectively. Since there was no way to assign a peak at 800cm^{-1} to absorption of CH_2-NH_2, CH_2 of fiber structure was supposed to bind with NH_2 of $NH_4SO_3NH_2$. As shown in Fig.6-26, 20%-treated sample exhibited a very typical change which had never shown by other samples shown above, i. e., spectrum observed after heating up to TDOP already revealed much deformed shape at 241°C with disappearance of peaks due to the structure of cellulose which was maintained even at FP showing broad peaks at 1600, 1410, 1210, 1030, 800 and 600cm^{-1} the assignment of which were described above except for a peak at 1030cm^{-1} due to S=O stretching of -SO_3H overlapped with a large absorption of cellulose in unheated sample and disclosed after disruption of the structure of cellulose. Thus, 20% $NH_4SO_3NH_2$-treated sample with sufficient flame retardance was charred in the earlier stage of the thermal degradation compared with the case of 20% $(NH_4)_2HPO_4$-treated sample with the highest flame retardance among samples used for this study, which suggests that $NH_4SO_3NH_2$ might act as a kind of catalyst for the thermal degradation and char formation.

(8) Sample treated with NaBr

As this treating reagent NaBr shows no typical absorption from 4000 to 400cm^{-1}, spectrum of sample treated with this compound without flame retardance was identical with that of unfinished sample, and spectral change with temperature rise was also similar to that of untreated sample except that a peak at 2950cm^{-1} typical of cellulose already decreased at TDOP though temperature is significantly lower than those of unfinished sample and also samples treated with other sodium salts. This is probably due to an effect of easily decomposable halide (figure is omitted).

(9) Sample treated with NH_4Br

In contrast to NaBr-treated sample, spectrum of unheated sample was significantly influenced by N-H stretching of NH_4^+ at around 3000 and 1400cm^{-1} and a typical band for C-H stretching of methylene bond at 2950cm^{-1} was almost overlapped to appear as a small peak (Fig. 6-27). As for the spectral change with proceeding of the thermal degradation, a similar tendency showing appearance and increase in a peak at 1700cm^{-1} and gradual decrease in a peak at 2950cm^{-1} was observed at TDOP and MDRP compared with that observed in the case of NaBr-treated sample though these temperatures of NH_4Br-treated sample are significantly lower than those of NaBr-treated sample by 70°C or more. Spectrum for residue after heating up to FP was similar but more flat with broad peak at 3300, 1700, 1600, 1400, 1200, 1000 and 800cm^{-1} all trace but peaks at 1700 and 1600cm^{-1} and became further flat at 500°C showing proceeding of char formation. Comparison of these curves to those of NaBr-finished sample, both are halide of sodium or ammonium, suggests that highly flame retardant ammonium halide is more decomposable and more easily chared at much lower temperature than sodium halide without flame retardance.

(10) Sample treated with H_3BO_3 and $Na_2B_4O_7$

H_3BO_3 and $Na_2B_4O_7$ showed complicated spectra with several large peaks, but little effect was given to the spectrum of cellulose except for small peaks at around 1600cm^{-1} from H_3BO_3 and at 820cm^{-1} from $Na_2B_4O_7$ observed with 20%-treated sample (Fig.6-28) but not with 5%-treated sample. Spectra of both 5%-treated and 20%-treated samples observed at TDOP were unchanged also in this case except for appearance of carbonyl group at 1700cm^{-1}, and those observed at MDRP showed decrease in every peak from the structure of cellulose but increase in peaks not only at 1700cm^{-1} from carbonyl group as observed in other cases but also at 3300-3400 and 1060cm^{-1} due to the absorption of both treating reagents, which can be explained that these absorption were overlapped by strong absorption of cellulose itself but disclosed by the cleavage of cellulose. At FP, a peak at 1600cm^{-1} due to the above mentioned char precursor increased, but all other peaks reduced and diminished to trace but that at 1700cm^{-1} from char precursor. Comparison between 5%-treated sample without flame retardance and highly flame retardant 20%-treated sample led us to conclude that there would not be much difference between thermal degradation behavior of both samples except that trace of peaks due to H_3BO_3 and $Na_2B_4O_7$ remained more clearly in 20%-treated sample because of larger amount of add-on. Such phenomenon is different from what was observed by, comparing other flame retardant finished samples treated with 5% and 20% solutions of reagents described above, which showed that flame retardant 20%-treated sample showed cleavage and char formation at much lower temperatures compared with behavior of 5%-treated samples without flame retardance. Such difference is probably attributed to the difference in the mechanism of flame retardation of H_3BO_3 and $Na_2B_4O_7$ which retard ignition by covering the surface of fibers with molten film of H_3BO_3 and $Na_2B_4O_7$ together with contribution of endothermic melting of these compounds simultaneously with evaporation of water of crystallization in $Na_2B_4O_7 \cdot 10H_2O$, in contrast to other cases which retard ignition by generating incombustible gases, e. g., NH_3, CO or CO_2, to dilute combustible gases, by blacking radicals with halogens, as well as by dehydrating from cellulose to accelerate char formation with P etc. to contribute to give self-extingushability to any flammable material.

(11) Sample finished with Pyrovatex CP alone

Being influenced by Pyrovatex CP, N-methylol dialkyl phosphonopropinamide, unheated Pyrovatex finished sample showed extra peaks at 1670cm^{-1} due to $-NH_2$ bending and C=O stretching by amide II of primary acid amide, $-CONH_2$, at 1550cm^{-1} from N-H bending by amide II of secondary acid amide -CONH- and at 830cm^{-1} due to absorption of aliphatic primary amine, $-CH_2NH_2$, and an ordinary peak for bound water of cellulose at 1640cm^{-1} was overlapped, which were all disappeared at TDOP showing a spectrum almost identical with that of unfinished sample except that increase in absorption by carbonyl group was larger showing undamaged cellulose itself. Spectral change at MDRP was also similar to that of unfinished sample with further increase in carbonyl group and reduction of intensities of specific absorption of cellulose itself. But spectra observed after heating up to FP and 500°C were considerably broadened and more flat (Fig. 6-29) compared not only with that of untreated sample but also with those of samples treated with nondurable treating reagents shown above, which suggests that durable flame retardant proceeds char formation more rapidly.

(12) Sample treated with Pyrovatex CP and additives {hexamethylolmelamine (M6) and H_3PO_4}

As shown in Fig. 6-30, unheated sample showed larger peaks at 1670, 1550 and 830cm^{-1} because of additional influence of a resin M6, which diminished at TDOP with apparent decrease in intensity of cellulose typical absorption at 2950cm^{-1} and appearance of a peak at 1700cm^{-1}, and spectrum for residue obtained after heating up to MDRP showed more disrupted structure of cellulose compared with that of sample treated with Pyrovatex alone. Spectra for residues obtained after heating up to FP and 500°C were identical with those of sample treated with Pyrovatex alone.

Comparison of spectra of samples between samples finished with and without additives suggested that flame retardant sample finished with additives with LOI value higher than 28% was decomposed more easily at lower temperature than flammable sample finished without additives with LOI value much lower than 28%.

(13) PROBAN finished sample

To observe effect of ammonia cure on PROBAN finished sample, spectral changes were observed before (Fig. 6-31) and after (Fig.6-32) ammonia cure. Unheated samples also showed peaks due to C=O stretching and N-H or $-NH_2$ bending of acid amides at 1670, 1550 and 820cm^{-1} as mentioned in the case of Pyrovatex finished sample. At TDOP, spectra of both samples showed none of spectral change in the structure of cellulose but a peak of carbonyl group appeared and the above 3 peaks still remained, and a peak at 1700cm^{-1} was larger and shaper after curing. At MDRP, reduction of intensity of absorption at 2950cm^{-1} and disruption of the structure of cellulose expressed by the deformation of spectrum in a range of 1450-1200cm^{-1} were observed in both cases to about the same extent. Thus, spectral changed at TDOP and MDRP were similar in both cases before and after ammonia cure even though temperatures are much higher when observed after ammonia cure, by more than 70°C for TDOP and 50°C for MDRP. However, spectra observed after FP shows much difference, i. e., broadened and flat spectrum similar to that of Pyrovatex finished sample was shown before curing, whereas ammonia cured sample gave a spectrum similar to that observed at MDRP exhibiting only a very slight decrease in each peak, which means that this sample quenched immediately after ignition showing a very favorable phenomenon from the safety. Spectra of both samples before and after curing were similar but more flat after curing when observed after heating up to 500°C , and these were identical with those of Pyrovatex finished samples showing favorable char formation.

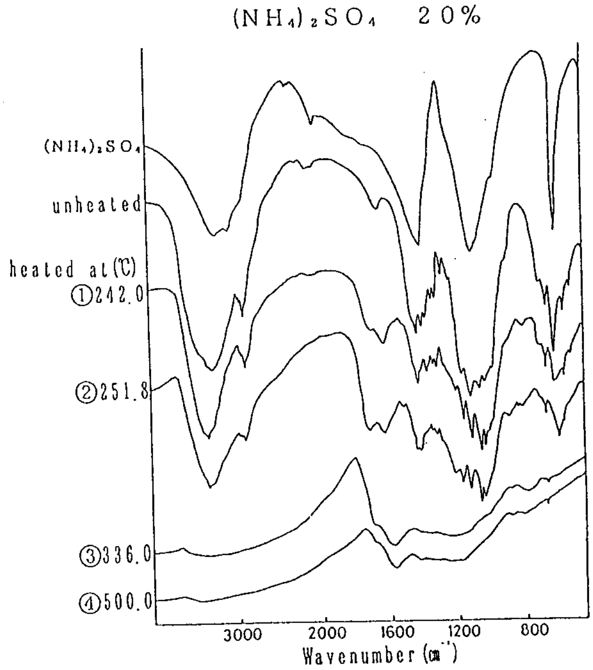


Fig. 6-25 IR spectral change in cotton fiber treated with 20% of $(NH_4)_2SO_4$.

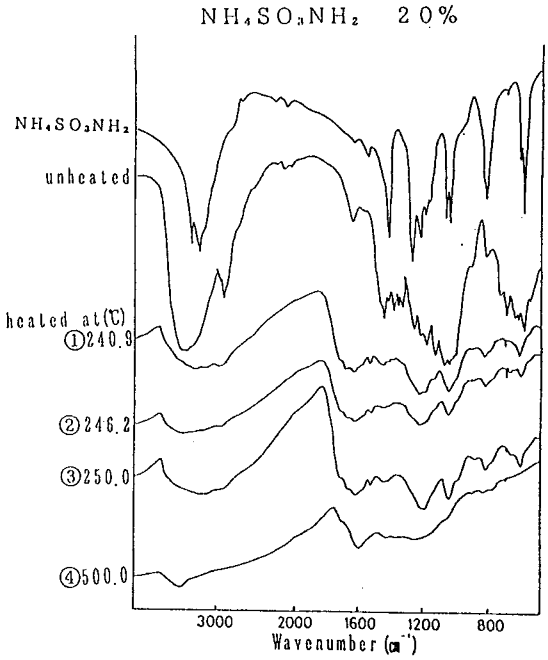


Fig. 6-26 IR spectral change in cotton fiber treated with 20% of $NH_4SO_3NH_2$.

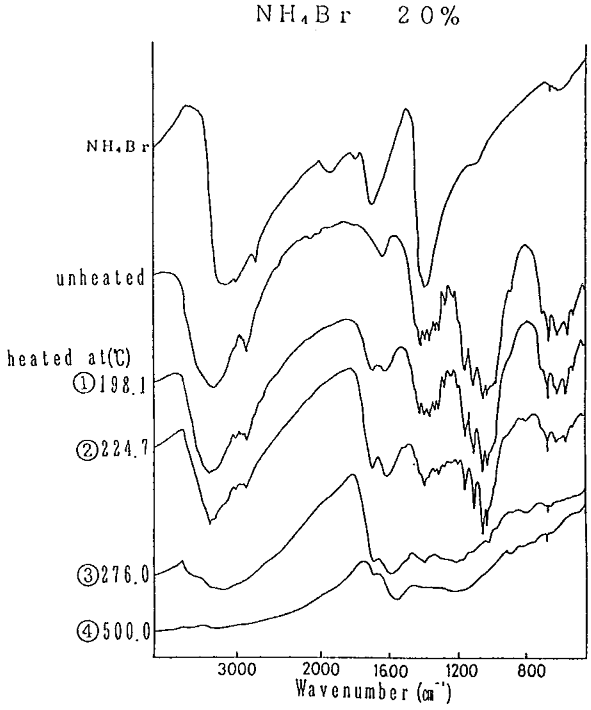


Fig. 6-27 IR spectral change in cotton fiber treated with 20% of NH_4Br.

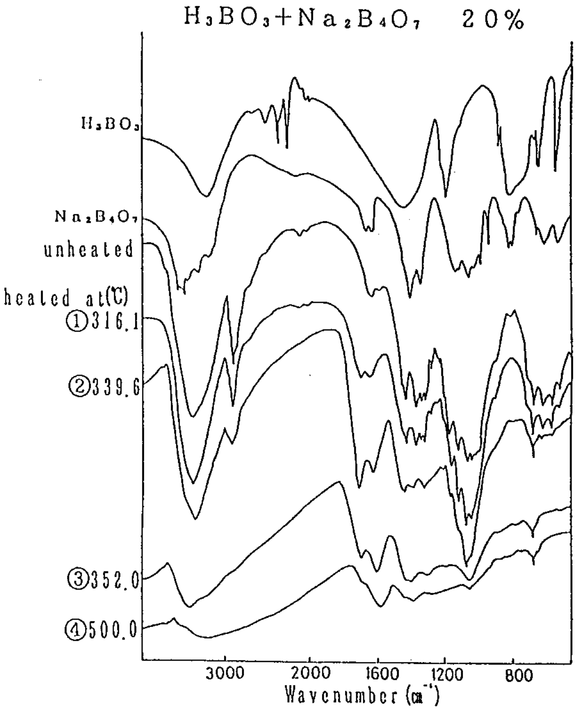


Fig. 6-28 IR spectral change in cotton fiber treated with 20% of H_3BO_3 and $Na_2B_4O_7$.

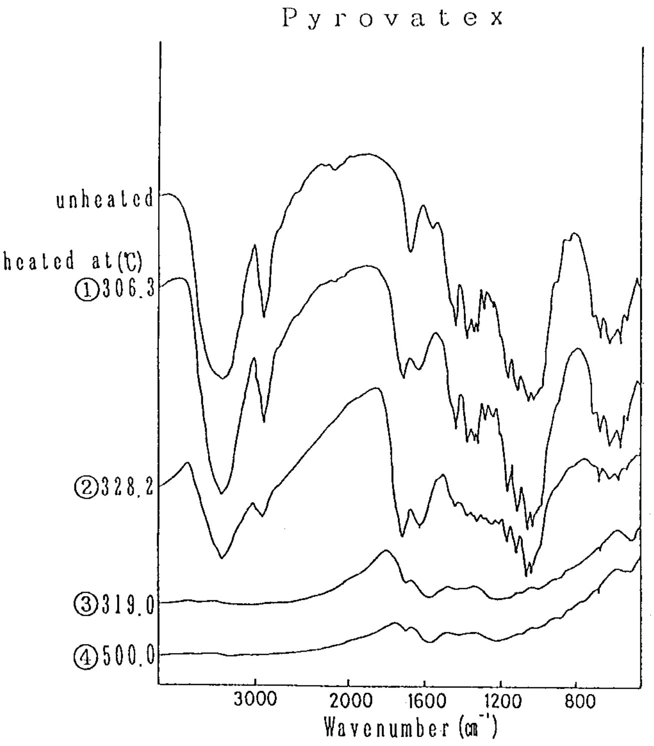


Fig. 6-29 IR spectral change in cotton fiber treated with Pyrovatex CP.

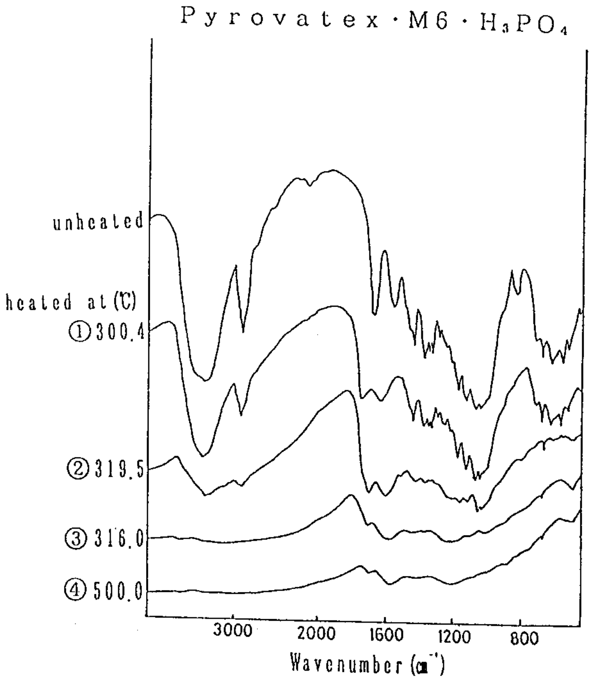


Fig. 6-30 IR spectral change in cotton fiber treated with Pyrovatex CP and additives.

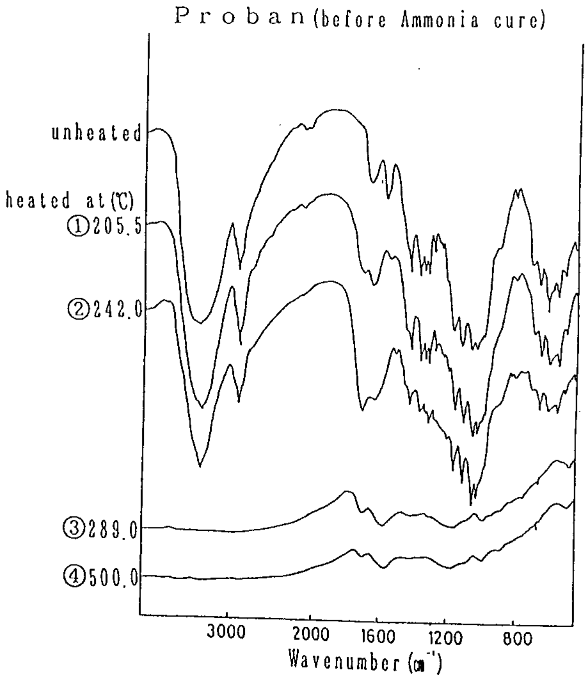


Fig. 6-31 IR spectral change in cotton fiber treated with THPS precondensate before ammonia cure.

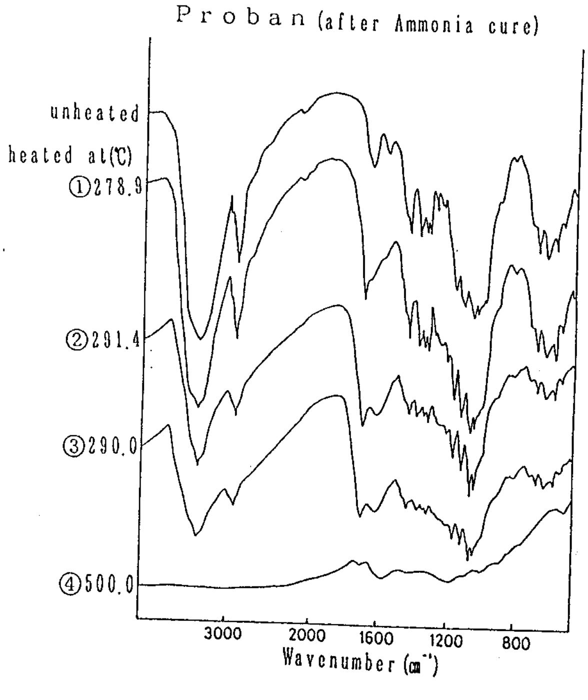


Fig. 6-32 IR spectral change in cotton fiber treated with THPS precondensate after ammonia cure (PROBAN finish).

3) Conclusion

Untreated cotton cellulose showed formation of carbonyl group already at TDOP but the structure of cellulose remained unchanged. Thermal treatment up to MDRP gave disruption of the structure of cellulose to some extent showing decrease in intensity of specific absorption of hydrocarbons. Ignition occurred immediately after TDOP, which gave almost complete disruption of the structure of cellulose leaving at 1700, 1600 and 1200cm^{-1} due to carbonyl group and C-H in-plane bending and skeletal vibration of benzene derivatives with conjugated double bonds as a char precursor. Thermal treatment up to 500°C also gave a spectrum similar to that obtained at FP.

Samples treated with urea or sodium salts containing a single element, N, P, S or Br gave IR absorption spectra and changing behavior with the proceeding of thermal degradation similar to those observed with untreated sample except that some treating reagents kept their specific absorption peaks up to 500°C . On the other hand, flame retardant samples treated with 20% solutions of ammonium salts containing P, S or Br in combination with N so as to hold sufficient add-on gave spectral changes at lower temperatures, which disclosed that the thermal degradation would be initiated in much earlier stage at lower temperatures to reach char formation much easily and effectively.

Boric acid and borax showed different behavior locating in flammable zone in spite of having high flame retardance, which is attributed to the flame retardation mechanism different from that for other flame retardant samples treated with ammonium salts etc. as shown above.

The overall conclusion is that the results obtained by the studies on thermal degradation behavior described in Chapter 6 was supported and confirmed by, and reflected on the results of IR absorption spectral observations attempted this time.

6-1-6 Thermal Degradation Behavior of PET Fiber and Effect of Flame Retardant Finishes

This section deals with thermal degradation behavior of PET to be described in connection with observation for thermal degradation of cellulosic fiber described in the previous section.

Since PET fiber is most widely used throughout the world, the flame retardation of this fiber is indispensable for the safety of the human life.

Therefore, we have carried out investigations for flame retardant finishes as well as for related studies from the fundamental and practical standpoints, which have been described in Chapter 3.

Thermal analytical observations were performed by using samples prepared according to the processes described in the above Chapter 3.

Attention was also paid to effects of Br and P on the thermal degradation behavior since Br and P are recognized to be effective for the flame retardation of PET.

It has been coincidentally believed that Br acts in the vapor phase by trapping free radicals OH • and H • considered to be responsible for the propagation of the flame as proposed by, for example, Rosser[4,21].

On the other hand, two contradictory opinions have competed by using different kinds of phosphorus based flame retardants, one of which has been supported for so long a time by that the activity of P was performed predominantly in the condensed phase as observed for most phosphorus containing additives[27,28,104]. The other one is based on the results obtained later from PET fibers containing triphenylphosphine oxide which indicate that phosphorus compounds are active in the vapor phase[61].

Therefore, the present study is focused on the thermal analytical observations to obtain some approaches to performances of Br and P on PET fabrics, if possible, to decide whether Br and P act in the solid-phase or in the vapor phase.

1) Experimental

(a)Materials

PET fabric was the same as that used for the investigation described in 3-2-3.

Treating reagents used this time were hexabromocycrododecane (HBCD), diphenyl ethyl phosphate (DPEP), diphenyl methyl phosphate (DPMP) and triphenyl phosphate (TPPA), and acetone as a solvent for these reagents.

(b) Methods

(1) Preparation of DPEP and DPMP

DPEP and DPMP were prepared as described in 3-2

(2) Treating method

Acetone solutions of 10% of HBCD, 40% of TPPA, 34% of DPEP, 32% of DPMP, mixtures of different ratios of HBCD and TPPA, (10% HBCD + 2.1% DPEP) and (10% HBCD + 2% DPMP) were prepared and PET fabric was treated as mentioned in 3-2

(3) Thermogravimetric analysis (TGA)

TG curve was obtained for each sample as described in 6-1-1.

TDOP, MDRP and FP were determined as described also in 6-1-1,

(4) Evaluation of flame retardance (LOI)

LOI value for each sample was evaluated by LOI method for PET described in 3-2-1

(5) Quantitative determination of Br

Br was quantitatively determined by the combustion at high pressure using Parr1108 Oxygen Combustion Bomb followed by Vorbards reverse titration method as mentioned in 3-2.

(6) Quantitative determination of P

P content in each sample was analyzed by the method described in 3-1-1.

2) Results and Discussion

(a) Evaluation of flame retardance of PET samples

Attention was drawn to the results of evaluation of LOI values for PET samples, i. e., even untreated PET showed LOI value, 23.0%, higher than cotton by 4% and all treated samples gave LOI values higher than the critical value 27-28% as shown in Table 6-5. Among treated samples, those containing both Br and P showed higher level of LOI compared with those containing higher Br or P though there found little difference in effects of Br and P each alone on the flame retardation of PET. It was also found that sample treated with 10% of HBCD, saturated solution, and 2.5% (1/4) of TPPA gave the best result of all samples investigated.

Table 6-5 List of TDOP, MDRP, FP and LOI value for PET untreated and treated with HBCD or / and TPPA

	TDOP	MDRP	FP	LOI
untreated	397.1 °C	419.0 °C	436.7 °C	23.0 %
treated with 10% HBCD	386.5 °C	422.5 °C	447.7 °C	28.7 %
treated with 40% TPPA	389.5 °C	419.4 °C	439.7 °C	28.3 %
treated with 10% HBCD + 2.5% TPPA	389.8 °C	422.5 °C	448.2 °C	34.4 %

(b) Effects of Br, P and combination of Br and P on decomposing behavior of PET fibers observed by TG curves

The alternative thermal analysis was carried out by TGA to observe how Br and P compounds influence the thermal degradation onset temperatures and the peak maximum temperatures at which the rate of decomposition reaches maximum.

As shown in Fig.6-33-A, TG curve of untreated PET fabric showed typical changes by addition of HBCD or TPPA. These curves showed two step reductions of different shapes getting lower with increases in HBCD and TPPA contents. The 1st reduction is due to the participation of decomposition of additives HBCD and TPPA respectively and 2nd reduction is resulted from the decomposition of PET itself.

TG curves for HBCD-containing samples exhibited remarkable lowering with rise of temperature between 1st and 2nd reductions, while TPPA containing samples gave TG curves kept at almost the same level after 1st reduction upto around 400°C. As mentioned above, as far as what are observed from these TG curves are concerned, HBCD gives considerable effect on PET substrate, probably accelerating the degradation of PET at lower temperatures.

Moreover, combined effects of HBCD and TPPA were reflected in the curves for the samples treated with mixed solution of HBCD and TPPA as shown in Fig.6-33-B, i.e., when the ratio of HBCD is higher, a curve is closer to the curve for the sample treated with HBCD alone, and vice versa. If the ratios of both components are the same, the curve falls just in between the curves for the sample treated with HBCD alone and for that treated with TPPA alone as illustrated in the figure. Thus TG curves reflect both effects of HBCD and TPPA depending on the mutual ratios for combination. However, the synergism of Br and P can be hardly observed on TG curves in this case.

In addition to the thermolytic behavior observed by visual changes in TG curves as shown above, more significant factors to be taken into consideration are the thermal degradation onset temperature and the temperature at which the rate of thermal decomposition reaches maximum, as well as residual amounts of samples remaining after the thermal decomposition. This is because information may suggest if or how the additives play some roles for the thermal decomposition of the substrate, especially in this case, the results of TGA were much expected to see if Br and P participate in the thermal decomposition of PET fibers and further how they contribute to the flame retardance of PET in the solid phase. Therefore, TG curves obtained by the thermal analytical observations were further considered as follows:

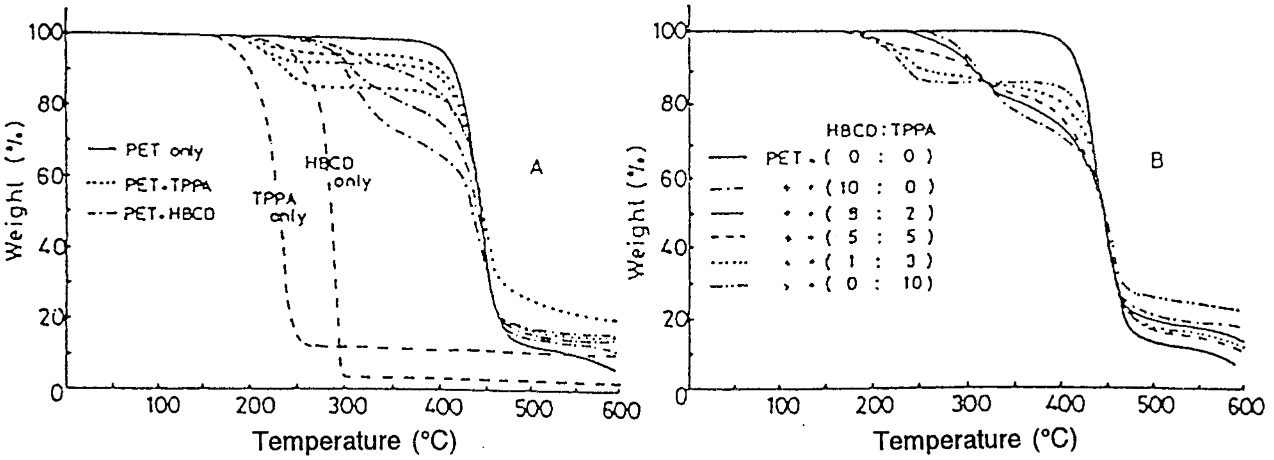


Fig. 6-33 Change in TG curve of PET observed by addition of HBCD and / or TPPA (A : with each alone, B : with combination of both in various ratios).

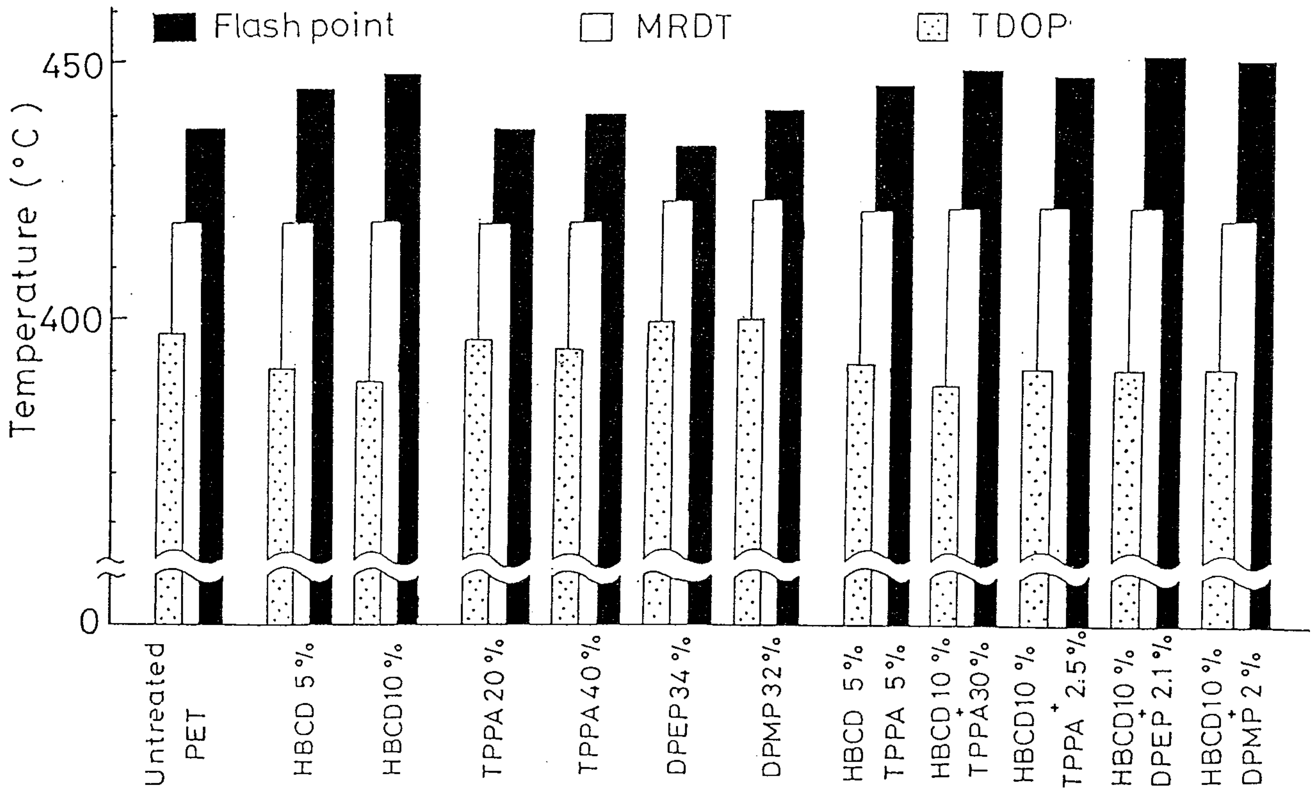


Fig. 6-34 Comparison among thermal degradation onset point, maximum rate of decomposition temperature and flash point.

(c) TDOP, MDRP and FP decided for PET samples

TDOP, MDRP and FP for each sample are listed in Table 6-5. It was obviously shown that all temperatures were located in much higher region even TDOP at nearly 400°C and FP at around

450°C. Generally, it has been recognized that synthetic fibers have lower heat resistances compared with that of cellulosic fibers, however, it was revealed, at least as for as the thermal degradation is concerned, that thermal degradation was initiated and ignited at considerably higher temperatures in the case of PET compared with cotton.

Fig. 6-34 is another illustration to show a positional relationship among TDOP, MDRP and FP more comprehensibly, in which temperature elevated almost linearly in the order of TDOP, MDRP and FP at the same temperature level in all cases irrespective of the kind of flame retardants as well as of concentrations of compounds.

(d) Relationship between LOI values and TDOP, MDRP or FP

LOI value vs TDOP, MDRP or FP was plotted for each sample to see if there was any relationship between flame retardance and these temperatures, e. g., it was expected that any characteristic difference or tendency might be observed with LOI values as observed between flame retardant samples and flammable samples in the case of cellulosic samples treated with nondurable inorganic compounds. But as shown in Fig. 6-35, all samples showed almost the same level irrespective of LOI values, higher or lower, for each of TDOP, MDRP and FP, which is a tendency entirely different from what was observed for the above mentioned cotton fabric treated with nondurable flame retardants, i. e., flame retardant samples with LOI values higher than 28% showed lower temperature for these 3 points, whereas flammable samples including untreated sample, with LOI values lower than 28% exhibited higher temperatures to demonstrate two groups of LOI vs temperature plots separated each other as shown in Fig. 6-3 and 6-4. The tendency shown by PET is similar rather to that shown by durable flame retardant finished cotton fabric treated with organic flame retardant compounds (see Fig. 6-16). The above mentioned fact will suggest that the mechanism of flame retardation for materials treated with inorganic compounds is significantly different from that for those treated with organic flame retardant compounds, whereas organic flame retardants donate similar effects on the flame retardation of flammable materials irrespective of natural or synthetic substrates.

There is still an important fact to be noted as to the order of these three points, i. e., in the case of cellulosic materials treated with nondurable inorganic compounds, flammable samples were ignited immediately or soon after TDOP before MDRP whereas flame retardant samples showed considerably retard ignition behind MDRP after production of large amounts of pyrolytic gases sufficient for ignition, on the other hand, in the case of PET samples, FP was behind MDRP in all cases irrespective of untreated and treated samples as well as of LOI values, which means that PET material can be hardly ignited probably because of liquidization due to melting, in this sense, PET samples can be recognized to be more flame retardant than cellulosic samples.

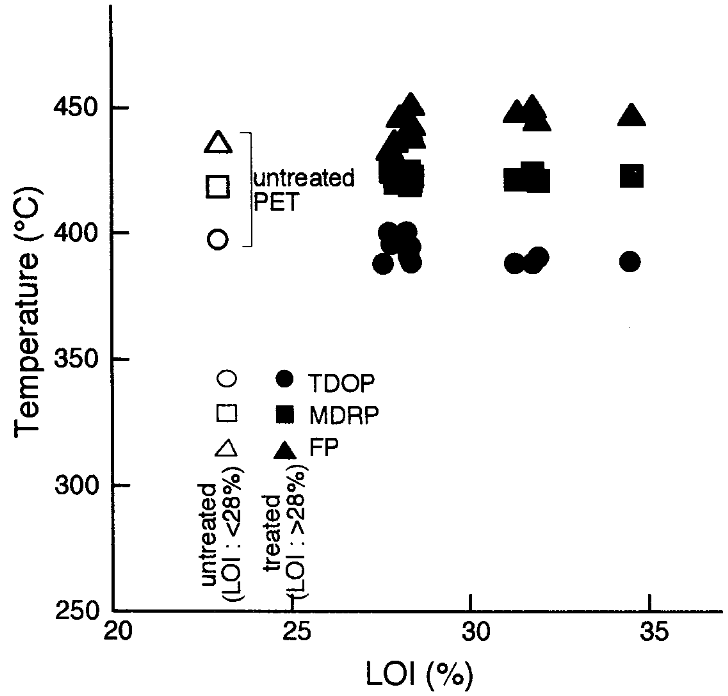


Fig. 6-35 LOI vs temperature plots of PET untreated (open marks) and treated (solid marks) samples at TDOP, MDRP and FP.

(e) Changes in Br and P contents observed with thermal treatment

It seemed to be of interest to see how much Br and P contents would change after heating, residues obtained after heating up to TDOP, FP and 600°C (Fig. 6-36).

Br was reduced down to undetectable a mount at TDOP by Vorhord's method though a very slight amount of Br was detected by another method as described in 3-2-2 as described below(Fig. 6-37), where as P remained in a very small amount even at 600°C. At TDOP, considerable difference was observed in residual amounts of P among samples ranging from 1mg to 8mg depending upon amounts of P initially contained, but such difference decreased down to 0.5-1.5mg after FP and little difference was observed at 600°C showing merely around 0.13mg/g irrespective of the initial P content, which clearly disclosed that retention of P was significantly larger between 3.7 times and 8 times, in samples containing Br in combination with P (retained ratio = 10%) compared with that in samples containing P alone (retained ratio = 1%). Such phenomenon seems to be closely connected with the flame retardation of samples by the synergistic effect of Br and P as described in 3-2-1.

Furthermore, attention should be paid to the fact that flame retardance was found to be the best in samples containing both Br and P although initial P contents were comparatively small, much smaller than those containing P alone, and Br was almost lost before reaching upto TDOP. This strongly confirmed that Br would act in the gaseous phase by blocking radicals of flammable pyrolytic products and P would contribute to char formation in the solid phase for self-extinguishing, for which comparatively small amount of P would be required, e. g., 1.5mg would be enough to donate sufficient flame retardance.

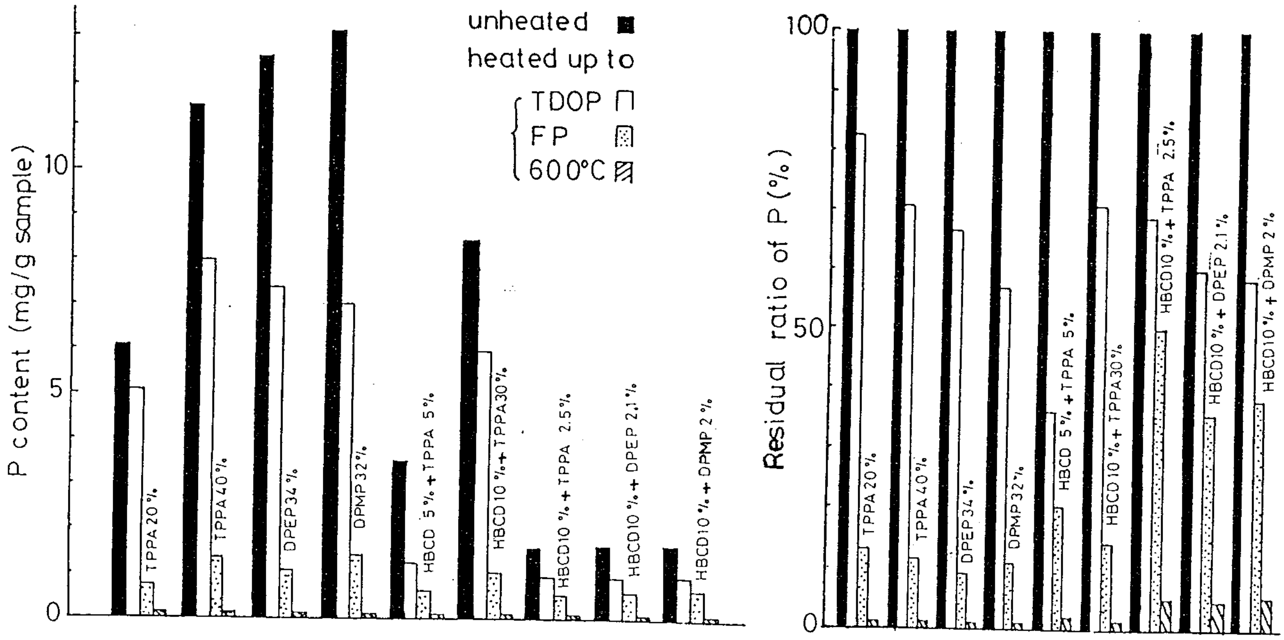


Fig. 6-36 Residual amounts (left) and ratios of residues (right) of P compounds-treated samples obtained after thermal treatment up to TDOP, FP and 600°C.

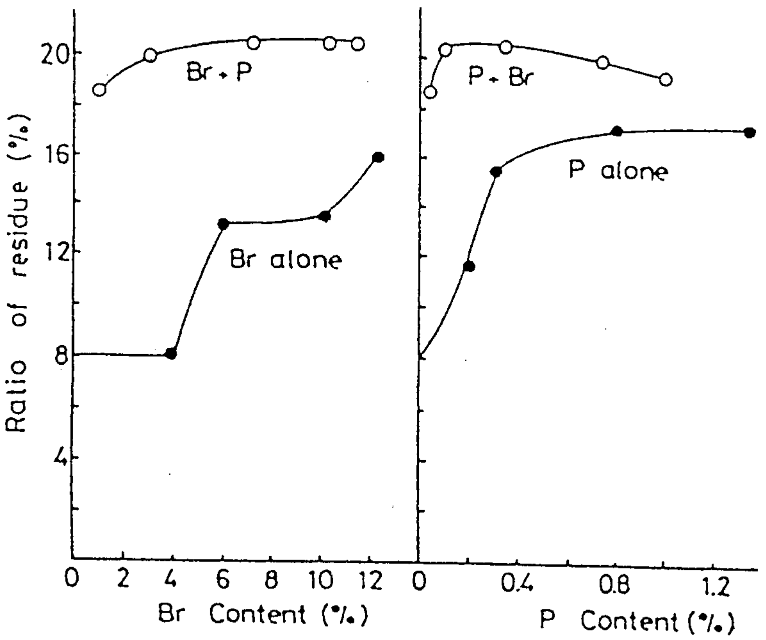


Fig. 6-37 Comparison of effects of Br or P alone with those of combination of both by residues obtained after thermal decomposition.

(f) Effects of Br, P and Br + P on residual amount of PET samples obtained after thermal decomposition

It is the most important factor to evaluate the flame retardance of any flame retardant finished samples from amounts of residues (char in many cases) after combustion. As shown in Fig. 6-37, residual amounts of the samples containing each Br and P alone increase with increase in Br and P contents and much further enhancements are also observed with combinations of both elements showing the synergistic effect also in this case.

Comparing the effect of Br with that of P at the same content, it has been clarified that P gives larger amount of residue with only 1/10 Br contest. This probably means that P component acts more effectively than Br in the solid phase with a small amount to accelerate char formation just as in the case of cellulosic fibers, while the activity of Br is minor in the solid phase with less participation in char formation. This will be explained more evidently by determining amounts of Br and P remaining in the residues after pyrolysis, which is a further project of the present studies. According to literatures available so far, Br acts as a free radical scavenger to inhibit the flame propagation [4,21], while P acts in the solid phase to promote char formation [27,28,104] at least in the case of cellulosic fibers. However, little has been made clear in the case of PET fibers. Therefore, as mentioned above, the purpose of the thermal analytical observations this time is to get some information to see how and to what extent Br and P act in the solid phase to contribute to the flame retardance of PET fibers.

The results obtained by the present investigations led us to conclude that Br contained in organic compounds such as HBCD incorporated in the PET molecule by the thermo-fix will act also in the solid phase as well as in the gas phase to participate in the flame retardance of PET fibers, which agrees with Bostic's opinion deduced from another angle [15]. This was proved by significant changes in the phase transition temperatures and increase in the residual amount left over after the pyrolysis.

3) Conclusion

The thermal degradation behavior was observed also for PET treated with HBCD as a donor of Br and TPPA, DPEP or DPMP to supply P, each alone or both together.

Thermogravimetric (TG) curve was obtained from each sample, from which TDOP and MDRP were determined and FP was determined separately. These 3 temperatures were compared among samples with different level of LOI values as well between flammable untreated sample and flame retardant treated samples, the results of which led us to conclude that each of TDOP, MDRP and FP of all samples rest at almost the same level irrespective of untreated and treated samples as well as of LOI values. Ignition of PET samples was considerably retarded even though in the case of flammable untreated sample, which is entirely different from what was shown by cellulosic samples.

Br and P contained in residues obtained after TDOP, FP and 600°C were determined, the results of which confirmed that Br would act in the gaseous phase for the flame retardation by blocking radicals of flammable pyrolytic gases, on the on the hand, P would work effectively in solid phase to gain sufficient flame retardance with the aid of Br.

6-1-7 Apparent Activation Energies of Thermal Degradation Observed for PET Samples

Since apparent activation energy (Ea) is closely related to the thermal degradation, the investigation was extended to observations for Ea of each sample to see if there is any relationship between Ea and flame retardance, though only overall Ea was obtained for each sample in this case.

1) Experimental

(a) Materials

PET fabric and treating reagents were the same as those mentioned in 3-2-3.

(b) Methods

Treating method for flame retardant finish was the same as described in 6-1-5.

Flame retardance of each sample was evaluated by LOI method as described in 2-2-2.

Ea of each sample was determined by Ozawa's method as described in 6-1-2.

2) Results and Discussion

(a) Comparison of Ea among samples

In this case, Ea of each sample was expressed by average value because of little difference in Ea throughout the process of thermal degradation which is different from what was observed in the case of cotton fiber shown above.

Fig. 6-38(upper figure) shows Ea of all samples, in which all treated samples required Ea higher than that of untreated sample, but participation of treating compounds were only 2% and 18% at highest. Samples treated with HBCD alone showed higher Ea compared with those treated only P-containing samples, of which TPPA needed higher Ea than DPEM and DPMP. Samples containing both Br and P showed Ea the level of which is similar to that of HBCD-treated samples, which looks as if P-containing compounds did not participate in Ea, e. g., sample treated with 10%

of HBCD + 30% of TPPA showed Ea nearly the same as that of sample treated with 10% of HBCD, though no wonder for other samples since they were treated with solutions containing very lower concentrations of P-containing compounds.

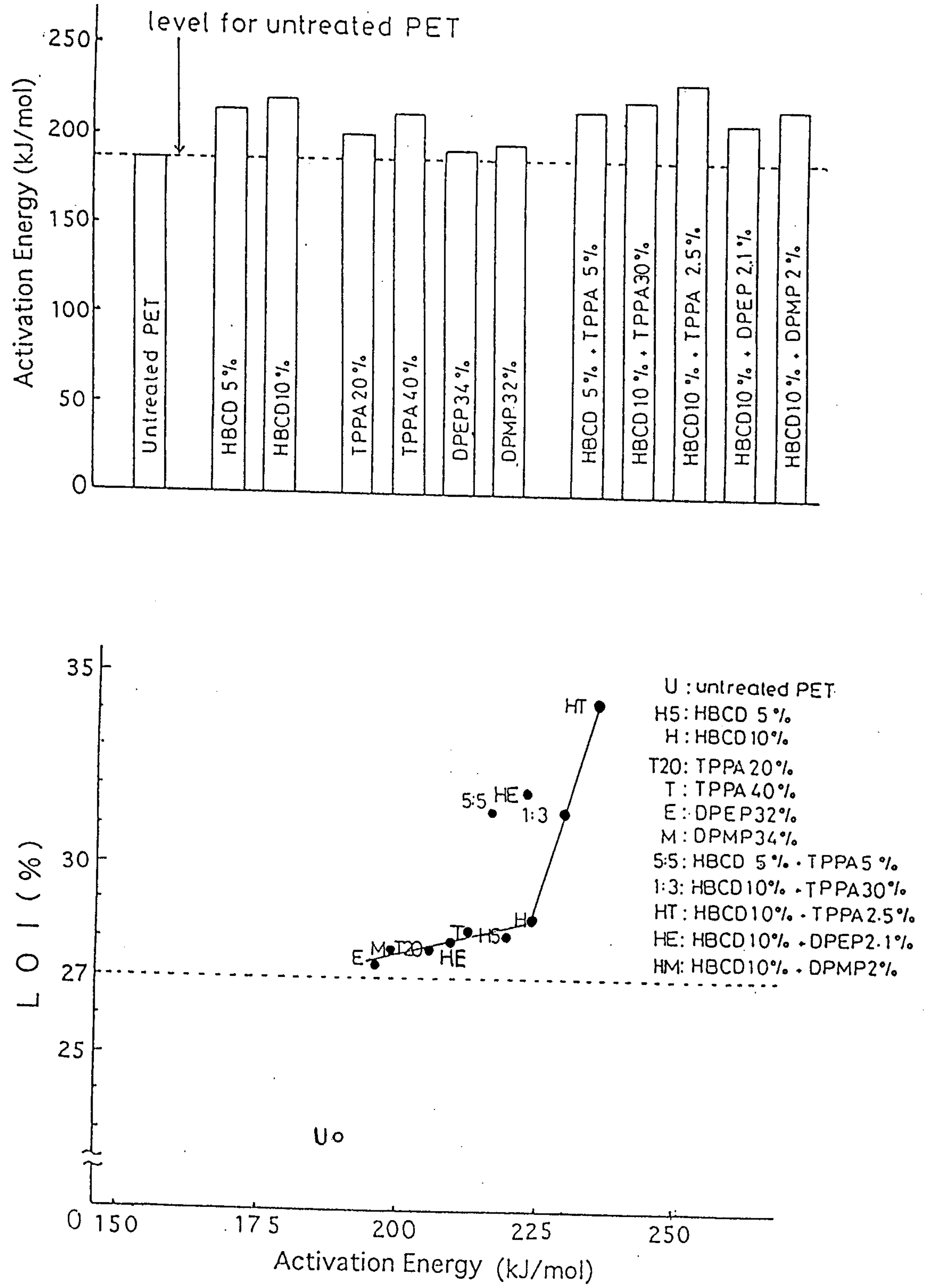


Fig. 6-38 Activation energy (Ea) of each sample (upper) and correlation between Ea and LOI value (lower).

(b) Correlation between Ea and LOI

LOI values were plotted for Ea to see if there was any relationship between flame retardance and Ea or between untreated and treated samples. As shown in Fig. 6-38(lower figure), there found an obvious discrimination between untreated sample without flame retardance and treated samples with flame retardance. Treated samples were separated into 2 groups, lower group consisting of those treated with single compound Br-containing or P-containing compound except for 1 sample containing both elements and upper group including samples treated with both compounds. In lower group, a correlation was observed between LOI and Ea in a narrow range of LOI, whereas in upper group, Ea of 2 samples overlapped with those of lower group though other 2 samples showed higher Ea values. However, except for 2 samples (5 : 5, HM), this Ea vs LOI plotting could be interpreted as consisting of 2 kinds of correlation with different angles taking off at a position of H.

(c)Comparison of Ea levels of PET samples with those of cellulosic samples

Comparison of the above mentioned Ea values observed for PET samples with those of cellulosic samples described in 6-1-2 disclosed that Ea values of both untreated PET and cotton fabrics were positioned in a same range 180-190kJ/mol, and those of treated PET samples and some, not all, of durable flame retardant cotton samples were located at a similar level ranging from 195-235kJ/mol, though nondurable flame retardant cotton samples showed considerably lower Ea resulted from easily decomposable nature of nondurable inorganic flame retardants

3) Conclusion

Ea values of PET samples were found to be in a range similar to that of cellulosic samples, but showed little difference throughout the process of thermal degradation suggesting that the thermal degradation proceeds more steadily compared with that of cotton fiber.

As to relationship between Ea and flame retardance, flammable untreated PET with LOI lower than 27% required the lowest Ea, and a characteristic correlation was observed between Ea and LOI values among treated PET samples with LOI values higher than 27%.

Part 2 Observation of Gaseous Phase

6-2 Pyrolytic Gas Generation Observed with Thermal Degradation

Introduction

In the previous part, the thermal degradation behavior of cellulosic and PET fibers was observed in the solid phase. On the other hand, this part subsequently deals with the vapor phase.

Since inhibition of pyrolytic gas generation is as inevitable as prevention of combustion itself to secure the safety of the human life, the attention should be paid to effects of flame retardant finishes on pyrolytic gas production. Therefore, pyrolytic gas species were detected both qualitatively and quantitatively from many kinds of treated and untreated cotton samples for comparison between pyrolytic gas products from flammable samples and these from flame retardant samples to prove effects of flame retardant finishes on the pyrolytic gas generation.

6-2-1 Pyrolytic Gas Generation Behavior from Cotton Cellulose Observed at Different Stages in the Process of Thermal Degradation

1) Effects of Nitrogen or / and Phosphorus

After demonstrating the thermal degradation behavior of cotton cellulose with or without the flame retardance by the thermogravimetric analyses, it seems indispensable to develop the thermogravimetric (TG) observation by analyzing pyrolytic gases to be formed in the process of thermal degradation.

Studies on the pyrolytic gas analysis of cellulosic fibers were already initiated in 1920's and considerable efforts have been made so far, particulaly in 1960's ~ 1970's [105-116].

However, the results from the pyrolytic gas analysis of polymers available so far have been obtained merely by rapid and uniform heating of the sample at any constant temperature to observe overall information of pyrolytic gases obtained at each fixed temperature.

But, it seemed more important and useful to analyze pyrolytic gases at different stages in the process of thermal degradation to dynamically observe pyrolytic gases to be formed and transformed with rising temperature during thermal decomposition. Chang[117] et al. have investigated pyrolytic gases from synthetic polymer substances by using TG method, but they measured gases by collecting only at the stage of maximum gas generation. No attention was paid to changes in amounts and gas species to be observed with temperature rise.

We performed dynamic observations for the pyrolytic gas formation in the process of thermal degradation by trapping gases at several representative temperatures, e. g., before and after the thermal degradation onset point, flash point and maximum degradation rate point on each TG curve followed by gas chromatographic analysis and gas chromatography-mass spectrometry. Samples used were cotton fabric untreated (sample A) and treated with urea (sample B) to supply nitrogen (N), disodium hydrogen phosphate (Na_2HPO_4) (sample C) as a phosphorus (P) donor and diammonium hydrogen phosphate {$(NH_4)_2HPO_4$} (sample D) to supply both N and P. The effect of flame retardance was shown by the fact that compared with flammable samples (A, B, C), pyrolytic gases from flame retardant sample (D) were extremely reduced both in amount and number of gas products decreasing with temperature rise even disappearing at 500°C in some cases, and only sample D showed a characteristic difference from other samples by the absence of a toxic gas acrolein as well as by the presence of a pyrolytic gas scavenger acrylonitrile, which is probably due to the synergistic effect of N and P. The above results evidently confirm that flame retardation is effective not only to inhibit combustion and pyrolytic gas generation but also to scavenge gases even already generated as shown by quenching behavior.

(a) Experimental

(1) Materials

(i) Fabric

The fabric material used for the present investigation was 100% cotton plain woven fabric (100 g/m^2), yarn count of which was 20 tex in warp and 16 tex in weft. Fabric sett was 171/5 cm in ends and 135/5 cm in picks. This fabric was purified by soxhlet extraction with chloroform - methanol (1 : 1 vol/vol) for 24 h and air dried.

(ii) Treating reagents

Reagents used for this study were 20% solutions of urea and Na_2HPO_4 as a N donor and a P donor respectively as well as of $(NH_4)_2HPO_4$ to supply both N and P.

(2) Methods

(i) Treatment of fabric

The cotton fabric was impregnated with the above mentioned solutions for about 5 min., padded after 2 dip - 2 nip process adjusting pick up to be about 90% and air dried.

(ii) Thermogravimetry

TG curve was obtained for each sample using Shimadzu TGA-40 by heating in N_2 with a flow rate of 30ml/min from room temperature to 100°C first, holding at 100°C until the evaporation of water was completed and followed by raising temperature up to 500°C at a heating rate of 20°C/min. Sample size was 4 ~ 5mg which was cut into powdery pieces with scissors. Differential thermogravimetric (DTG) curves were simultaneously obtained by Shimadzu DT-40 to see differential values of produced gases.

(iii) Determination of thermal degradation onset point (TDOP), maximum degradation rate point (MDRP) and flash point (FP)

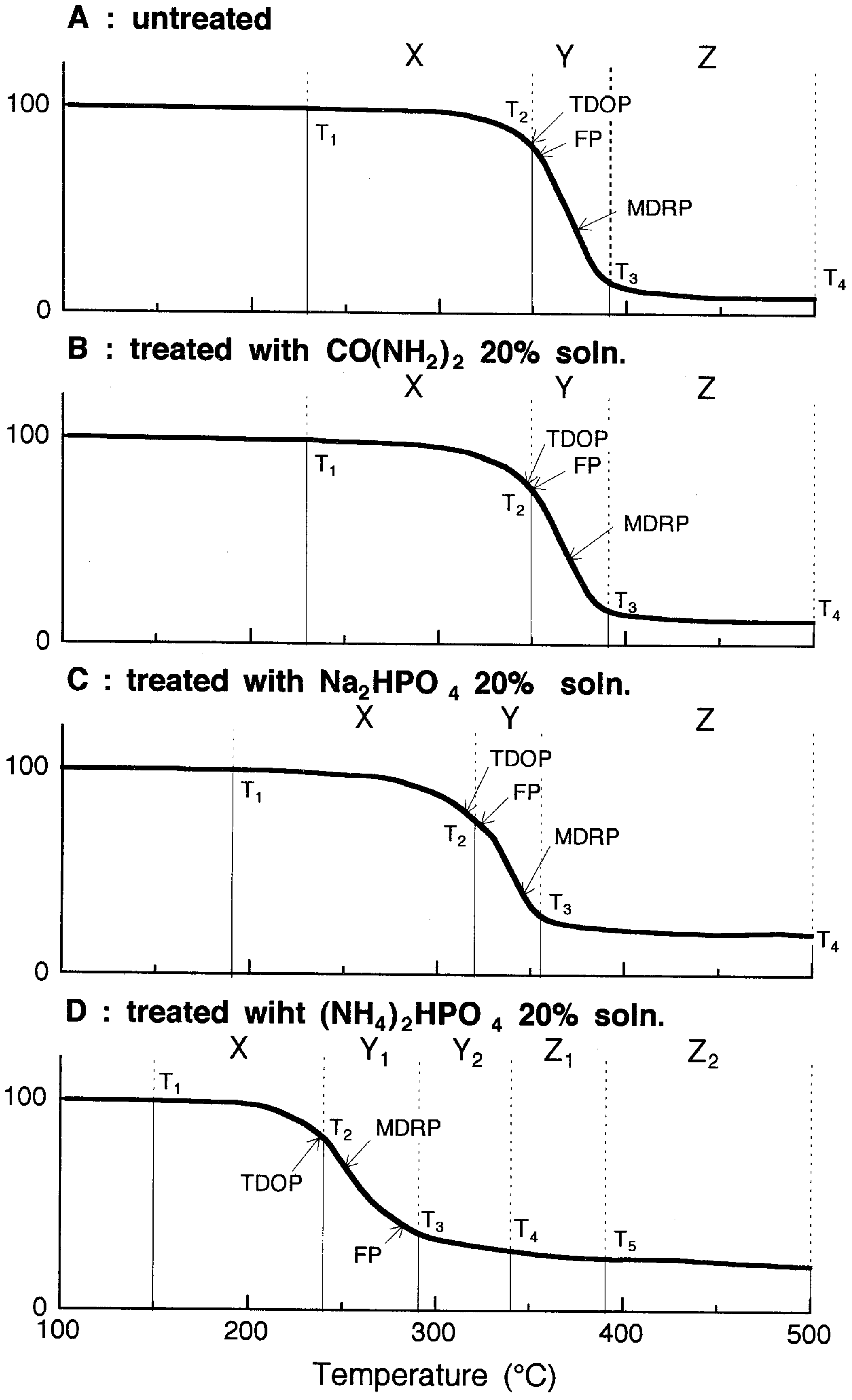
Theses three temperatures were determined as described in the previous chapter.

(iv) Determination of pyrolytic gas collecting temperatures

Taking TDOP, MDRP and FP determined as mentioned above and shapes of TG curves into consideration, temperatures at which pyrolytic gases to be collected were determined on each TG curve as shown in Table 6-6 and Fig. 6-39.

Table 6-6 List of LOI value and pyrolytic gas collecting temperatures (T) in combination with TDOP, FP and MDRP in various stages X, Y and Z on TG curve of each sample.

			X			Y					Z
	Sample	LOI (%)	T1 (°C)	TDOP (°C)	T2 (°C)	FP (°C)	MDRP (°C)		T3 (°C)		T4 (°C)
A	untreated	18.9	230	350	350	353	374		390		500
treated with 20% soln. of											
B	$CO(NH_2)_2$	22.2	230	347	350	350	369		390		500
C	Na_2HPO_4	22.2	190	314	320	322	346		355		500
			X			Y1			Y2	Z1	Z2
			T1 (°C)	TDOP (°C)	T2 (°C)	MDRP (°C)	FP (°C)	T3 (°C)	T4 (°C)	T5 (°C)	final temp. (°C)
D	$(NH_4)_2HPO_4$	43.4	150	238	240	251	283	290	340	390	500


A : untreated

B : treated with $CO(NH_2)_2$ 20% soln.

C : treated with Na_2HPO_4 20% soln.

D : treated wiht $(NH_4)_2HPO_4$ 20% soln.

Fig. 6-39 Mutual positions of (T), TDOP, MDRP and FP on TG curve of each sample.

(v) Collection of pyrolytic gases at various stages in the process of thermal degradation

Pyrolytic gases generated in the process of the thermogravimetry were collected at various temperatures on TG curves (see Table 6-6 and Fig. 6-39) as follows : Heating was stopped at each desired temperature and pyrolytic gases flowing out with carrier gas (N_2) were trapped in a Porapak Q - packed trap connected to a carrier gas outlet. This trap was chilled in a dry ice - ethanol bath beforehand. In this case, throughout the gas route except for a part of reaction tube inserted into a furnace and trap itself was kept at 200°C or higher to avoid the condensation of gases passing through the route. In order to fractionate pyrolytic gases in each temperature range in the process of thermal degradation, gases should be collected between two decided temperatures, e. g., 100°C ~ T1, T1 ~ T2, T2 ~ T3 and T3 ~ 500°C. But, it was confirmed by the preliminary experiments that it was impossible to collect each gas fraction accurately at every restricted temperature range and any favorable reproducibility could not be expected since there was a delay between gas generation and trapping because of the volume of reaction tube in TG apparatus. Therefore, in every case, heating was started from room temperature, stopped at each desired temperature shown in Fig. 6-39 to collect the total amount of gases generated from the thermal degradation onset to each desired temperature, i. e., the gas analysis was performed for 100~T1(X), 100~T2(X+Y) and 100~T3(X+Y+Z), and values for Y or Z stages were obtained by (X+Y)-X or (X+Y+Z)-(X+Y).

The furnace was removed simultaneously with the termination of heating to cool down to around 200°C to avoid both effects of remaining heat and condensation of gases.

On the other hand, introduction of carrier gas was continued for 5 min to flow out pyrolytic gases completely. It has been preliminarily confirmed that 5 min is enough for complete removal of gases throughout the gas route.

The trapped gases were released instantaneously in a silicon oil bath heated up to 190 ~ 200°C for 30 sec. and introduced into gas chromatographic (GC) analyzer (see below) for the quantitative analysis of pyrolytic gases as well as into a gas chromatographic - mass spectrometric (GC-MS) analyzer (see below) for the identification of each pyrolytic gas. Releasing temperature was selected to be able to release any gas even with the highest boiling point among the pyrolytic gases and releasing time was determined as the result of a preliminary experiment.

(vi) GC analysis

The pyrolytic gases released as mentioned above were introduced into GC Type 063 (Hitachi Seisakusho) with a FID detector to which a glass column 3mm in diameter packed with Porapak Q of 80~100 mesh was connected. The temperature was raised to 200°C at a heating rate of 5°C/min under a nitrogen flow of 40~60ml/min. The injection inlet was kept at 200°C. The data were treated with Chromatopack C-RIB (Shimadzu Seisakusho).

(vii) GC-MS analysis

On the other hand, the pyrolytic gases trapped and released in the same manner as in the case of GC analysis were also introduced into GC-MS Type JMS-DX300 (Nihon Denshi) for which a glass column packed with Porapack Q the same as that for the above GC analysis was used. The data was analyzed by JMA3000 (Nihon Denshi). Electron ionization (EI) and chemical ionization (CI) methods were adopted for identification of gases at an ionization voltage of 70eV. GC-MS analysis was carried out from 50°C to 240°C at a heating rate of 4°C/min. The repetition was made by a 6-sec cycle in a scan range of 15~300 m/z. The temperature of the separation and the ionization chamber were set at 260°C and 200°C respectively. The ion acceleration voltage was 3.5kV and the flow rate of He was adjusted to 40ml/min. Repetition ion current chromatograms were used for the identification of gases. The structure of each pyrolytic gaseous product was identified from pseudo-molecular ions and mass fragments. The identification was also confirmed with authentic compounds.

Not only pyrolysis but also gas chromatographic and mass spectrometric analyses were repeated 5~10 times for each sample and the results were averaged.

The amount of each pyrolytic compound was shown as an amount per 1g of the substrate (cotton cellulose) in each treated sample after the gravimetric determination of its add-on and moisture content.

(viii) Determination of flame retardance

The flame retardance of each sample was evaluated as mentioned above.

(b) Results and Discussion

(1) Evaluation of flame retardance

As shown in Table 6-6, not only untreated sample A but also samples B and C containing single N or P respectively gave LOI values lower than 28%. Only sample D containing N in combination with P showed LOI value much higher than 28% probably because of the synergistic effect of both elements.

(2) Change in pyrolytic gas generation with temperature rise in the process of thermal degradation visualized by gas chromatograms

The pyrolytic gases were quantified by GC analysis and identified by GC-MS analysis as described above.

Fig. 6-40 shows gas chromatograms of the untreated cotton cellulose as well as of samples treated with Na_2HPO_4 and $(NH_4)_2HPO_4$ (sample treated with urea is omitted because of similarity with the untreated sample).

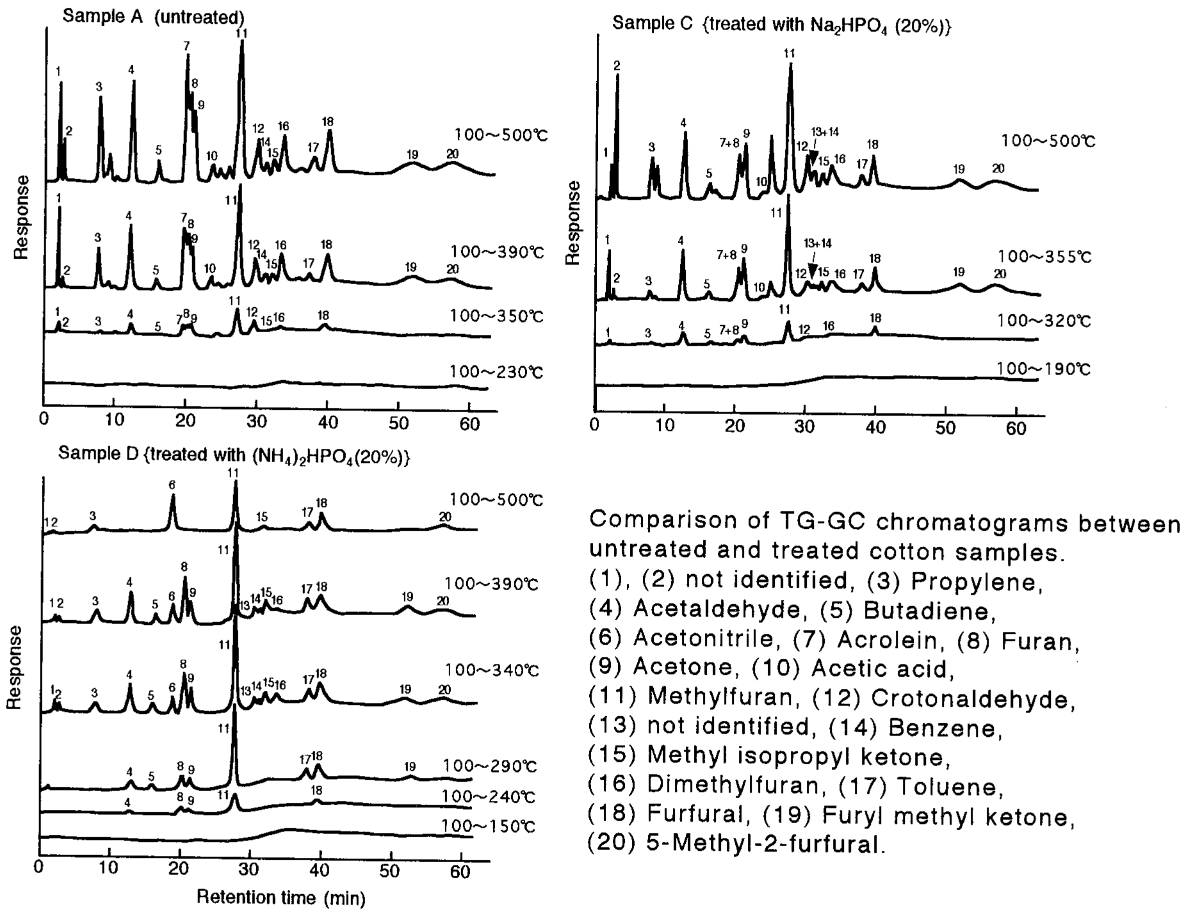
No peak was observed in all cases in fractions collected at T1 before the degradation onset, but several small peaks, more than 10 peaks in the case of the untreated sample, appeared after TDOP in X range and peaks increased in both number and area with temperature rise. But, attention was drawn to $(NH_4)_2HPO_4$-treated sample D which exhibited much less gases in both number and area. This is an obvious visual evidence for the fact that flame retardant sample clearly inhibits the pyrolytic gas generation. Such differences in gas generation behavior among these samples are observed in more details below.

In the case of untreated sample A, all gas species but acetic acid, benzene and toluene were already shown at or after TDOP in stage X, particularly acetaldehyde, furan, acetone, methylfuran and crotonaldehyde can be seen as obvious peaks. Attention should be paid to that acrolein, an extremely toxic gas, was generated already in this stage. Soon after MDRP, all gas species appeared in large amounts in stage Y, specially acetaldehyde, furan, acetone, methylfuran, dimethylfuran, furfural as well as acrolein extremely increased during 40°C temperature rise. Up to the final temperature, 500°C, additional increase was found in each gas in stage Z, particularly enhancement of acrolein was noticeable.

Na_2HPO_4-treated sample C gave qualitatively similar but quantitatively less peak areas compared with those of the untreated sample except that peaks 7 (acrolein) and 8 (furan) also 13 (hexane) and 14 (benzene) were not separated each other and combined as a single peak respectively, which were, in addition to crotonaldehyde and furfural, considerably less than those from the untreated sample. In stage Z, every peak showed further increase from those in stage Y, particularly increases in propylene and crotonaldehyde were marked. As shown above, samples treated with compounds containing single N or P exhibited reduction more or less quantitatively but little difference was found qualitatively when compared with the untreated sample. Comparison of N (from urea) and P (from Na_2HPO_4) revealed that P gave a little larger effect.

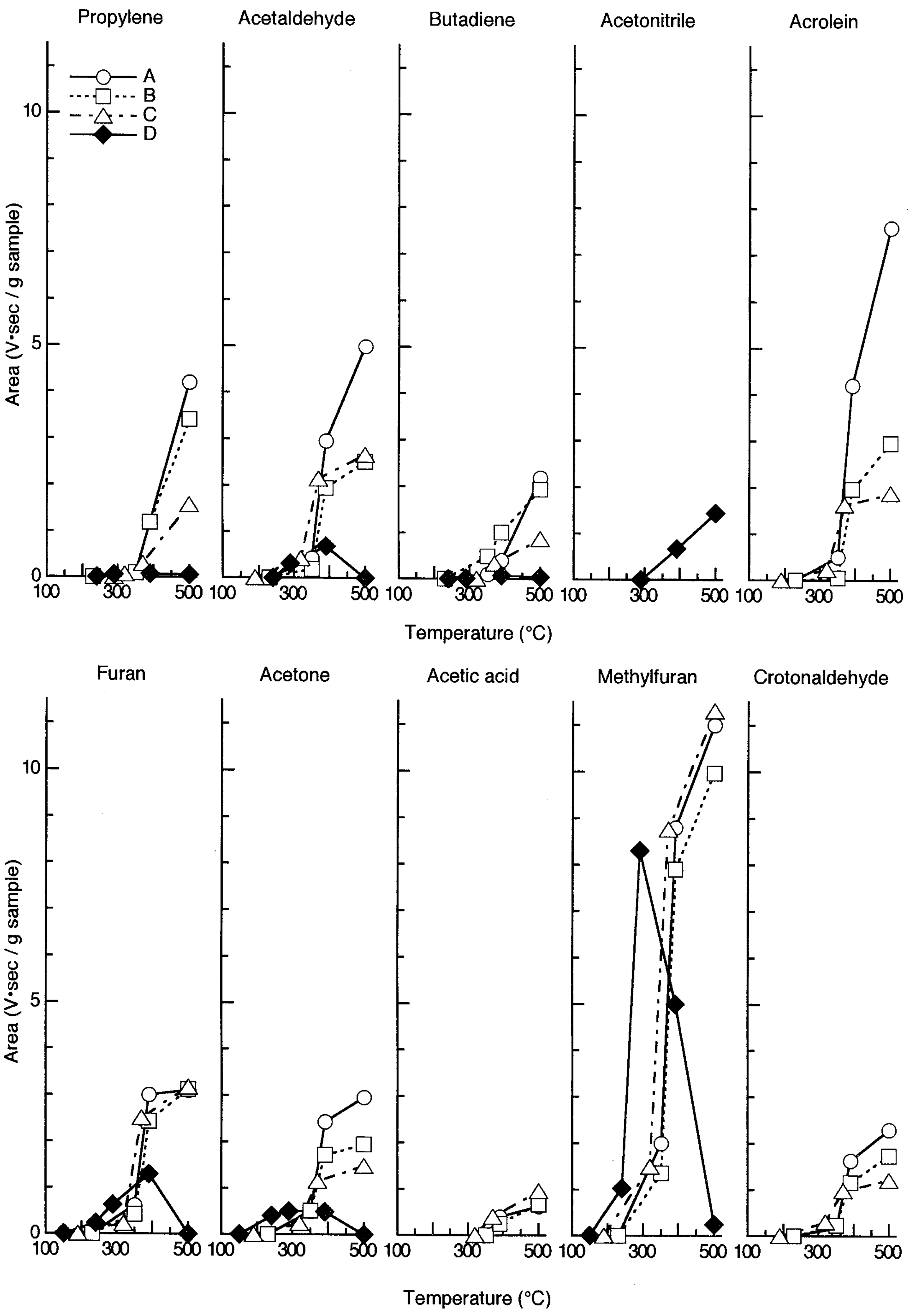
On the other hand, $(NH_4)_2HPO_4$ - treated flame retardant sample D containing both N and P showed patterns considerably different from the above mentioned samples without flame retardance. In stage X, there found only slight peaks of furan, methylfuran, acetaldehyde and furfural also a trace of acetone. Stages Y and Z were divided into 2 parts in this case because of a long and gentle slope of TG curve of this sample. Even in the maximum gas generation stages, i.e., the latter half of stage Y (Y2) and the first half of stage Z (Z1), both number and amounts of gas products are considerably less than those of other 3 kinds of samples. Moreover, attention was particularly drawn to the fact that hazardous acrolein (7) disappeared and a flammable gas-scavenger acetonitrile (6) which was never observed from other samples, newly detected at 340°C and showed obvious increase with temperature rise. In contrast to other 3 samples which showed increase in every gas species with temperature rise, this sample showed remarkable decrease in both number and amount except that only acetonitrile exhibited a marked increase in the final stage, where almost half number of gas species disappeared, i. e., only 7 gas species survived with much less amounts, whereas acetonitrile showed much more enhancement even at 500°C, which is extremely favorable phenomenon for the flame retardation.

Such phenomena, presence of acetonitrile and absence of acrolein, are believed to be resulted from the synergistic effect of N and P, which agrees with the result from pyrolysis by high frequency heating to be described below.



Comparison of TG-GC chromatograms between untreated and treated cotton samples.
(1), (2) not identified, (3) Propylene,
(4) Acetaldehyde, (5) Butadiene,
(6) Acetonitrile, (7) Acrolein, (8) Furan,
(9) Acetone, (10) Acetic acid,
(11) Methylfuran, (12) Crotonaldehyde,
(13) not identified, (14) Benzene,
(15) Methyl isopropyl ketone,
(16) Dimethylfuran, (17) Toluene,
(18) Furfural, (19) Furyl methyl ketone,
(20) 5-Methyl-2-furfural.

Fig. 6-40 Comparison of gas chromatograms between untreated and treated cotton cellulose as well as between samples with LOI < 28% (sample A and C) and sample with LOI > 28% (sample D).



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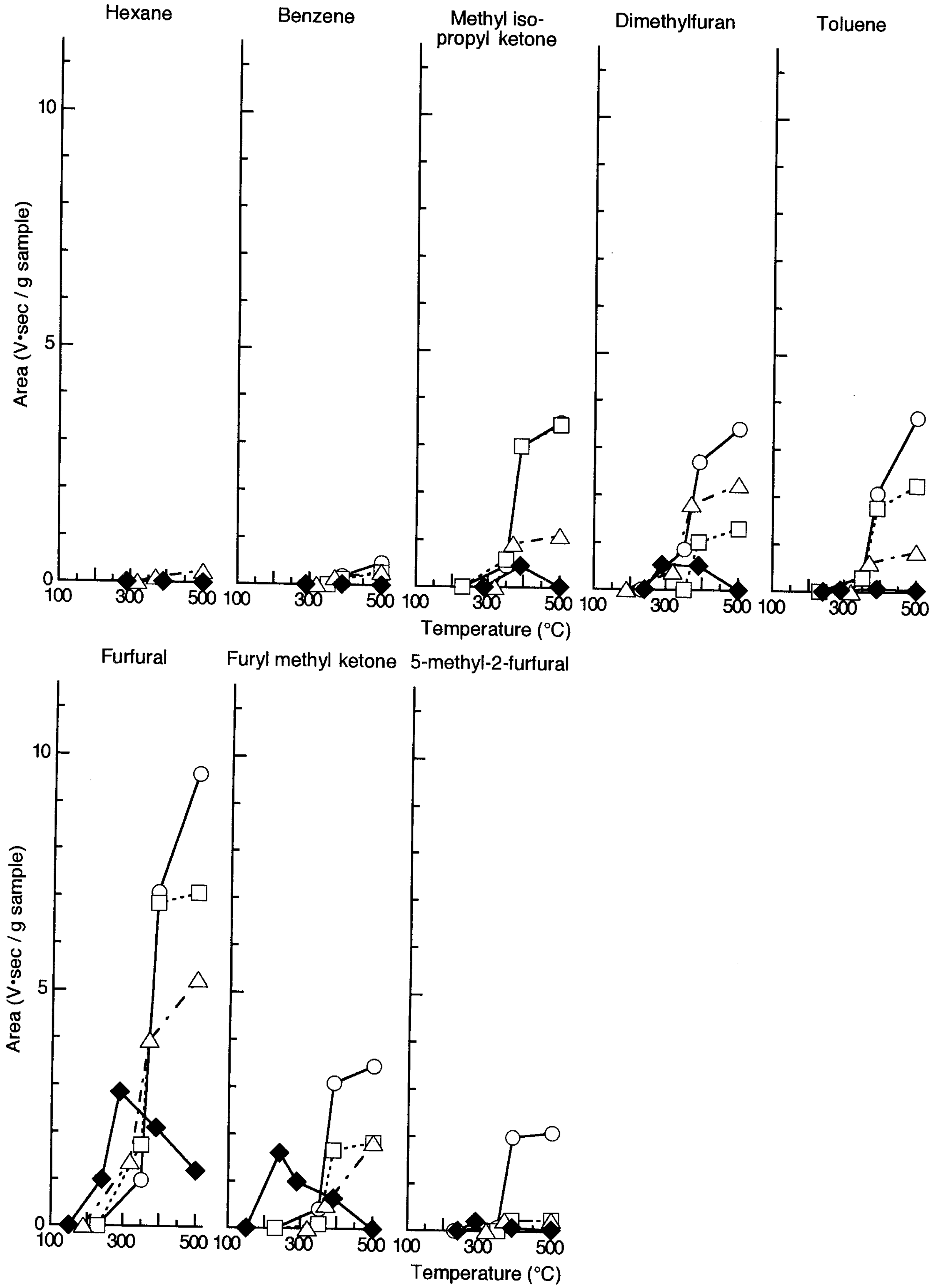


Fig. 6-41 Quantitative change in each pyrolytic gas species observed with temperature rise in the thermal degradation process. { A : untreated sample, B : sample treated with 20% solution of urea, C : sample treated with 20% solution of Na_2HPO_4, D : sample treated with 20% solution of $(NH_4)_2HPO_4$}

(3) Quantitative observation of each gas species varying with temperature and effect of treating reagents on pyrolytic gas generation

More accurate quantitative values were obtained from the peak areas of the gas chromatograms shown above at each selected temperature range. These values are illustrated in Fig. 6-41 for each gas species individually for the relative comparison among 4 kinds of samples, untreated sample (A), sample treated with urea (sample B), sample treated with Na_2HPO_4 (sample C) and sample treated with $(NH_4)_2HPO_4$ (sample D) . Gases are arranged in the order of retention times at which their peaks appeared on the gas chromatograms.

As shown in the figure, treated samples B, C and D gave less amounts compared with untreated sample A in all gas species but a few exception, specially $(NH_4)_2HPO_4$ - treated sample D showed the least amounts or trace even undetectable throughout the heating process, and also decrease or even disappearance of all gases but very useful acetonitrile at the final stage . Comparing sample B containing N alone with sample C containing only P for a comparison of both effects, the latter showed a larger inhibiting effect on gas generation. The most attractive findings, absence of acrolein and presence of acetonitrile are indicated more clearly and more concretely here in contrast to other three cases.

Paying attention to each gas species in more details in combination with comparison among samples, change in each gas product is considered as follows. Comparison of propylene with acrolein regarded to be produced by oxidation of propylene revealed that oxidized product was much more formed in the case of untreated sample A, whereas the oxidized product was undetectable in sample D. Since the amounts of acrolein from samples B and C are significantly less than that of the untreated sample as shown here, it seems to be worth treating, even with single N or P containing compounds though the flame retardance itself is not sufficient in these cases. Butadiene, a diolefin, could be cleaved into 2 olefin molecules, but might be rather converted to propylene because of absence of ethylene at least as far as the result of the present study is concerned. As for acetonitrile highly responsible for the flame retardance appeared in significant amounts showing a linearly increasing tendency up to 500°C or higher, contrary to the result of entire absence in all other cases. A quite opposite result was exhibited in the case of acrolein as shown in the next column, i. e., the entire absence was shown by sample D in contrast to high yields from other samples. Another attention should be paid to furan family, furan, methylfuran and dimethylfuran as well as to furfural. According to the generally supported thermal degradation mechanism of cellulose, glucofranose is an intermediate product in the route from cellulose molecule to form flammable gas fragments. Taking this mechanism into consideration, glucofranose could be converted to furfural, 5-methyl 2-furfural and methylfuran or dimethylfuran followed by further conversion to furan through cleavage of methyl group. In this case the most attracting finding is that the amounts of methylfuran are exceptionally marked in all cases, which probably because the conversion from glucofranose to methylfuran is easiest and rapid, and further cleavage is difficult and slower owing to the stability of this compound. But we notice typical different behavior between flame retardant sample D with LOI higher than 28% and other samples A, B and C with LOI lower than 28%, i. e., samples A, B and C showed remarkable increase with rising temperature, particularly, urea-treated sample B even slightly exceeded the untreated sample, whereas sample D exhibited rapid decrease at higher temperature.

Not only in the case of methylfuran, sample D showed such decreasing tendency even disappearing at 500°C in some other gas species in contrast to increasing tendency observed with other three samples, which is an obvious evidence that sample D with the synergistic effect of N and P acts not only to inhibit pyrolytic gas generation but also scavenge already generated gas products by the aid of the action of a scavenger, acetonitrile. Thus, flame retardant sample can be drastically characterized by the pyrolytic gas generating behavior.

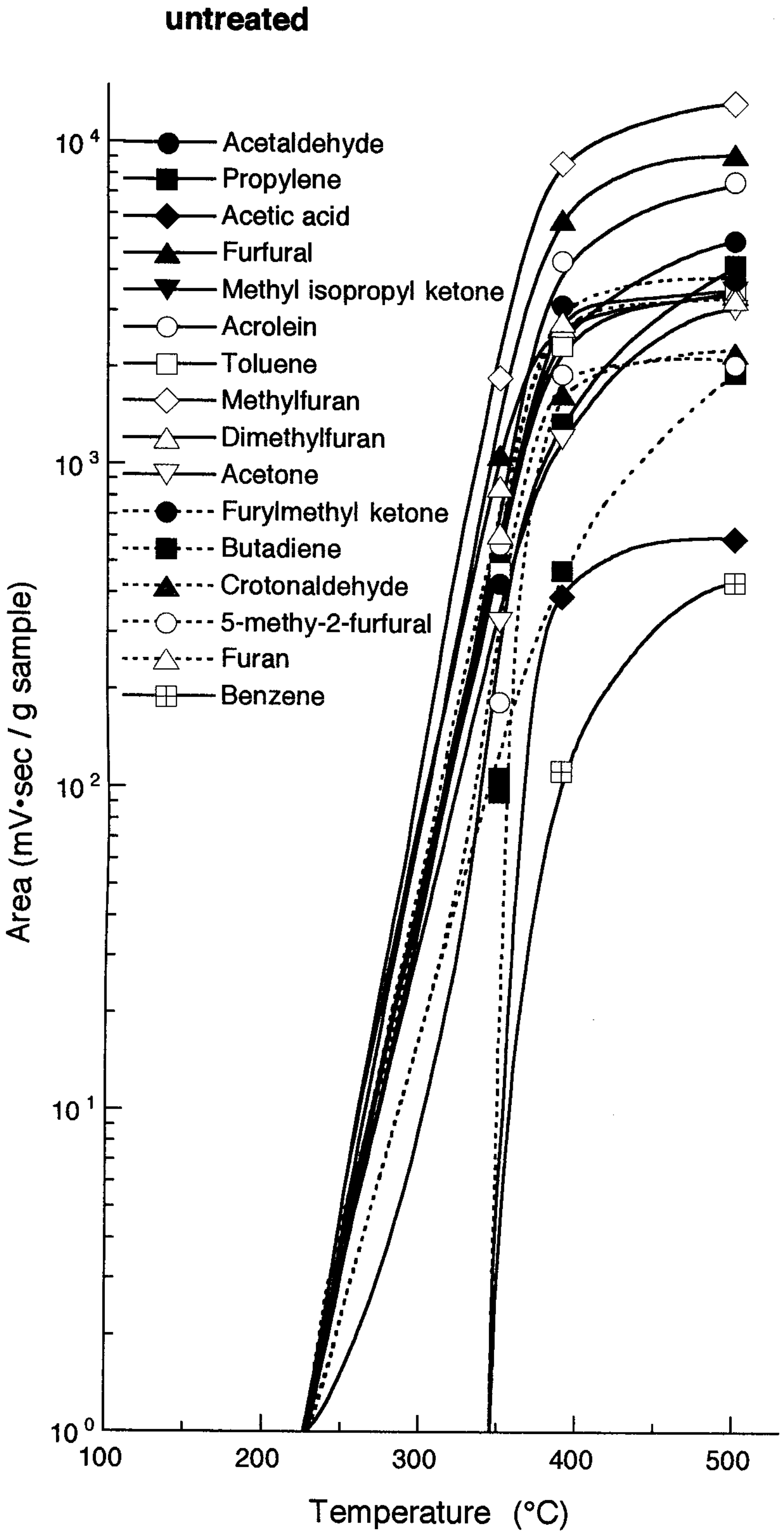
(4) Area vs temperature curves to clarify relative comparison of pyrolytic gas generation behavior among gas species as well as between flammable sample and flame retardant sample

To observe change in gas generation at each selected temperature for relative comparison among gas species as well as to see both qualitative and quantitative differences between samples with and without flame retardance, area vs temperature curve for each gas product was shown in Fig. 6-42 (area is indicated by the logarithmic scale). A merit of this figure is to enable us to compare the amounts of all pyrolytic gases collected at each stage from each individual sample. Untreated sample A was selected as a representative flammable material to be compared with flame retardant sample D.

Sample A shows continuous increase in every gas species, of which the highest amount is shown also by methylfuran followed by furfural > acrolein > acetaldehyde > propylene, in contrast, the least amount by benzene, only about 1/10 the amount of propylene, and acetic acid, a little more, 1/20 that of furfural and the rest 10 gas species compactly align in a range between 1/6 - 1/3 the level of methylfuran when compared at the final temperature. Above all, the fact to which attention should be focused first is that the amount of a hazardous toxic gas, acrolein falls to 3rd position. This information can explain persuasively that hazard of fire is not only combustion itself but also producing pyrolytic gases containing such toxic gases in combination with CO.

On the other hand, flame retardant sample D disclosed an entire different behavior, all gas species were generated at much lower temperature, i. e., methylfuran, furfural, furyl methyl ketone, furan and acetone at 200~250°C, acetaldehyde, dimethylfuran, toluene and butadiene, at 250~300°C and the rest 6 species, at 300~400°C. All species but one decreased after showing the maximum values in a range of TDOP and FP, 240~300°C (methylfuran, furfral and furylmethyl ketone) or at a higher range, 340~390°C (other 10 species). acetone showed a plateau between 240~390°C. One exceptional gas, a potential extinguisher acetonitrile alone exhibited an increasing tendency with temperature rise. The highest amount is shown by methylfuran followed by furfural also in this case, but comparing with the yields given by untreated sample A, the maximum amounts are 2/3 for methylfuran and less than 30% for furfural respectively. Methylfuran was reduced down to 1.5% at 500°C though furfural maintained 65% of the peak value. The lowest amounts were shown by hexane and benzene which generated at higher temperature range showing a peak at around 400°C and disappeared at 500°C. Other several species, furan, acetone, furylmethyl ketone, acetone and methyl isopropyl ketone were also rapidly reduced to finally reach zero level. Other several species also more or less decreased at the final stage. Contrary to the case of untreated sample A, it should be emphasized again that no acrolein was found in this case.

In contrast to the decreasing or disappearing tendency observed with the above mentioned gas species, a pyrolytic gas scavenger, acetonitrile which was absent in every sample without flame retardance, appeared at higher temperature range and kept increasing with temperature rise showing significant amount at the final stage, which is very favorable phenomenon for the flame retardation and security.



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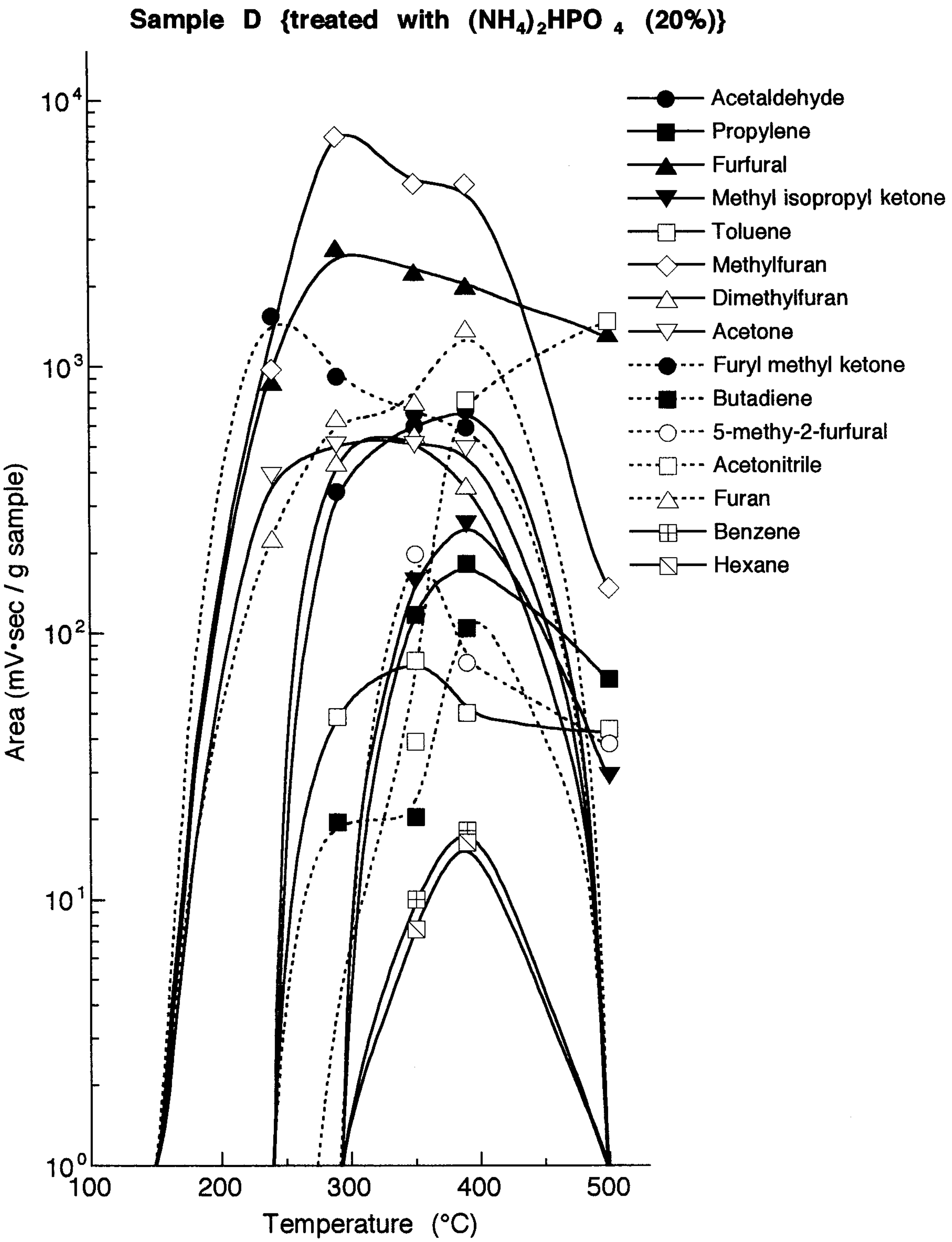


Fig. 6-42 Area vs temperature curves of all gas species from individual samples for comparison of pyrolytic gas generation behavior between flammable and flame retardant samples.

(c) Conclusion

The results reveals that flame retardant sample D showed extremely less amounts and less number of gas products compared with other flammable samples, and some gases decreased with temperature rise even disappearing at 500°C when other three samples showed further increase. Moreover, considerable amount of toxic acrolein gas was observed from samples A, B and C, but not detected from sample D, and acetonitrile, an effective pyrolytic gas scavenger, was found only from sample D.

The results of the present study confirmed that the flame retardation works not only to inhibit combustion and subsequent gas generation but also scavenge pyrolytic gases already formed to reduce or quench them.

In conclusion, since the hazard of fire is not only from burning itself but also from pyrolytic gases including toxic gases as described above, the above results that absence of toxic acrolein and presence of pyrolytic gas scavenger acetonitrile were revealed only by flame retardant sample have confirmed the necessity of flame retardant finish for any flammable material.

2) Effects of Nitrogen or / and Halogens

Since the hazard of fire is brought not only by combustion itself but also by pyrolytic gases which may cause the vital disaster, we have studied on the pyrolytic gas generation to see if flammable materials treated with compounds containing nitrogen or/and phosphorus and halogens which are effective flame retardant elements can inhibit the generation of hazardous pyrolytic gases and described in the previous section. In the case, it was thought to be more significant to obtain more dynamic information about the variation of gas generation changing with temperature rise in the process of thermal degradation. Therefore, we collected pyrolytic gases at several points on each TG curve to obtain both qualitative and quantitative determinations of pyrolytic gases generated at various stages in the degradation process.

We firstly treated cotton cellulose with compounds containing nitrogen (N) or phosphorus (P) each singly (urea and Na_2HPO_4) and both together $\{(NH_4)_2HPO_4\}$ to observe effect of N or / and P on the variation of pyrolytic gas generation in the process of thermal degradation, the results of which were described in the previous section.

Successively, it was further thought to be of interest to extend this work to see the effect of halogens instead of P on the thermal degradation of cotton cellulose this time.

For the contribution of halogens to the flame retardation mechanism, Rosser [118], Simmons et al. [119], Warren [120] and Lewin et al. [121] have provided that the action of halogens is attributed to trapping combustible gas radicals. Lyonis et al. [122] have also suggested that phosphorus-halides complex acts much more effectively. Garn et al. [106] and Sugiura [123] investigated pyrolytic gas products from cellulose fibers treated with compounds containing halogens and P. On the other hand, Tesoro et al. [124-126] and Miller et al. [127-131] used cotton / polyester blended samples treated by bromination in combination with phosphorylation using a bromine (Br) -containing organic phosphate and also observed considerable increase in flame retardance evaluated by LOI value.

Since our studies on the effect of flame retardant elements on the flame retardation have been based on the presence or absence of N, the present study deals with the effects of halogens with and without N on pyrolytic gas generation behavior not at a fixed temperature, but observed at various stages in the process of thermal degradation of cotton cellulose. The previous study (Part 1) was followed by investigations carried out with the same cotton fabric treated with compounds containing urea or halogens as sodium, calcium and ammonium salts to see the effects of halogens, singly and in combination with N.

(a) Experimental

(1) Materials

(i) Fabric

Fabric material was 100% cotton plain woven fabric the same as that used for the investigation reported above.

(ii) Treating reagents

Reagents used for the present study were urea as a compound containing N alone, sodium and calcium salts of halogens, NaCl, $CaCl_2$ and NaBr as compounds containing halogens only and ammonium salts of chlorine (Cl) and Br, NH_4Cl and NH_4Br as compounds containing both N and halogens. All compounds were used as 20% solutions and additional 5% solutions were prepared for $CaCl_2$, NH_4Cl and NH_4Br because 20% solution of these three compounds gave high flame retardance with LOI values of > 28% as shown in Table 6-6.

(2) Methods

(i) Treatment of fabric

The cotton fabric was treated with the solutions mentioned above in the same manner described in the previous section.

(ii) Thermogravimetry and determinations of TDOP, FP and MDRP

Thermogravimetric (TG) curve was obtained, and TDOP, FP and MDRP were determined for each sample as described in 6-1-1. and shown in Table 6-7.

Table 6-7 List of LOI value TDOP, MDRP, FP and pyrolytic gas collecting temperatures at various stages on thermogravimetric (TG) curve of each sample.

		X		Y	Z				
Sample	LOI (%)	T1 (°C)	T2 (°C)		T3 (°C)	T4 (°C)	TDOP (°C)	MDRP (°C)	FP (°C)
A untreated	18.9	230	350		390	500	350	374	353
treated with									
B $CO(NH_2)_2$ (20% soln.)	22.4	230	350		390	500	347	369	350
C NaCl (20% soln.)	20.8	250	340		390	500	335	367	340
D NaBr (20% soln.)	20.3	250	300		350	500	265	312	276
e $CaCl_2$ (5% soln.)	23.5	220	270		350	500	245	250	300
E $CaCl_2$ (20% soln.)	31.6	220	270		350	500	245	249	310
f NH_4Cl (5% soln.)	21.3	170	250		390	500	330	366	350
F NH_4Cl(20% soln.)	28.3	170	250		390	500	330	360	370
g NH_4Br (5% soln.)	23.7	170	250		350	500	194	294	266
		X		Y1 Y2		Z			
		T1 (°C)	T2 (°C)	T3 (°C)	T4 (°C)	T5 (°C)			
G NH_4Br (20% soln.)	38.2	160	230	270	350	500	194	218.5	267

(iii) Determination of gas collecting temperatures on each TG curve and collection of gases at these temperatures

To observe the variation of pyrolytic gas generation changing with temperature rise in the process of thermal degradation, gas collecting temperatures were selected on each TG curve as described in Part 1 and shown in Table 6-6 and illustrated in Fig. 6-43.

Pyrolytic gases were collected at these selected temperatures by trapping in Porapak Q packed traps chilled in a dry ice-ethanol bath in the manner also described in the previous section 1).

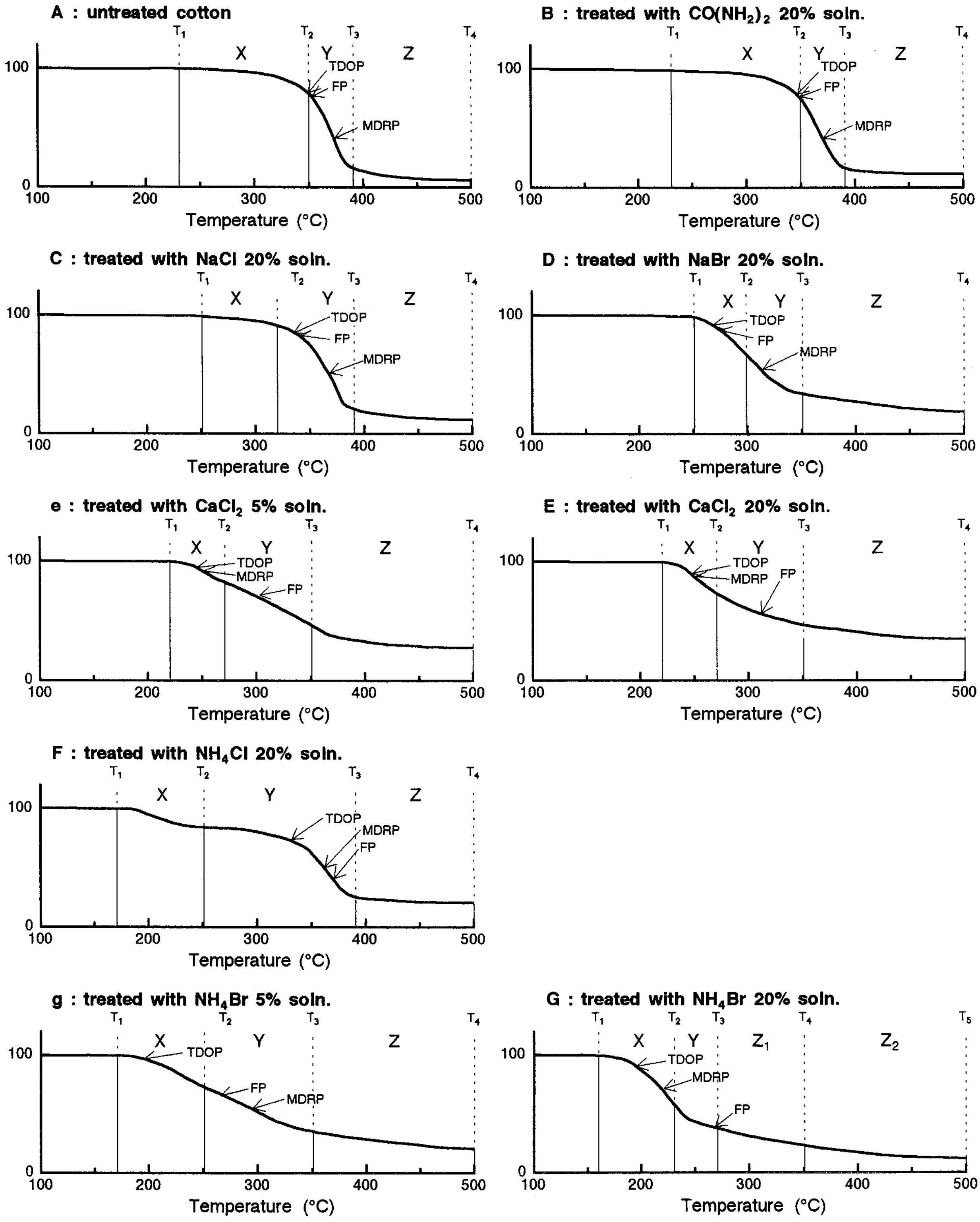


Fig. 6-43 Pyrolytic gas collecting temperatures in relation to TDOP, MDRP and FP on TG curve.

(iv) Qualitative and quantitative determination of collected gases

The collected pyrolytic gas products were released in silicon oil at 190 - 200°C for 30 sec. and introduced into a GC analyzer for the quantitative determination as well as into GC-MS analyzer for the identification of each pyrolysis gas species under the conditions the same as mentioned in Part 1.

Pyrolysis and gas chromatographic analysis as well as mass spectrometry were repeated 5 - 10 times for each sample to confirm the reproducibility and the averaged values are shown. Every amount of pyrolytic product was expressed as an amount per 1g of cotton cellulose used for this experiment in each sample after the gravimetric determination of its add-on and water content.

(v) Determination of flame retardance

In order to see if there is any characteristic difference in the pyrolytic gas generation behavior between flammable samples and flame retardant samples, flame retardance of each sample was determined as LOI (limiting oxygen index) value as described in 2-1-2.

(b) Results and Discussion

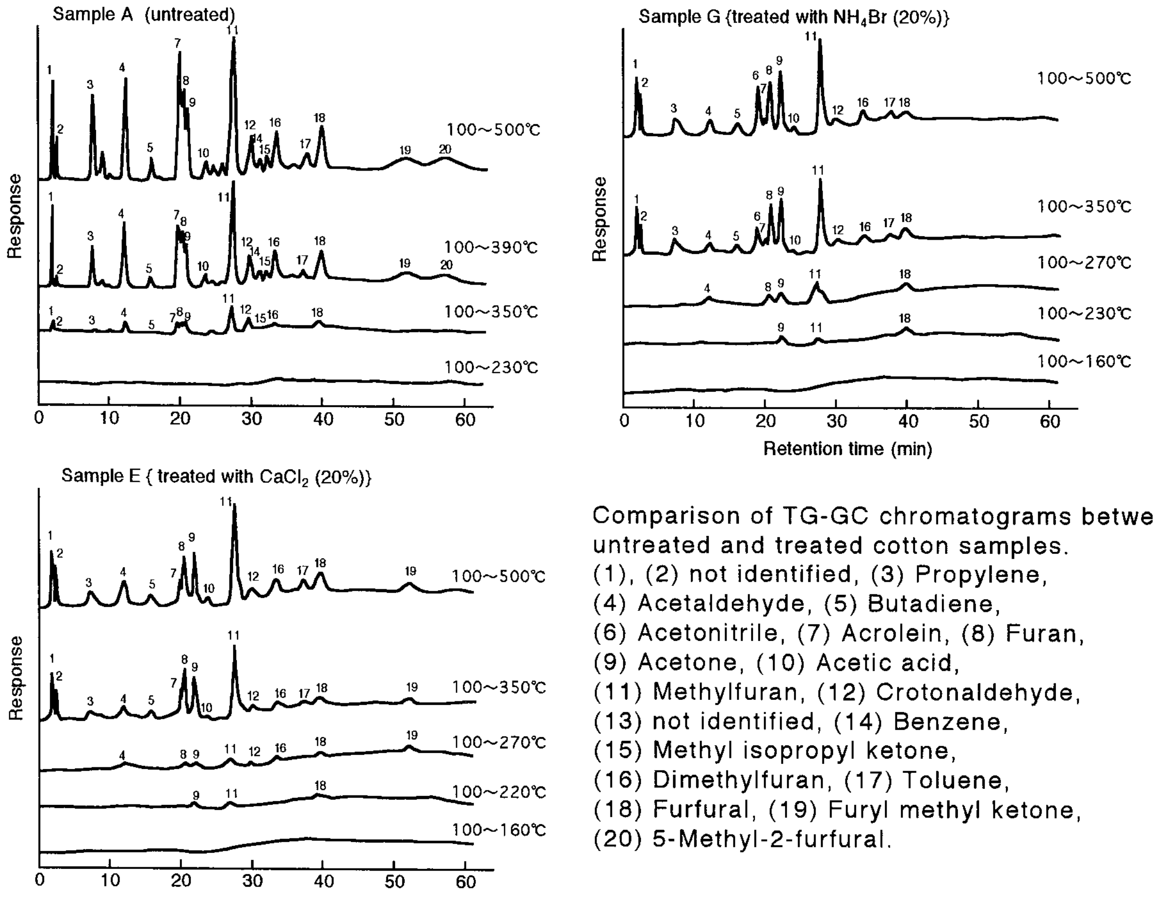
(1) Evaluation of flame retardance

According to the criterion for flame retardance recognized as 28% by Nakanishi et al. [14], samples treated with urea or sodium salts of halogens containing nitrogen or halogens alone respectively as well as with any 5% solutions should be evaluated to be more or less flammable without flame retardance because of their LOI values lower than 28%, though more or less higher than that of untreated sample A.

On the other hand, flame retardant samples with LOI values higher than 28% are only those treated with 20% solutions of $CaCl_2$, NH_4Cl and NH_4Br, particularly, LOI value of NH_4Br-treated sample containing nitrogen and bromine extremely exceeds the critical value which means highly flame retardant. High LOI value of sample E even though with Cl alone without any participation of N is probably due to the well known deliquescence of $CaCl_2$ allowing cellulosic fiber molecules to absorb considerable amount of water which provides effective contribution to retard the initiation of combustion, so called ignition.

(2) Change in pyrolytic gas generation with temperature rise in the process of thermal degradation and comparison between flammable and flame retardant samples

Fig. 6-44 shows gas chromatograms of untreated sample (A) as a representative of flammable samples and flame retardant samples with 2 highest LOI values treated with 20% solutions of $CaCl_2$ (E) and NH_4Br (G) respectively.



Comparison of TG-GC chromatograms between untreated and treated cotton samples.
(1), (2) not identified, (3) Propylene,
(4) Acetaldehyde, (5) Butadiene,
(6) Acetonitrile, (7) Acrolein, (8) Furan,
(9) Acetone, (10) Acetic acid,
(11) Methylfuran, (12) Crotonaldehyde,
(13) not identified, (14) Benzene,
(15) Methyl isopropyl ketone,
(16) Dimethylfuran, (17) Toluene,
(18) Furfural, (19) Furyl methyl ketone,
(20) 5-Methyl-2-furfural.

Fig. 6-44 Comparison of gas chromatograms between untreated and treated cotton cellulose.

The gas chromatogram of the untreated sample is the same as that shown in Part 1. More than 10 gas products appeared at 350°C and increased in both amount and number of species with temperature rise. Twenty species were detected though the first 2 were not identified, of which propylene, acetaldehyde, acrolein and methylfuran were found in marked amounts. Particularly, attention should be paid to that acrolein, a hazardous toxic gas, was produced in a significant amount already in X stage which confirms the hazard of fire to be also caused by pyrolytic gas generation.

On the other hand, flame retardant samples with high LOI values show remarkable reduction of acrolein, and disappearance of benzene, methyl isopropyl ketone and 5-methyl-2-furfural, furthermore furyl methyl ketone disappeared from sample G, though the onset of gas generation is lower in the case of flame retardant samples compared with flammable samples as represented by the untreated sample. Such inhibited generation of acrolein is of course absolutely favorable.

Moreover, every peak clearly exhibited remarkable decrease in amount. Above all, the focus of attention should be a fact that an effective flammable gas scavenger, acetonitrile, was produced only from sample G treated with 20% solution of NH_4Br containing both nitrogen and a halogen Br appearing in the latter half of Y stage. Such phenomena, the marked reduction of acrolein though not entire absence, and presence of acetonitrile, are obviously owing to the synergistic effect of nitrogen and bromine.

(3) Quantitative observation of each gas species varying with temperature, and effects of treating reagents on pyrolytic gas generation

Fig. 6-45 shows comparisons of relative amounts of samples observed for each individual pyrolytic gas product varying with temperature rise for the relative comparison among all samples. The gas species are arranged in the order of retention time.

As an overall tendency, it is obvious that untreated sample A showed the highest value in all gas species but a few exception, followed by sample B, C or D with LOI values lower than 28%. On the other hand, sample E, F and G treated with 20% solutions of $CaCl_2$, NH_4Cl and NH_4Br respectively with LOI values higher than 28% exhibited low area values. Particularly, sample G with the highest LOI value showed the lowest values in almost all gas species though the gas generation onset is earlier at lower temperatures compared with those of samples with LOI lower than 28%. Samples e, f and g treated with 5% solutions of reagents corresponding to the above mentioned E, F and G gave LOI lower than 28% because of insufficient contents of flame retardant elements, which resulted in showing higher area values compared with those of samples E, F and G.

Concerning individual gas products, it is highly required to pay attention to the generation of a toxic gas acrolein. Flammable untreated sample A obviously showed a distinguished value followed by sample B treated with urea decreased to less than 40% though without flame retardance. On the other hand, flame retardant samples E and F treated with 20% solution of chlorides gave only 1/2 the amount from sample B, particularly sample G with the highest LOI treated with 20% solution of NH_4Br exhibited much more reduction down to less than 6%. Such reduction of hazardous gas acrolein compared with those of other samples is very favorable phenomenon, which is probably due to the synergistic effect of N and Br. However, comparison of this effect with that of N and P shown in the previous section 1) reveals that the synergistic action of N and P is much more effective than that of N and Br since acrolein entirely disappeared from sample with the synergistic effect of N and P but not in the case of sample G containing N and Br. As to furan, the values of flammable samples A and B overlapped on a level the same as that of acrolein from sample B, whereas flame retardant samples E, F and G all showed just 1/2 those of sample A and B.

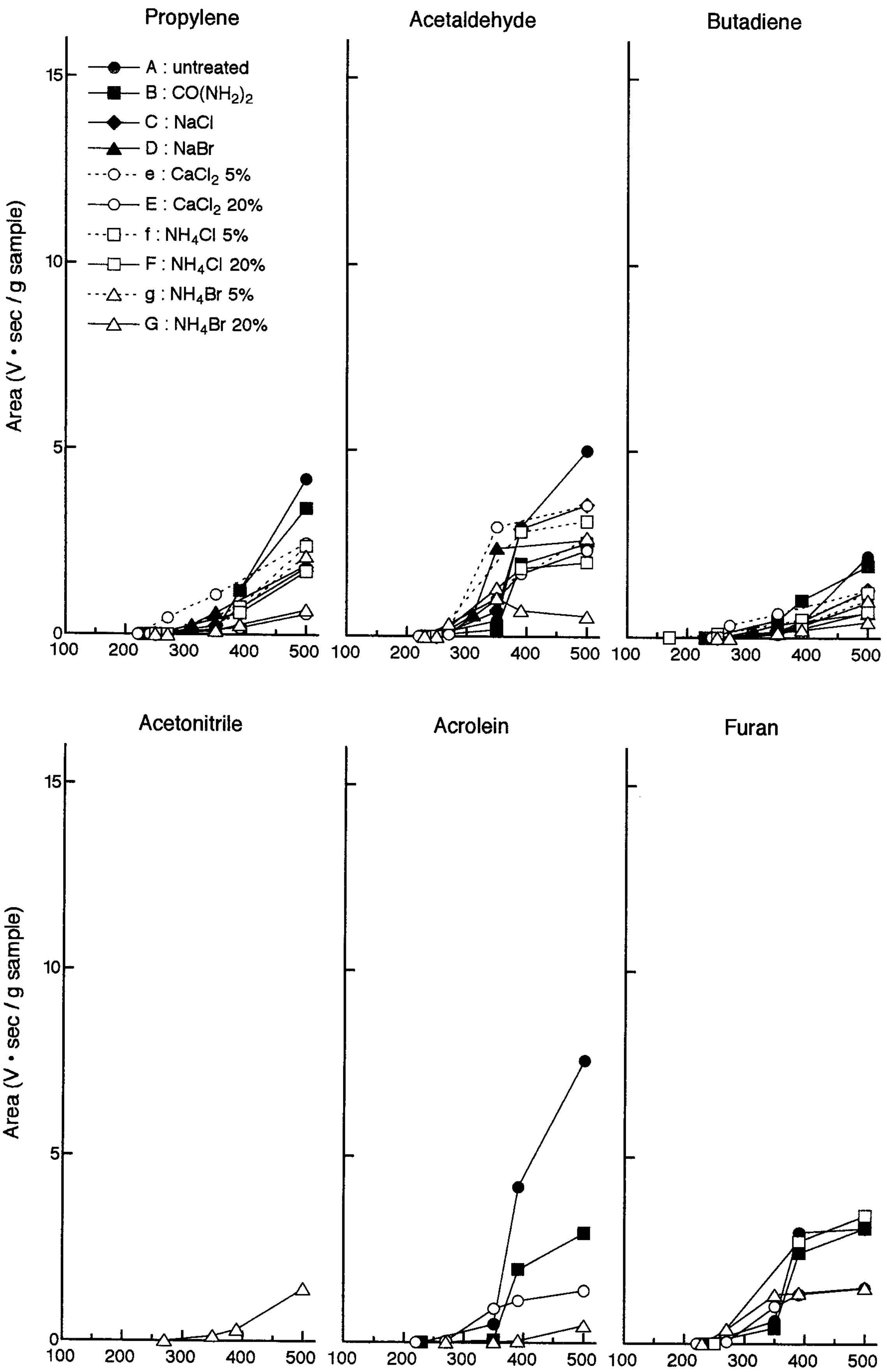
In the case of samples treated with sodium salts (C and D) and 5% solutions (e, f and g) having LOI values less than 28%, acrolein and furan did not allow sufficient separation and appeared as a combined peak on each chromatogram which are shown as the summed values in Fig. 6-45. At any rate, it can be supposed that the amounts of acrolein from these samples can be estimated at fairly less than that from the untreated sample. Thus, the above fact obviously confirmed a merit of treating any flammable sample with these compounds since all treated samples more or less inhibited the generation of very toxic acrolein.

The fact that acetonitrile, a pyrolytic gas scavenger as mentioned above, was detected only from sample G is quantitatively shown in this figure, which can be due to the synergistic effect of N and Br though less than that observed in the case of N and P described in the previous section 1).

The amounts of acetone and acetic acid, both possessing acetyl group all settled compactly on the same level particularly acetic acid was detected in only slight amounts, even undetectable in the case of NH_4Br-treated sample.

Methylfuran showed the largest amounts also in this case, and special attention was drawn to the fact that the amounts of methylfuran from samples containing chloride including sodium salt of Br exceeded the untreated sample. Sample e treated with 5% solution of $CaCl_2$ showed the highest amounts, 1.6 times and almost 1.4 times those from the untreated sample at 390°C and 500°C respectively. Samples treated with NH_4Br exhibited lower values, especially sample G treated with 20% solution gave the amount only 1/3 that of the untreated sample.

In contrast to furfural, 5-methyl-2-furfural with addition of a methyl group to furfural showed the amounts only 4% (urea-treated sample) - 25% (NaBr-treated sample) of those of furfural and even undetectable in the cases of samples C, e and E containing sodium and calcium chlorides and also sample G treated with 20% solution of NH_4Br.



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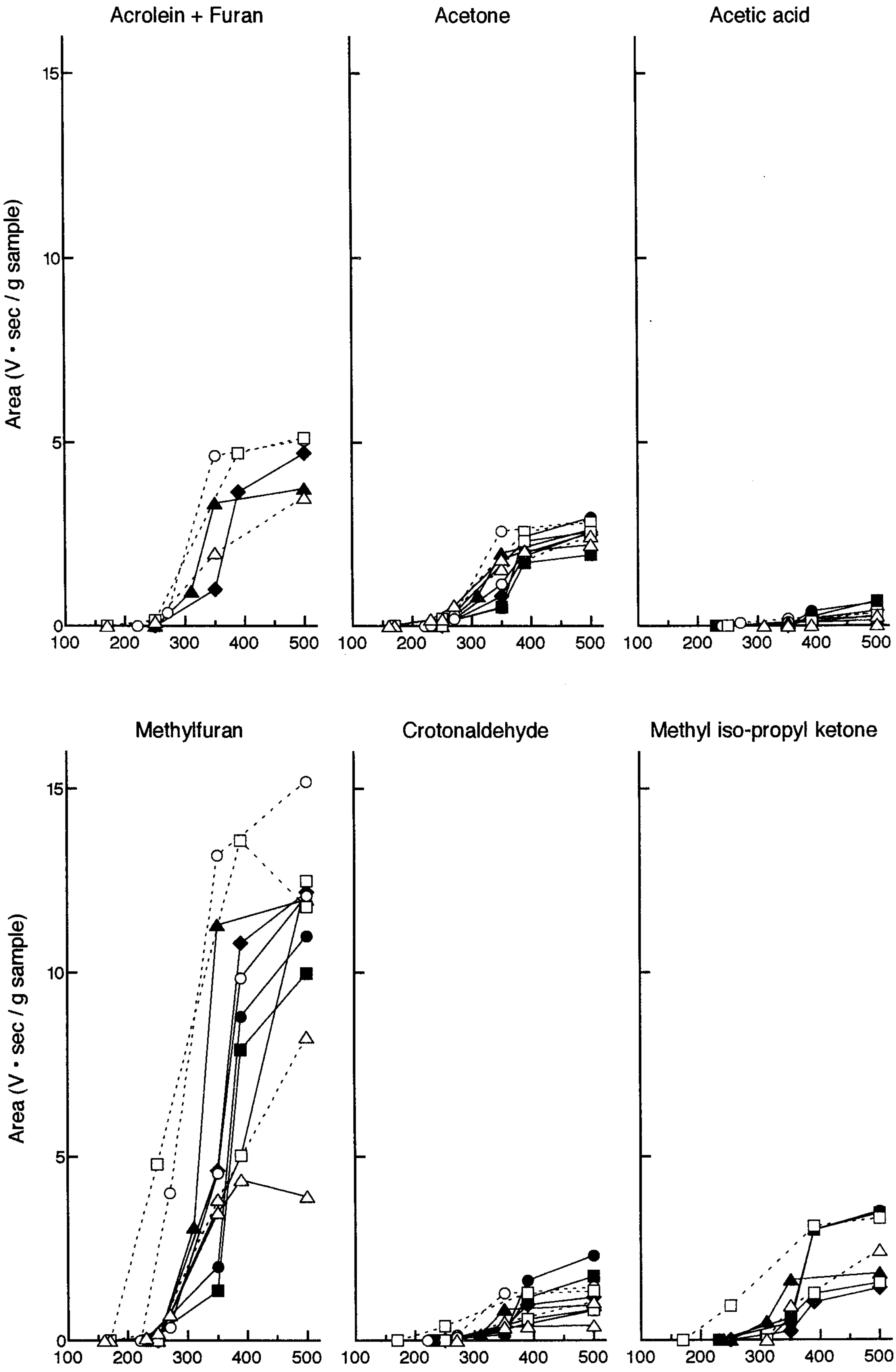

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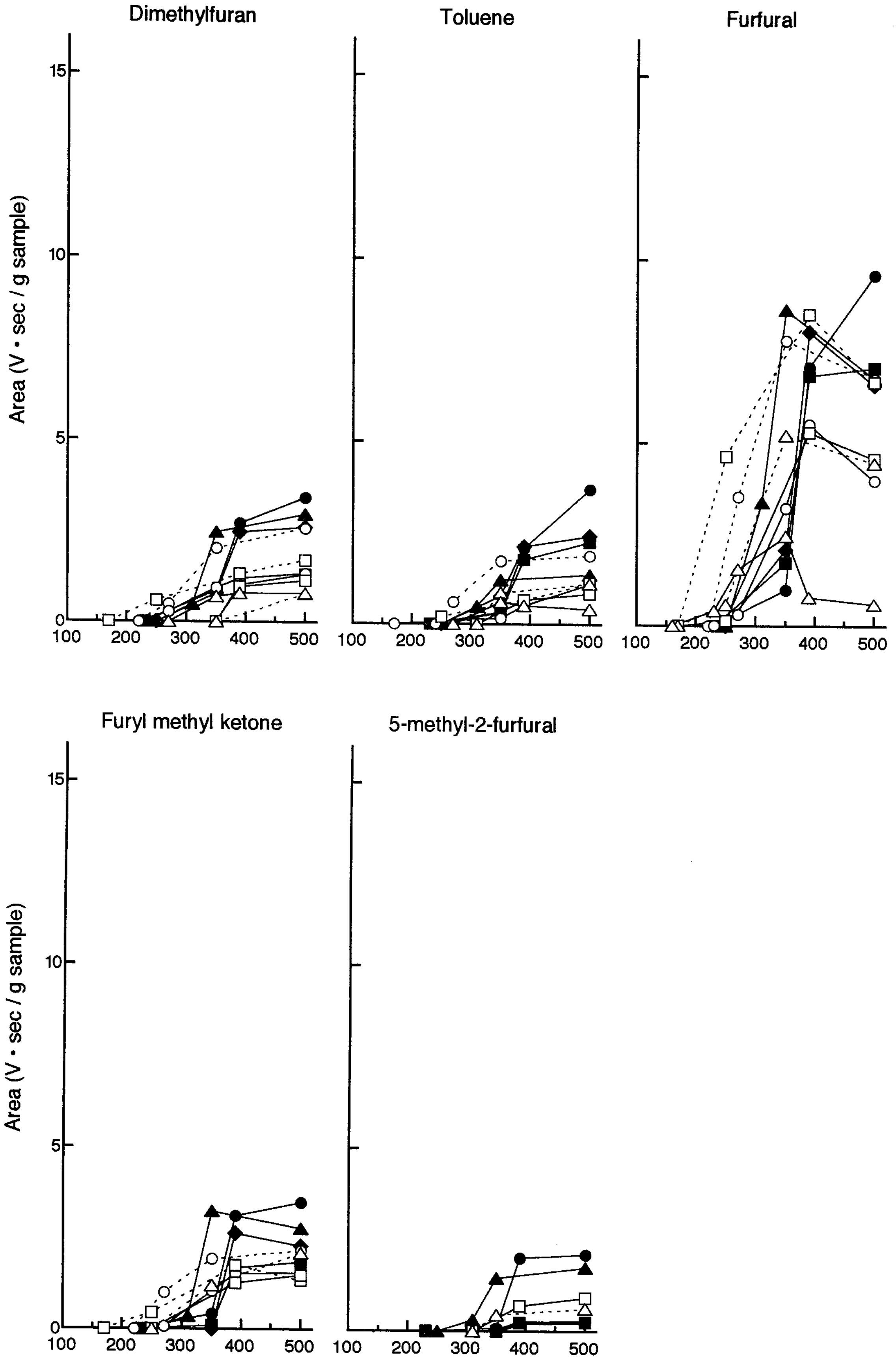
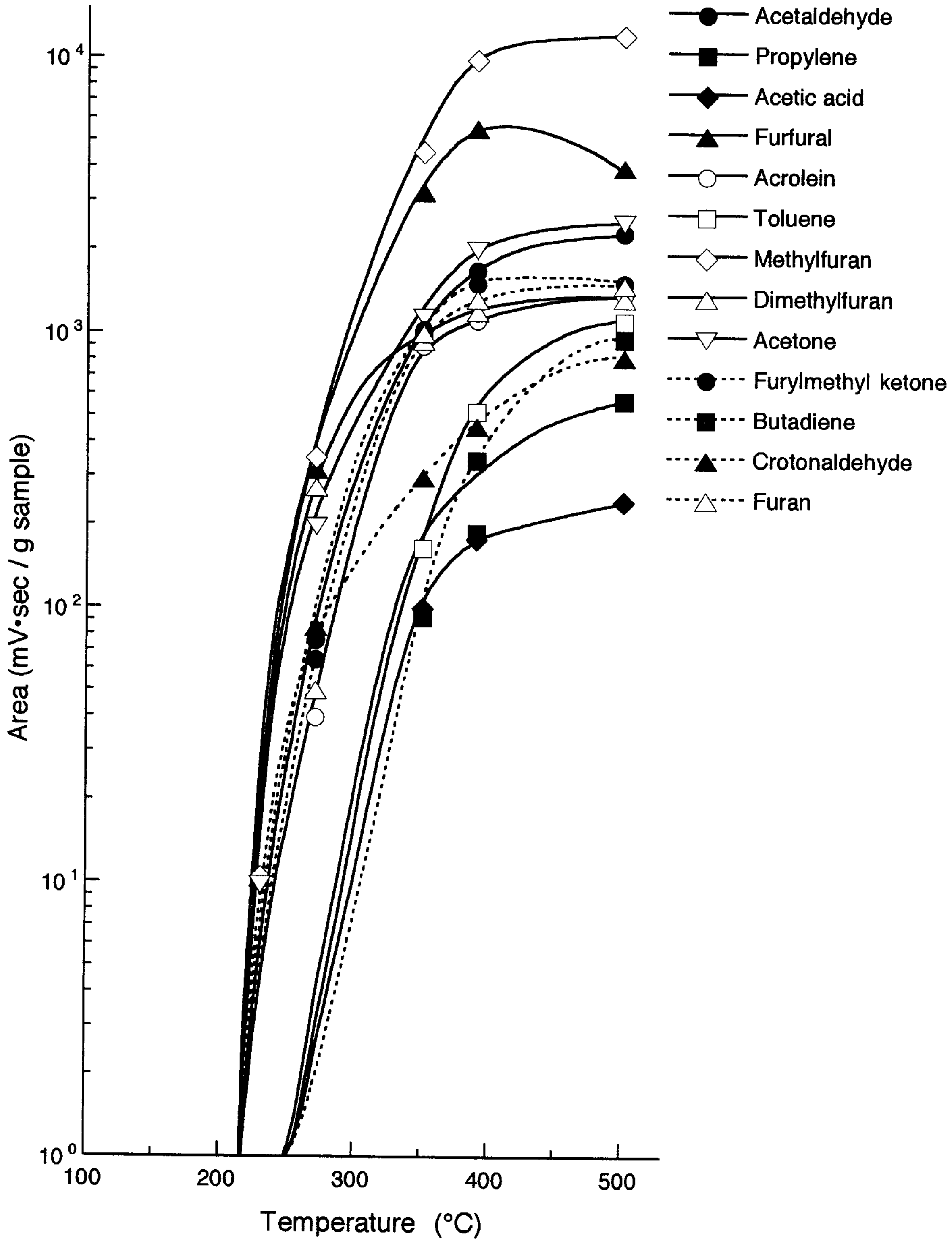


Fig. 6-45 Quantitative change in each pyrolytic gas species observed with temperature rise in the thermal degradation process.

Sample E {treated wiht $CaCl_2$ (20%)}



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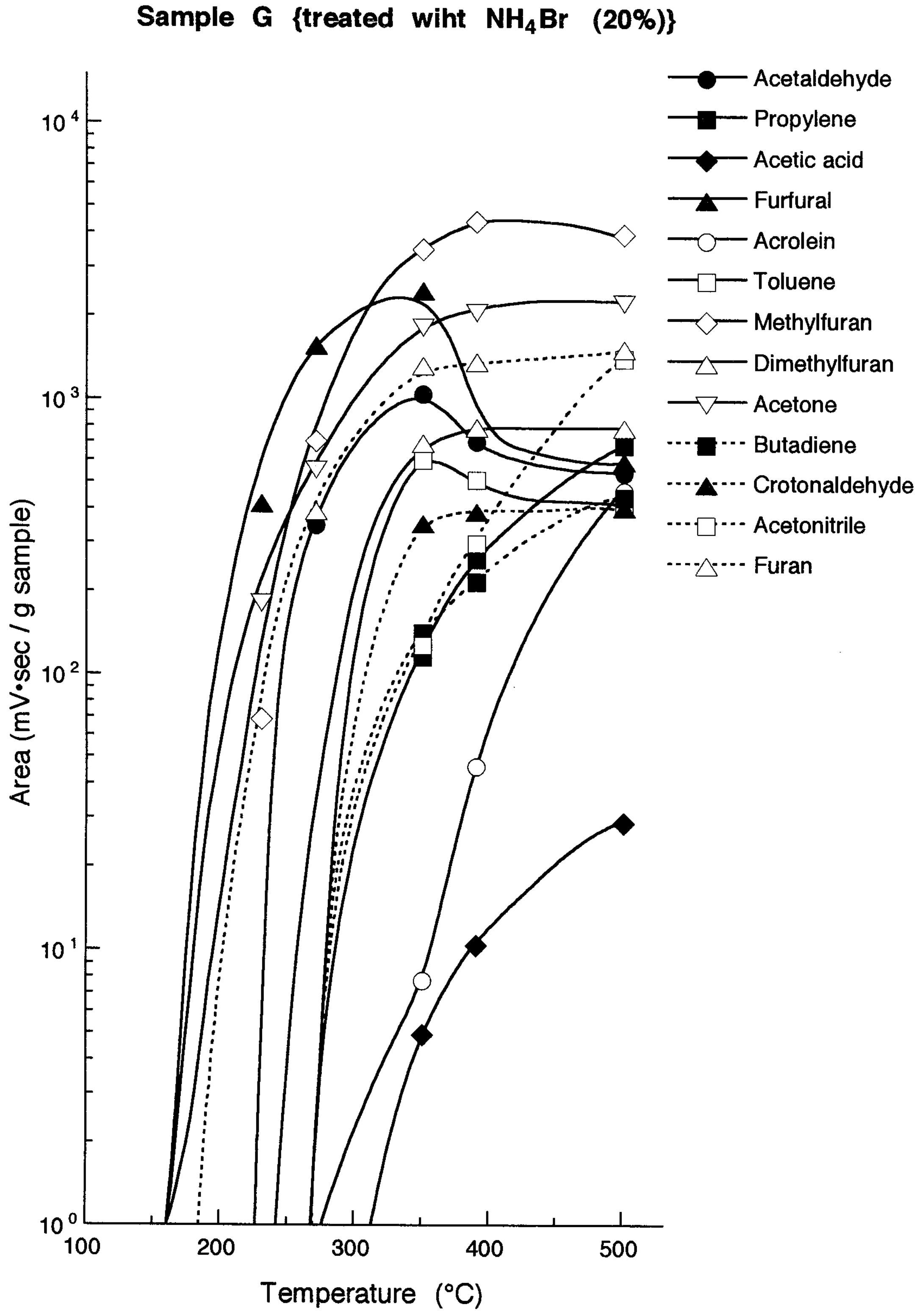


Fig. 6-46 Area vs temperature curves of all gas species from individual samples for comparison of pyrolytic gas generation behavior between flammable and flame retardant samples.

(4) Area vs temperature curves for relative comparison of pyrolytic gas generation behavior among all gas products from each sample as well as difference between flammable and flame retardant samples

Fig. 6-46 shows area vs temperature curves of all gas species generated from individual samples to compare gas generation behavior among all gases produced from each sample and to see any difference between behavior of flame retardant sample and that of flammable sample. In this case, untreated sample A was selected as a representative flammable sample and sample E and G with the highest LOI values as representative flame retardant materials for the comparison between with and without flame retardance.

As already shown in the previous section, untreated sample A showed 18 peaks in the gas chromatogram of which 16 species were identified and every gas product is quantitatively plotted on the logarithmic scale against temperatures. All gases showed rapid increase from 230°C to 390°C, particularly between 350-390°C followed by gradual ascending slope.

Expressing the peak area by mV·sec/g sample, the largest 3 species are methylfuran (11000), furfural (9500), acrolein (7500) followed by acetaldehyde (5000). On the other hand, acetic acid and benzene are only 5.5% and 3.6% of methylfuran respectively. The rest 10 species compactly align between 4000 and 2000. Furan and acetone are almost overlapped each other.

In contrast to such flammable sample, flame retardant samples showed different behavior as follows : Sample E treated with 20% solution of $CaCl_2$ with LOI value considerably higher than 28% gave 13 gas species, less than that of the untreated sample by 3 gas species, methyl isopropyl ketone, 5-methyl-2-furfural and benzene. Attention should be paid to considerable decrease in a hazardous gas acrolein. As to other gas products, all species but methylfuran showed also reduction compared with the untreated sample, i. e., only methylfuran exhibited about 9% increase unusually but other species showed more or less decrease, acetone down to 86%, acetaldehyde to 56%, butadiene and propylene to 47-45%, furfural and furyl methyl ketone to 42-41% respectively, dimethylfuran, crotonaldehyde and acetic acid down to 38-37% and toluene down to 29%. The overall reduction seems to be considerable though all gases but furfural showed increasing tendency with temperature rise. In the case of another flame retardant sample G treated with 20% solution of NHBr with the highest LOI exceeding 38%, more reduction with disappearance of several gas species, was observed, i. e., at the final point 500°C, decreases in the amounts of acetic acid and furfural reached down to 5-6% and those of toluene and acetaldehyde down to about 11%, those of butadiene, propylene and crotonaldehyde to 17-20%, that of dimethylfuran to 29%. Methylfuran with the largest yield showed a reduction down to 1/4 that of the untreated sample though the above mentioned sample E produced much more amount exceeding that of the untreated sample. Above all, what the attention should be focused on is that a gas scavenger acetonitrile was generated only from this sample having the synergistic effect of N and Br. Such ability for the formation of acetonitrile observed with this sample G seems to bear comparison with that shown by the sample with the synergistic effect of N and P reported in Part 1. But, obvious difference is found between decreasing tendencies shown by both samples, i. e., the sample containing N and P exhibited marked decrease in all gas species but acetonitrile, even disappearance of many gas species at 500°C, whereas only 3 species showed some reduction in the case of the sample containing N and Br. Such difference in area vs temperature curves also confirms lower synergistic effect of N and Br compared with that of N and P mentioned in the previous section.

(c) Conclusion

In conclusion, the overall characteristics of pyrolytic gas generation behavior is that flame retardant samples E, F and G with LOI values higher than 28% treated with 20% solution of $CaCl_2$, NH_4Cl and NH_4Br respectively showed less amounts of almost all gas products with disappearance of some gas products, particularly sample G with the highest LOI because of the synergistic effect of N and Br exhibited the least amounts in every gas species with disappearance of more species though such inhibiting ability of the synergistic effect of N and Br on the pyrolytic gas generation is comparatively less than that of N and P reported in Part 1. As to the generation of pyrolytic gas scavenger acetonitrile, one of the important factors for the flame retardance, the generated amount from sample G containing N and Br is less than that of P-containing sample in combination with N. The above results, also taking the above mentioned generation of acrolein into consideration probably suggest that the synergistic effect of N and Br observed by this study is less than that of N and P shown by the previous study described in Part 1.

6-2-2 Overall Pyrolytic Gas Production by Instantaneous Heating

1) Effects of Nitrogen an Phosphorus

In addition to the observations for pyrolytic gas generations by collecting gas products at gradually rising temperatures with proceeding of the thermal degradation, alternative investigation was thought to be required to get some more practical information, i. e., in the case simulating any instantaneous exposure to high temperature heat source such as fire outbreak. Further investigations were attempted by instantaneous heating to observe overall pyrolytic gas production and effects of flame retardant finishes.

(a) Experimental

(1) Materials

(i) Substrate

One hudred % Cotton fabric the same as that used for the previous investigations was purified by Soxhlet extraction with chloroform-methanol (1:1 vol/vol) for 24 h in the case.

(ii) Reagents

Compounds used for treatments are shown in Table 6-8. Ammonium hydroxide (NH_4OH) and urea were used as nitrogen sources, phosphoric acid (H_3PO_4) as phosphorus sources, and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] as a compound containing both nitrogen and phosphorus in the same molecule. N-source and P-source compounds were combined for studying the effect of the combination of N and P in comparison with $(NH_4)_2HPO_4$.

Table 6-8 Limiting Oxygen Index (LOI) of untreated and treated cotton samples.

Reagent		LOI (%)
	Untreated	18.9
20%	urea	22.2
20%	NH_4OH	19.0
5%	H_3PO_4	28.1
20%	H_3PO_4	46.1
20%	Na_2HPO_4	22.2
20%	urea + Na_2HPO_4	23.5
5%	urea + H_3PO_4	24.8
20%	urea + H_3PO_4	46.1
20%	NH_4OH + H_3PO_4	43.1
5%	$(NH_4)_2HPO_4$	24.4
20%	$(NH_4)_2HPO_4$	43.4

(2) Methods

(i) Treatment

Five percent and 20% solutions of the above mentioned reagents were prepared, with which the purified cotton fabric was treated as mentioned in 6-2-1.

(ii) Pyrolysis Gas Chromatography (PGC)

★ Apparatus

A high-frequency induction-heating-furnace pyrolyzer, Type JHP-2 (Nihon Bunseki Kogyo) was connected with a gas chromatograph (GC) Type 063 (Hitachi Seisakusho) with a FID detector to pyrolyze and analyze pyrolytic gases simultaneously. The data were treated with Chromatopack C-R1B (Shimadzu Seisakusho)

★ Conditions for analysis

Pyrolysis: Three kinds of Pyrofoiles (foils made of ferromagnetic derivatives, Nihon Kagaku Kogyo) for 445, 590 and 764°C were selected for representative pyrolysis. A 200-300μg portion of a sample, precisely weighted, was wrapped with a foil and pyrolyzed by high frequency heating. The furnace temperature was 160°C and the pipe temperature was 210°C.

The thermal treatment was carried out in N_2 flow by the instantaneous pyrolysis which reaches the fixed temperature within 0.2 s. This is to avoid or minimize the influence of oxidation and secondary decompositions.

GC analysis: Gas products were analyzed by GC with the same column under the same condition described in 6-1-1.

PGC-MS analysis: Gases produced by instantaneous pyrolysis mentioned above were identified by PGC-MS analysis under the condition the same as that described in 6-1-1.

(iii) Evaluation of Flame Retardancy

Flame retardance of each sample was evaluated by LOI method as mentioned in the previous sections.

b) Results and Discussion

(1) Temperature Dependence of Pyrolytic Gas Formation

The purpose of this experiment was to determine the optimal heating conditions with reliability for the present study. An attempt was made to observe pyrolytic gas formation in three temperature ranges, i.e., 400-500°C, around 600°C and 700-800°C.

The result of GC analysis clearly showed a temperature dependence of pyrolytic gas formation as illustrated in Fig. 6-47. The amounts of hydrocarbons with low boiling point increased with a rise of temperature and showed a remarkable increase in a temperature range higher than 700°C. This tendency is similar to that shown by Hofmann and Raschorof [11]. On the contrary, the amounts of acetol, dimethylfuran, furfural, 5-methyl-2-furfural, and peaks n.i. (not identified) No.8 and No.19 decreased with a rise of temperature. No.19 decreased with a rise of temperature. No.19 gas was characterized by fragment ions of m/z = 29, 57 and 69, and by molecular weight of 114 which is the highest among those of the pyrolytic gaseous compounds detected in this study. The same pyrolytic product was observed from cellulose by Wedley [12] as a not-identified product.

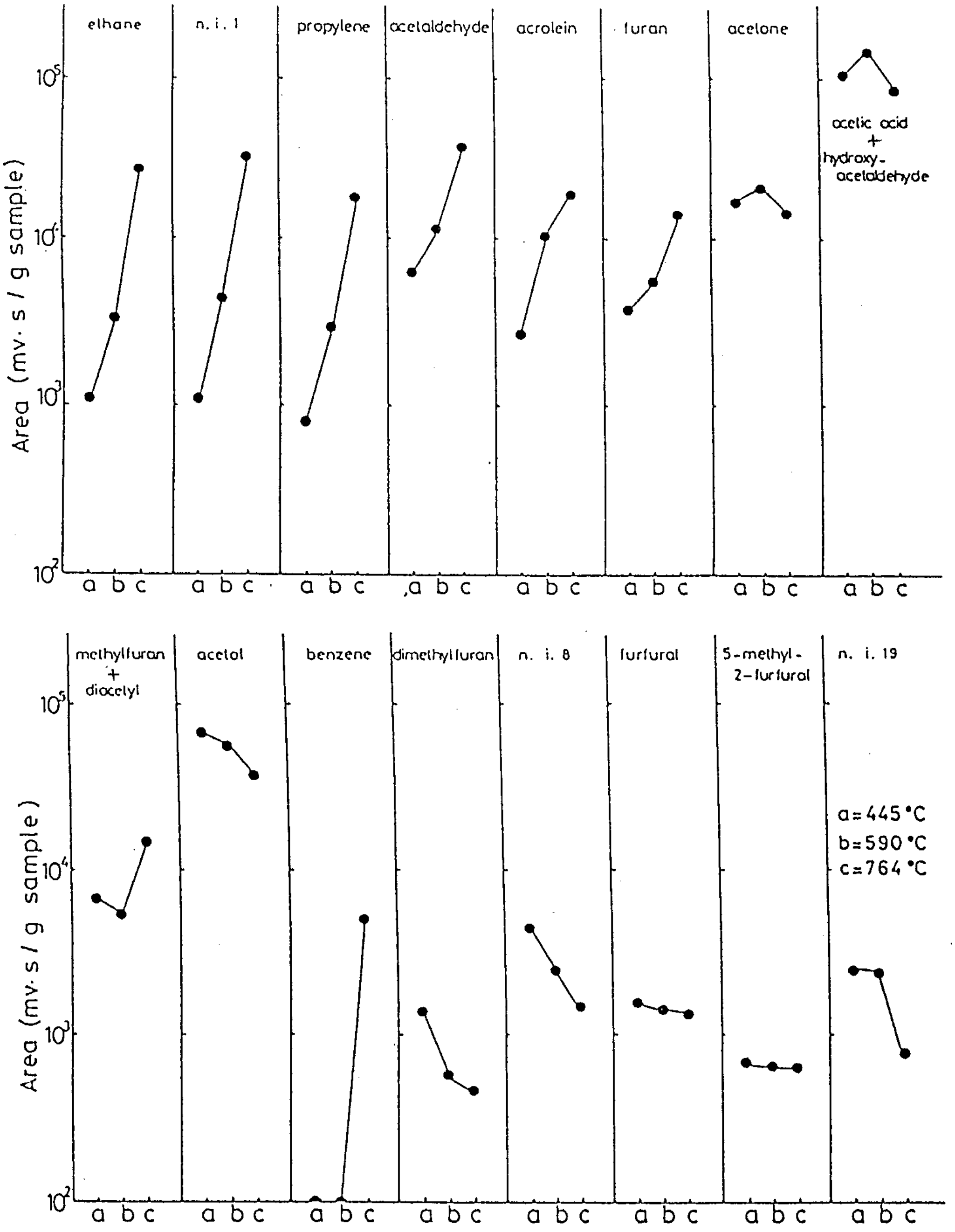


Fig. 6-47 Temperature dependence of the formation of gaseous products from cotton fibers. Pyrolyzed at (a), 445°C ; (b), 590°C ; (c), 764°C.

The comparison of furan (without -CH_3 group), methylfuran (with one -CH_3 group) and dimethylfuran (with two $-CH_3$ group) showed that the amounts of furan and methylfuran increased whereas that of dimethylfuran decreased as the temperature rose. Such a tendency means that the scission of $-CH_3$ group from dimethylfuran occurred to form methylfuran and/or furan. The decrease in the amount of furfural suggests another route to furan by removal of -CHO group from furfural.

The amounts of compounds with boiling point from 60°C to around 115°C, i.e., acetone, hydroxyacetaldehyde and acetic acid, showed maxima at around 600°C and decreased at 700°C or higher. The amount of benzene increased markedly, as much as 50 times, above 700°C. This suggests that the formation of benzene is attributed to the double-bond formation between C atoms through dehydration of cellulose in thermal decomposition.

Above findings show that the thermal decomposition was insufficient in a range of 400-500°C and too much proceeded in a range of 700-800°C. Therefore, the pyrolysis temperature of about 600°C is the most appropriate for the purpose of this study.

(2) Effect of N and P on Pyrolytic Gas Formation

(i) Effects on LOI

The LOI value was chosen as an indicator of flame retardance to examine the relationship between flame retardance and the pyrolytic gas formation. A high LOI value means that the material requires higher concentration of oxygen to keep burning, and the LOI of 27-28% is regarded as the critical level for the material to be flammable.

Table 6-8 shows that samples treated with compounds containing N or P alone except those treated with H_3PO_4 had LOI values lower than the critical level, 27-28%. High LOI values of H_3PO_4-containing samples can be attributed not only to P element but also to high moisture content owing to hygroscopicity of H_3PO_4. High flame-retarding effect was also observed for the sample treated with 20% $(NH_4)_2HPO_4$, probably because of the synergism of N and P. However, those treated with a mixture of urea and Na_2HPO_4 showed little flame-retarding effect though this mixture contains both N and P. This fact suggests that the contribution of N and P together to flame retardance requires a proper composition of the elements to show the synergism for flame retardation. It was also found that the insufficient add-on of flame retardants failed to give flame retardancy.

Taking the above results into consideration, attention was paid to the relationship between LOI values and pyrolytic gas formation. PG chromatograms of untreated and treated samples obtained by PGC-MS analysis showed approximately 46 peaks of pyrolytic gaseous compounds. Of these, we paid attention to 19 compounds definitely identified and two unidentified compounds, No.8 and No.18, which showed markedly different behavior in the formation between flame retardant samples and flammable samples with low LOI values.

Fig.6-48 shows relative amounts of these pyrolytic gaseous compounds from various samples. The amount from the untreated sample is indicated by a broken line for each product. In this figure, the following different behavior is observed between the untreated sample and the samples containing N and/or P, and also between samples with high LOI values and those with low LOI values.

(ii) Reduction of Flammable Gas Formation

The amounts of propylene, acetaldehyde, butadiene, acrolein, acetone, hydroxyacetaldehyde, acetol, benzene, dimethylfuran, ethane and n.i. No.8 from flame retardant samples were considerably less than those from flammable samples with low LOI values (see Table 6-8), e.g., acetaldehyde and benzene decreased to 1/8 - 1/13; acetol to 1/30 - 1/40; and, acetone, hydroxyacetaldehyde, dimethylfuran and n.i. No.8 entirely disappeared.

(iii) Inhibition of Acrolein Generation

Samples without flame retardance such as those treated with urea or NH_4OH, containing N alone, showed little change in the generation of acrolein. Those treated with Na_2HPO_4 alone or urea + Na_2HPO_4 showed only a small decrease. On the other hand, flame retardant samples treated with $(NH_4)_2HPO_4$, H_3PO_4, urea + H_3PO_4 and NH_4OH + H_3PO_4 etc. showed much larger reduction. Byrne et al. [105] suggested that the presence of P and/or N might inhibit the formation of acrolein.

(iv) Increase in the Amount of Unsaturated Compounds

Methyl vinyl ketone, furan and its derivatives, i.e., methylfuran, furfuran and 5-methyl-2-furfural containing carbon-carbon double bonds produced from the treated samples showed an increase in amount as compared with those from the untreated sample. A larger increase was observed for the samples containing N and P with higher LOI values. These products are likely to be related to char formation, because the findings well correspond to the observation of IR absorption spectra of residual condensed phase obtained by the thermal treatment of cellulose-ammonium phosphate [114].

Since peaks of methylfuran and diacetyl could not be resolved from each other, combined values are indicated in Fig. 6-48. However, the amounts of methylfuran can be calculated from the relative molar ratios of methylfuran and diacetyl based on the intensity ratios in the fragmentation patterns obtained by PGC-MS analysis. The molar ratio of methylfuran is around 10% for the untreated sample, 24% for samples containing P alone, 38% for those containing N alone and up to 66% for those containing both N and P. The result by Hofmann and Raschorof [108] also showed a similar tendency, i.e., finished samples generated methylfuran twice as much as unfinished sample.

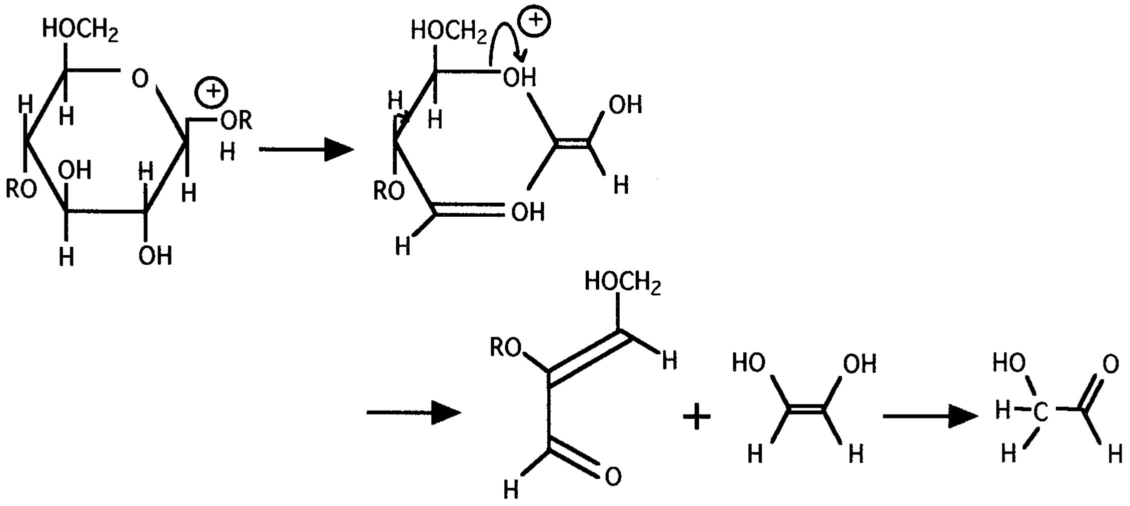
(v) Acetonitrile Generation

Acetonitrile to which we paid a special attention in the previous section 6-2-1 is an extremely useful substance for flame retardation as a radical scavenger in the vapor phase. Acetonitrile was detected neither from untreated sample nor from those treated with compounds containing N or P alone, but was generated from samples containing both N and P. It is notable that samples with high LOI values treated with 20% $(NH_4)_2HPO_4$, NH_4OH + H_3PO_4 and urea + H_3PO_4 gave the largest amounts, whereas samples with low LOI values because of the low level of add-on yielded much less amounts of acetonitrile even though they contain both N and P. This fact confirms a close relationship between the formation of acetonitrile and the flame retardancy.

According to Garn and Denson [106], acetonitrile is formed from acetic acid, a pyrolytic product from cellulose, and ammonia generated from flame retardants, e.g. ammonium salts, with the aid of catalytic action of P. Acetonitrile is converted into nitrogen oxides which play a role to give the self-extinguishability by acting as an inhibitor for radical side chain reactions. In contrast to our results, Hofmann and Raschorof [108] reported the production of very toxic and explosive acrylonitrile from fabric finished with a durable flame retardant Pyrovatex CP produced by Ciba Geigy Co.. This difference is probably due to the difference between ammonium salts and the organic phosphonocarbamate containing $-CH_2CH_2CONHCH_2OH$. Acrylonitrile was detected also in our investigation for a sample treated with Pyrovatex.

The quantitative change in the amount of acetic acid is important in connection with the formation of acetonitrile. Acetic acid was detected as a shoulder of the peak of hydroxyacetaldehyde for the untreated sample and samples treated with compounds containing N or P alone. On the other hand, hydroxyacetaldehyde disappeared and only acetic acid became detectable for samples treated with $(NH_4)_2HPO_4$ (Fig. 6-49).

According to Byrne et al., [105], hydroxyacetaldehyde is formed for 1,2-ethenediol, an intermediate pyrolytic product generated by the splitting of a glucose unit through the following process:



The pyrolysis of the untreated sample or samples containing N or P alone will proceed mainly through this route.

On the other hand, it has been considered that acetic acid is formed from ketene, a dehydration product of hydroxyacetaldehyde, by the addition of water generated during the pyrolysis of cellulose. When samples treated with $(NH_4)_2HPO_4$, containing N and P together, are pyrolyzed, this process seems to proceed mainly to form acetic acid.

The compound n.i. No.18 is also worth paying attention since it was detected in a very large amount only from samples containing $(NH_4)_2HPO_4$ and/or H_3PO_4. This product showed fragment ions of m/z = 39, 53 and 68, typical for furan. The molecular weight determined by CI-MS was 96 which is the same as that of furfural.

(vi) Comparison of Total Amounts of Pyrolytic Gases

Fig.6-50 shows the total amounts of pyrolytic gases from the samples. The untreated sample gave the largest amount and those treated with NH_4OH (B) and Na_2HPO_4 (D) containing N or P alone showed slightly lower level of gas formation. Such findings are consistent with their low LOI values, whereas samples containing urea (A, E, F, G) showed less amounts than B or D though they contain N alone and LOI values are low just as samples B and D. All samples with high LOI values gave less amounts of pyrolytic gases. Sample J treated with 20% $(NH_4)_2HPO_4$ showed the least amount exhibiting a synergistic effect of N and P present in the same molecule.

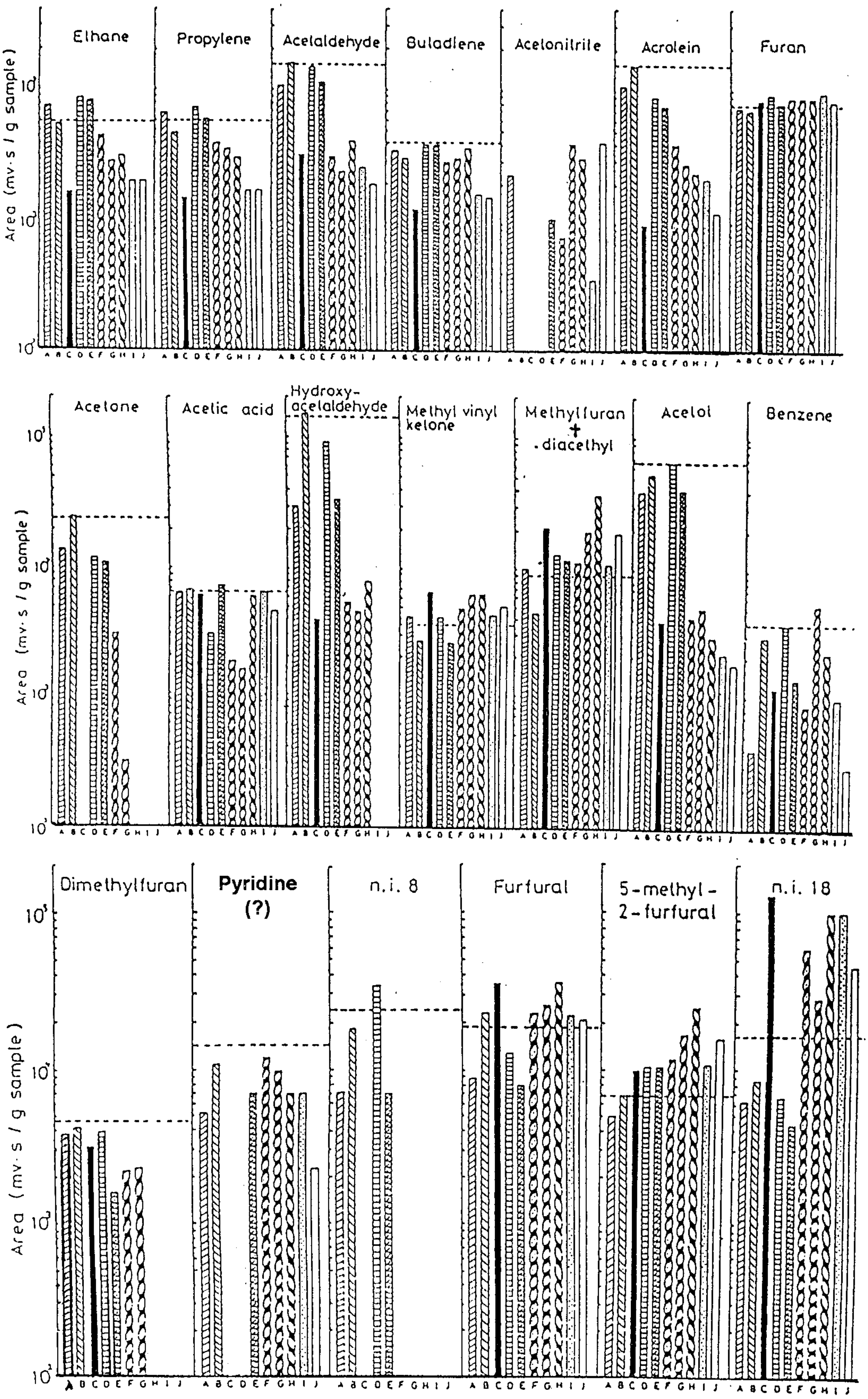


Fig. 6-48 Gaseous products from untreated and treated cotton samples, ----, untreated, treated samples with : (A), 20% urea : (B), 20% NH_4OH : (C), 20% H_3PO_4 : (D), 20% Na_2HPO_4 : (E), 20%urea + Na_2HPO_4 : (F), 5% urea + H_3PO_4 : (G), 20% urea + H_3PO_4 : (H), 20% NH_4OH + H_3PO_4 : (I), 5% $(NH_4)_2HPO_4$ and (J), 20% $(NH_4)_2HPO_4$.

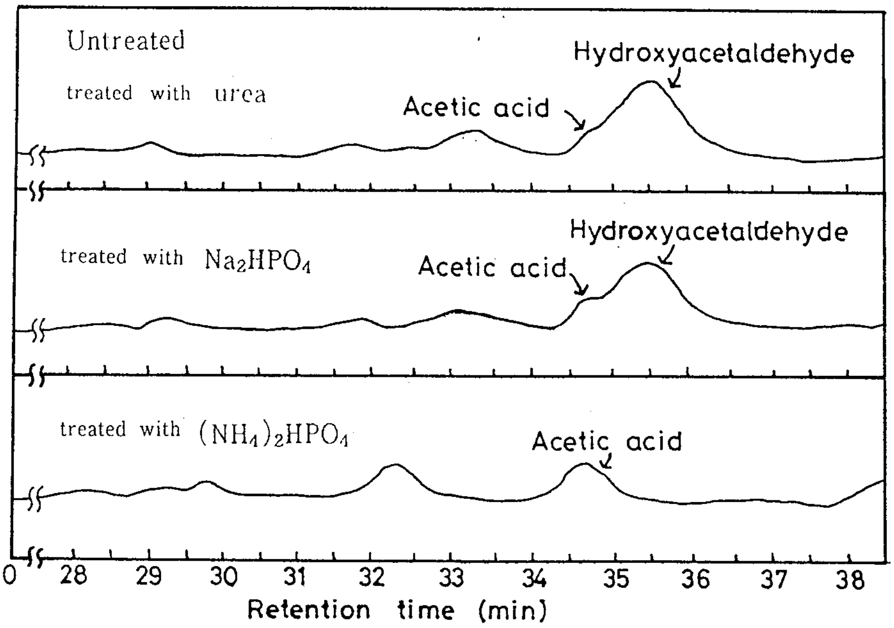


Fig. 6-49 Mutual change in amounts of acetic acid and hydroxyacetaldehyde pyrogramatically observed in untreated and treated cotton samples.

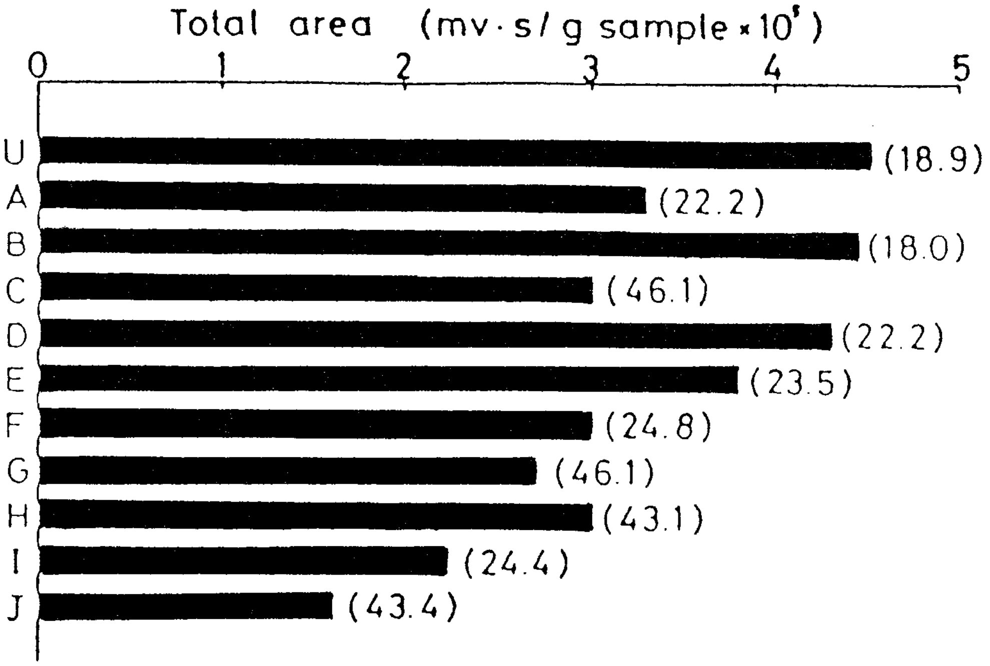


Fig. 6-50 Total amount of pyrolytic gases. (U), Untreated.
Treated samples with : (A), 20% urea : (B), 20% NH_4OH : (C), 20% H_3PO_4 : (D), 20% Na_2HPO_4 : (E), 20%urea + Na_2HPO_4 : (F), 5% urea + H_3PO_4 : (G), 20% urea + H_3PO_4 : (H), 20% NH_4OH + H_3PO_4 : (I), 5% $(NH_4)_2HPO_4$ and (J), 20% $(NH_4)_2HPO_4$.

2) Effects of Halogens on Pyrolytic Gas Production from Cellulose

Continued from the above mentioned investigation on effects of nitrogen and phosphorus on pyrolytic gas production by combustion of cellulosic fiber, this study was focused on the effects of compounds containing both halogen and nitrogen.

As to the contribution of halogens to the flame retardation mechanisms, Rosser, Simmons et al [118,119], Warren [120] and Lewin et al [121] have provided their opinions for the actions of halides in the flame retarding mechanism respectively, Lyons et al [122] have also suggested that effects of halogens in the presence of phosphorus could be attributed to the formation of phosphorus-halides complex which acts much more effectively for trapping radicals than halides of halogen oxides alone. Furthermore, Tesoro et al. [124-126,132] and Miller et al. [127-131,133] observed that cotton/polyester blend samples showed considerable increase in LOI values by combination of phosphorylation and treatment with a bromine-containing-organic phosphate. These results seem to suggest the synergistic effect of halogens and phosphorus on the flame retardation of flammable fibers.

On the other hand, Garn et al [106] and Sugiura [123] investigated pyrolytic gas products from cellulosic fibers treated with compounds containing phosphorus and halogens.

However, there has been little information concerning the effects of each flame retardant element in connection with the flame retardance. Therefore, the present investigation was undertaken to extend the previous study to deal with effects of halogens. Bromine and chlorine were chosen for comparing their effects with that of phosphorus with regard to the synergism with nitrogen.

(a) Experimental

(1) Materials

(i) Cellulosic Material

Cotton fabric was purified by Soxhlet extraction with chloroform-methanol (1:1 vol/vol) for 24 h as mentioned in the previous section.

(ii) Reagents

NaCl and $CaCl_2$ as chlorine-containing compounds, NaBr as a bromine-containing compound, and NH_4Cl and NH_4Br as representative compounds for nitrogen-halogen combination in a molecule.

Simultaneously, urea, a nitrogen source, and hydrogen chloride, a halogen source, were mixed together to compare the effect of nitrogen and halogens existing in a molecule as NH_4Cl, with that of both elements combined by mixing two compounds as urea and HCl containing nitrogen and a halogen separately.

(2) Methods

(i) Treatment of Cotton Fabric

Cotton fabric was treated with 5% and 20% solutions of the above reagents as described in 6-2-1.

(ii) PGC and PGC-MS were performed as described in the previous section.

(iii) Conditions for Pyrolysis and for analysis were the same as those mentioned in the previous section.

(iv) Evaluation of Flame Retardancy

LOI of each sample was determined as described in 2-1-2.

(b) Results and Discussion

(1) Evaluation of Flame Retardance

Prior to investigating pyrolytic gas formation from the untreated and treated samples, the flame retardance of the samples was evaluated to observe the relationship between flame retardance and pyrolytic behavior. The LOI values are shown in Table 6-9 in which add-on and water contest of each sample are simultaneously shown as factors affecting to the flame retardance.

As shown here, a sample treated with urea, containing nitrogen alone, showed low LOI values. All samples containing halogens in the absence of nitrogen also gave no flame retardance except for a sample treated with 20% of $CaCl_2$, which shows a high water content.

On the other hand, those treated with 20% of ammonium halides, containing both nitrogen and halogens, showed high LOI values. Especially the LOI value of the sample treated with 20% NH_4Br is extremely high. But the sample treated with a mixture of urea and HCl did not show any flame retardance even though it contained both nitrogen and chlorine.

The pyrolytic behavior of each sample was examined by taking the above results into consideration, with attention to how these LOI values, with or without flame retardance, affected the pyrolytic gas formation.

Table 6-9 Add-on level, water content and LOI of untreated and treated cotton samples.

	Reagent	Add-on level (%)	Water content(%)	LOI (%)
A	untreated	-	7.5	18.5
B	$CO(NH_2)_2$ 20% soln.	8.2	16.9	22.4
C	$CO(NH_2)_2$: HCl = 1 : 1 20% soln.	2.7	12.8	22.7
D	NaCl 20% soln.	19.3	6.6	20.8
E	NaBr 20% soln.	13.5	9.5	20.3
f	$CaCl_2$ 5% soln.	2.0	9.9	23.5
F	$CaCl_2$ 20% soln.	15.2	15.7	31.6
g	NH_4Cl 5% soln.	2.5	9.0	21.3
G	NH_4Cl 20% soln.	12.0	10.8	28.3
h	NH_4Br 5% soln.	2.6	6.4	23.7
H	NH_4Br 20% soln.	14.5	6.7	38.2

(2) Effect of Halogens on Pyrolytic Gas Production

The type and amounts of pyrolytic gases, as determined by PGC-MS analysis, were similar when the untreated sample and the nitrogen- or halogen compound-treated samples were compared. In contrast, the samples treated with compounds containing both nitrogen and halogen in the same molecule showed markedly different pyrolytic behavior from that of the untreated sample. Such tendency is similar to that observed in the case of nitrogen and phosphorus as described in the previous section. On the other hand, the PGC analysis gave more detailed information about the pyrolytic behavior. Fig. 6-51 shows relative amounts of representative pyrolytic gases from the untreated samples and those treated with compounds containing nitrogen and/or halogens. The amounts of gases were calculated from peak areas of pyrograms obtained by PGC analysis. The level of each gas from the untreated sample was indicated by a horizontal line.

As the result of overall comparison of the pyrolytic behavior of treated samples with that of the untreated sample, the following five tendencies were observed.

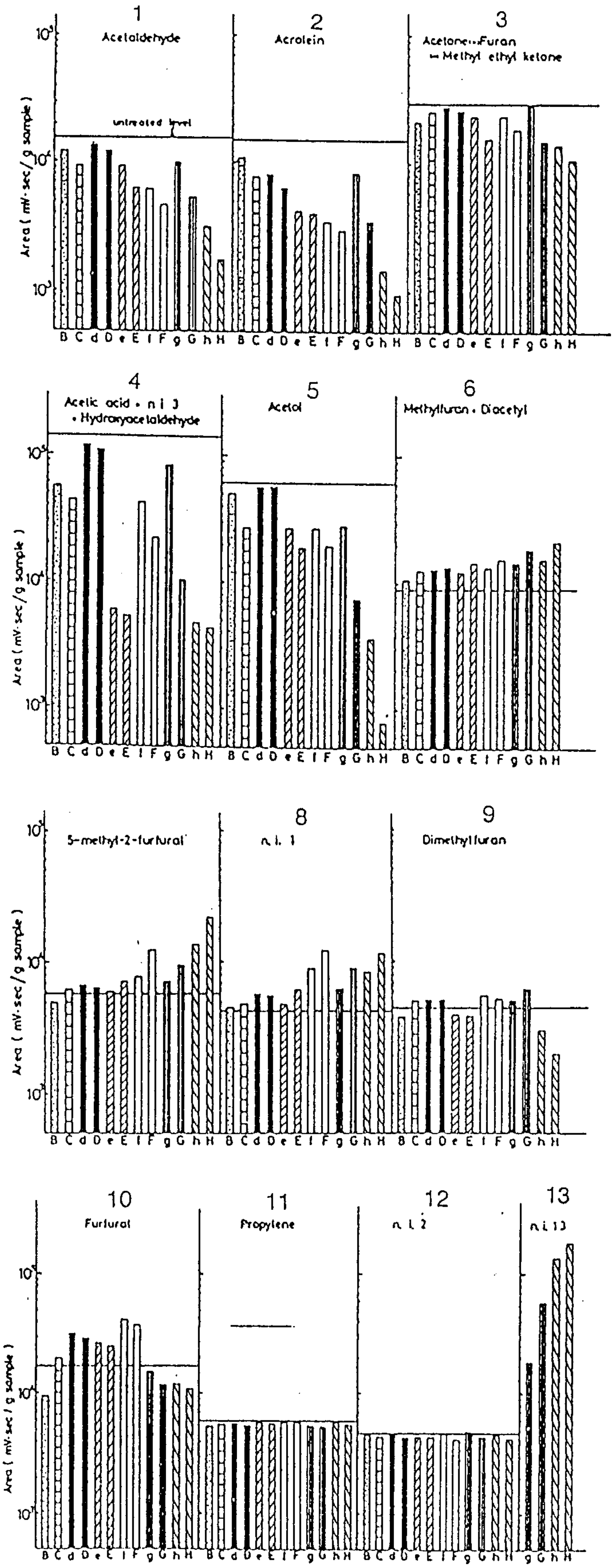


Fig. 6-51 Pyrolytic gas products from untreated and treated samples. - level for gases from untreated sample.
The treated samples B ~ H are the same as those indicated in Table 6-9.

(i) Reduction in Gas Production

A decreasing tendency in amounts was observed for (1) acetaldelyde, (2) acrolein, (3) furan + acetone + methyl ethyl ketone, (4) acetic acid + hydroxyacetaldehyde + non-identified (n.i.) compound No.3 (presumed molecular weight is 66) and (5) acetol. Here, (3) and (4) were shown as combined amount of the above mentioned three compounds because the present PG chromatograms lacked sufficient resolution for accurate determination of each component. Compositions of (3) and (4) from every sample are as follows.

As to (3), this fraction from the untreated sample contained all three compounds, but that from all treated samples contained only one or two components out of the three as shown in Table6-9. Furan was detected from all samples in the presence of nitrogen, but not from those in the absence of nitrogen. It was also found that methyl ethyl ketone ($CH_3COC_2H_5$) was detected from the samples containing chlorine, while acetone (CH_3COCH_3) from those containing bromine. Thus, a difference in components of flame retardants, i.e., chlorine and bromine, gave two kinds of ketones which differ in alkyl groups, CH_3 and C_2H_5, from each other.

On the other hand, in the case of (4), the aforementioned three compounds were observed with all treated samples but 2-3 samples which showed only trace.

Comparing the amounts of compounds (1) - (5), the untreated sample itself showed some difference, i.e., (1) and (2) are almost the same, (3) is about twice, (5) is 4 times and (4) even 10 times those of (1) and (2). The flame retardant samples treated with 20% solutions of $CaCl_2$ (F), NH_4Cl (G) and NH_4Br (H) gave a large reduction of gas formation. Especially sample H with the highest flame retardancy showed the largest reduction, which exhibited the most remarkable inhibiting effect on pyrolytic gas formation. But 5% solutions of the same flame retardants (f. g. h) gave less reduction probably because of insufficient add-on. The above finding proves that the flame retardance and the reduction of gas formation show a good agreement.

It should be emphasized that the samples treated with NH_4Br, both 5% and 20% solutions, performed a remarkable inhibiting effect on a toxic gas acrolein reducing down to 1/4 - 1/6 of those from the samples treated with NH_4Cl and even to 1/7 - 1/10 of that from the untreated sample.

Concerning the effect of bromides on (4), it is characterized that not only NH_4Br but also NaBr, both containing bromine, gave effective reduction. The samples treated with NH_4Br showed the highest inhibiting effect also on the generation of acetol. Especially an inhibiting action of sample H was such outstanding as 1/8 the amount from the untreated sample. The sample treated with 5% of NH_4Br, though without any flame retardance gave a reduction larger than those given by other treated samples. Such effect is considered to be resulted from the synergism of N and Br in

NH_4Br molecule probably due to the generation of both NH_3 and HBr. The inhibiting effect of Br compounds is better than that of Cl compounds though both are halogens.

(ii) Increase in Unsaturated Ring Products

A contrasting tendency was observed for (6) methylfuran + diacetyl. (7) 5-methyl-2-furfral and (8) non identified No.1. They showed an increase compared with those from the untreated sample. A common characteristic shown by these gases is that the amounts of these gases from F, G and H are more than those from these samples in contrast to what was shown in the previous article, i.e., a large reduction in gas formation was observed with these samples F, G and H.

Methylfuran and diacetyl were shown as a combined amount (6) because of insufficient resolution on PGC chromatogram. But relative molar ratios of both components were calculated on the basis of intensity ratios as follows: the molar ratio of methylfuran was only 10% for the untreated sample, but the treated samples showed an increasing tendency, e.g., those treated with NaCl, urea, NH_4Cl and NaBr showed 18%, 38%, 48.7% and 54.5% respectively. Further increase was observed for NH_4Br-treated samples, i.e., 68.9% when treated with 5% solution and 86.1% with 20% solution. Thus, the ratio of methylfuran was larger in the case of samples containing Br and N than those containing phosphorus and nitrogen described in the previous section. Especially NH4Br which contains bromine and nitrogen in the same molecule with the synergistic effect showed higher ratio.

Comparing these (6), (7) and (8) in more detail, much evident increases were observed for the samples F, G and H with high LOI values. This suggests that these pyrolytic products probably contribute to the flame retardance in such a way that ring compounds possessing double bounds could be precursors of char which contributes to the self-extingushability. This phenomenon agreed with the result observed with the samples containing P and nitrogen together as described in the previous section.

(iii) Increasing and Decreasing Behavior

Deimethylfuran and furfural showed both increasing and decreasing behavior depending on the treating compounds. In the case of dimethylfuran, only those treated with bromine compounds, NaBr and NH_4Br, especially with NH4Cl gave a large decrease in this gas showing the inhibiting action, while the samples containing chlorine, i.e., NaCl, $CaCl_2$, NH_4Cl and also urea + HCl showed an increase nearly to the same extent.

On the other hand, furfural exhibited some reduction only from N-containing samples, urea and ammonium halides, i.e., NH_4Cl and NH_4Br. All other sodium and calcium halides containing halogens alone gave much larger increase compared with that shown by the untreated sample.

Attention should be paid also to considerable decrease in dimethylfuran and furfural simultaneously with a large increase in methylfuran and methylfurfural in the presence of bromine and nitrogen. Such phenomena probably mean the scission of methyl group from dimethylfuran and the transfer to furan as well as to furfural to form methylfuran and methyfurfural.

(iv) Behavior of Ammonium Halides

Non-identified No.13 which corresponds to No.18 shown in the previous section showed typical behavior. This substance was presumed to be a furan derivative because of its deduced molecular weight, 96 the same as that of furan, as well as of fragment ions of furan specific m/z 39, 53 and 68. This substance was detected only from those treated with ammonium halides, NH_4Br and NH_4Cl this time. But, as described in the previous section, this was also detected from those containing phosphorus and N even without flame retardance, and not detected from any samples containing other salts even with high flame retardance. Therefore, this substance could be considered as a pyrolytic gas specifically formed from $[NH_4]$- containing compounds irrespective of the flame retardance.

As the result of investigation on the pyrolytic gas formation for every sample with a special attention to the effect of flame retardance on the pyrolytic behavior, a typical difference in behavior was observed between flame retardant samples and those without flame retardance. That is, only flame retardant samples gave clear reduction or enhancement in pyrolytic gases compared with other samples, especially the synergistic effect of nitrogen and halogens is well reflected in the pyrolytic gas formation. They showed the reduction of flammable gases and increase in unsaturated aromatic hydrocarbons as precursors of char. Such behavior agrees well with that observed in the case of the synergism of nitrogen and phosphorus described in the previous section.

(3) Overall Observation for Relationship between Total Amounts of Pyrolytic Gases and Flame Retardances

Individual relationship between the total amount of pyrolytic gases of each sample and its LOI value was compared to each other to get the conclusion from the overall standpoint. The result is shown in Fig. 6-52.

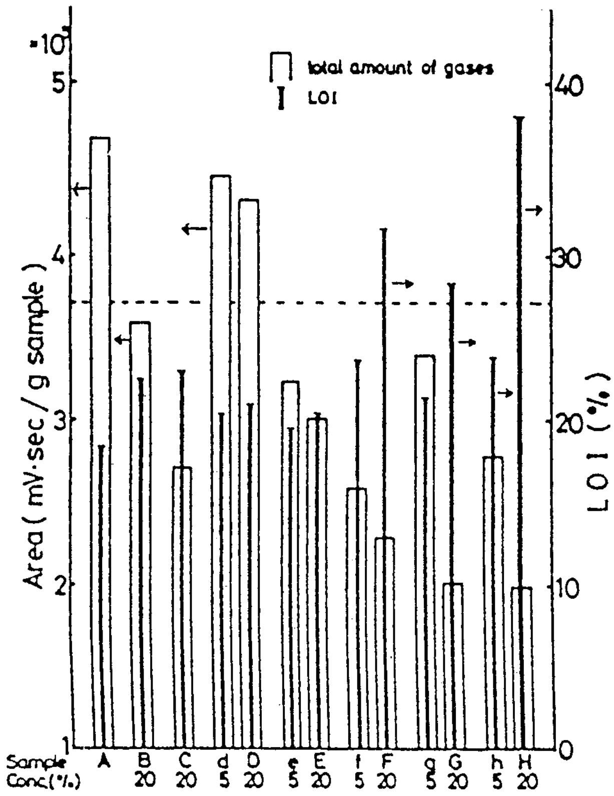


Fig. 6-52 LOI values and total amounts of pyrolytic gases from untreated and treated cotton fibers.
Samples A ~ H are the same as those indicated in Table 6-9.

Comparing LOI values among samples, samples F, G and H gave LOI values higher than 28 showing flame retardance. Comparison between G and H which showed the synergistic effect of nitrogen and halogens revealed that bromine gave considerable higher flame retardance than chlorine showing the highest LOI value. On the other hand, LOI value of $CaCl_2$ (F) was also higher than 30 which is second to H even in the absence of nitrogen. All the rest gave LOI values considerably lower than 28, showing little flame retardance. By corresponding these LOI values to the total amounts of pyrolytic gases detected from all samples, the following tendency was observed.

The samples having flame retardance all showed remarkable reduction of generated gases. In particular, ammonium halides having the synergistic effect of nitrogen and halogens gave the least amounts of pyrolytic products, only less than 40% of the amount from the untreated sample, which showed the best inhibiting effect.

Even though treated with the same flame retardants, samples g and h without any flame retardance, because of insufficient add-on, gave much more gases twice as much as those from the flame retardant samples G and H with sufficient add-on. The samples treated with NaCl without flame retardance gave large amounts. Whereas the levels for other sample treated with NaBr, a mixture of urea and HCl and 5% solutions of $CaCl_2$ and NH_4Cl were 50-68% of that for the untreated sample even though LOI values of are low. Sodium halides, NaBr and NaCl, showed LOI values approximately on the same level. But, the level of gas formation is entirely different, i.e., NaBr gave considerable reduction from the level of the untreated sample while NaCl showed much less inhibition for the gas formation.

As described above, it has been generally clarified that not only flame retardant samples but also some halides showed inhibiting effect on the pyrolytic gas formation even without flame retardancy.

(4) Comparison between Halogens and Phosphorus

It seems worth comparing effects of halogens with that of phosphorus observed between each alone and in combination with nitrogen. Comparison was attempted between the result obtained from the sample treated with Na_2HPO_4 containing phosphorus alone and that from the samples treated with sodium halides (NaCl, NaBr) containing halogens alone. Comparison was also made between the result from $(NH_4)_2HPO_4$- treated sample containing phosphorus and nitrogen and that from the samples treated with ammonium halides (NH_4Cl, NH_4Br). The following differences and similarities were observed.

(i) Qualitative Comparison

Ethane and acetylene were detected from the samples containing phosphorus alone and phosphorus + nitrogen but not from those containing halogens alone and in combination with nitrogen. Acetone was detected from the samples containing each one of phosphorus and bromine both with and without nitrogen but not from those containing chlorine. Furan generated from all samples but those containing bromine alone. Methyl ethyl ketone was detected only from those containing chlorine. On the other hand, methyl vinyl ketone was formed from those containing phosphorus alone and in combination with nitrogen, but not from those containing halogens with and without nitrogen.

(ii) Quantitative Comparison

★ Inhibition of Flammable and Toxic Gas Formation

The amount of acetaldehyde from the sample containing phosphorus alone was similar to that from the untreated sample, but those containing halogens alone gave less amounts. The samples containing phosphorus or bromine in combination with nitrogen gave the amount about 1/8 of that from the untreated sample, while NH_4Cl showed less effect (1/4). The amount of acrolein formed from the sample containing phosphorus alone was about 50% of that from the untreated sample, also found 65% for the samples containing chlorine alone, and 40% for those containing bromine alone, which means that bromine is the most effective to reduce toxic gas such as acrolein. When combined with nitrogen, phosphorus + nitrogen reduced to 7% showing the largest contribution, whereas halogens gave less effect, i.e., bromine + nitrogen to 9% and chlorine and nitrogen 35%.

The samples containing phosphorus and chlorine each alone gave acetol almost to the same amount as that from the untreated sample but bromine gave much less amount (1/3.5). In the case of the synergistic effect with nitrogen, $(NH_4)_2HPO_4$ gave a much reduced amount down to 1/38 of that of the untreated sample, and NH4Br showed an even further reduction to 1/85 while NH4Cl only to 1/8.5. Propylene was reduced by the synergistic effect of phosphorus and nitrogen but not by halogens both with and without nitrogen.

★ Increasing Tendency to Formation of Ring Products with Double Bond

The samples containing phosphorus or halogens each alone and in combination with nitrogen showed an increasing tendency to the formation of aromatic products with a double bond such as methylfuran and methylfurfural. In the case of methylfuran, the molar ratio of this product was simultaneously taken into consideration for each samples. The samples containing bromine both with and without nitrogen showed the largest amount, and those containing phosphorus or chlorine each alone gave considerable less amount, approximately 1/2 of that given by bromine-containing samples. Comparing chlorine-containing samples and phosphorus-containing samples, the former gave a little more amount than the latter. But when phosphorus and chlorine were present in combination with nitrogen, the effect of phosphorus and nitrogen came next to bromine + nitrogen, while chlorine + nitrogen gave the least amount, less than 1/2 of that from the sample containing bromine and nitrogen.

On the other hand, in the case of methylfurfural, the sample containing phosphorus alone gave the largest amount and those containing halogens each alone showed less amount, about 70%. Whereas the synergistic effect with nitrogen revealed that bromine + nitrogen gave the highest effect showing more than twice as much as the amount given by the aforementioned phosphorus-containing sample, but another halogen chlorine showed only 40% in combination with nitrogen, and phosphorus + nitrogen exhibited a value about 70% of that shown by bromine + nitrogen.

As mentioned above, the flame retardance evaluated by LOI value of each sample agreed with the pyrolytic behavior, which shows that the synergistic effects of phosphorus or halogens in combination with nitrogen are clearly reflected in the flame retardance as well as in the pyrolytic gas formation. The synergistic effect of halogens and nitrogen also agreed with that of phosphorus and nitrogen described in the previous section. But, comparing the effect of bromine, chlorine and phosphorus each alone, bromine showed the largest effect while chlorine and phosphorus similarly gave less effects, though the synergistic effects of these three elements and nitrogen are approximately on the same level in the case of instantaneous pyrolysis.

(c) Conclusion for 1) and 2)

As flame retardant elements for cellulosic fibers, phosphorus {in the case of 1)} and halogens {bromine and chlorine in 2)} have been selected for this study in combination with nitrogen and investigated how they influenced pyrolytic gas generation alone or in combination with nitrogen for the synergistic effect. The results are concluded as follows:

Quantitative observations disclosed obvious differences between samples with and without flame retardance for each pyrolytic product, which showed an agreement between LOI value and the pyrolytic behavior. The flame retardant samples treated with 20% solutions of H_3PO_4 + urea, NH_4OH + H_3PO_4, $(NH_4)_2HPO_4$, $CaCl_2$, NH_4Cl or NH_4Br exhibited remarkable reductions of flammable gas production and marked increase in products which contribute to char production to enhance the self-extinguishability.

Furthermore, comparison of the total amount of pyrolytic gases from each sample with LOI value showed that the flame retardant samples having high LOI values largely inhibit pyrolytic gas formation as shown in Fig. 6-53. Samples other than those untreated and treated with urea and NaCl also show reduction of pyrolytic gas formation to some extent even though they showed LOI values lower than 28%. Comparing halogens with phosphorus described in the previous section, bromine showed the largest effect, while chlorine and phosphorus gave similar but less effects. The synergistic effect of phosphorus or halogens and nitrogen is well reflected not only in the flame retardance but also in the pyrolytic gas generation, which can meet the requirements for the target of this study.

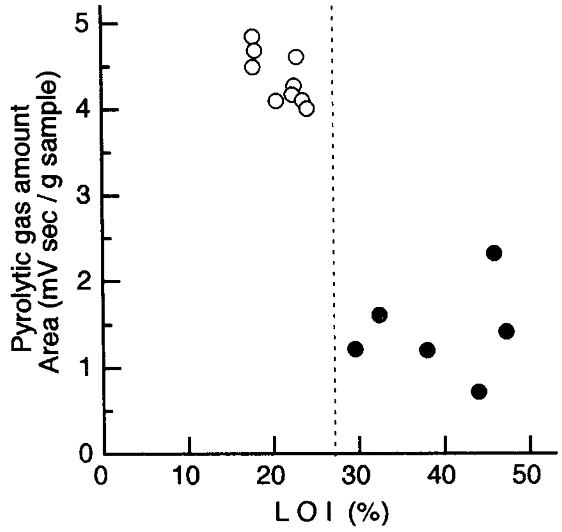


Fig. 6-53 Comparison between total pyrolytic gas amounts generated from flammable cotton fiber with LOI values < 28% (indicated by ○) and those from flame retardant cotton fiber with LOI values > 28% (indicated by ●).

6-2-3 Generation of smoke, CO and CO_2 from cotton cellulose and comparison between effect of inorganic flame retardants and that of organic flame retardants

The results mentioned in the previous section were all obtained by time consuming quantitative and qualitative analytical observation, which denied accurate analysis for pyrolytic gases from samples treated with any organic flame retardant because of the formation of very complicated and not identifiable intermediate pyrolytic products. But, it was thought to be necessary to obtain some information about pyrolytic gases from samples treated with organic flame retardant to compare with those from samples treated with inorganic compounds. Therefore, amounts of smoke, CO and CO_2 generated from cotton samples treated with organic and inorganic flame retardant were measured to compare the amounts of gases among samples[32].

1) Experimental

(a) materials

(1) Fabric

One hundred % cotton fabric the same as that described above for the previous investigations was used also for this investigation.

(2) Treating reagents

All organic and inorganic flame retardants were the same as those described in 2-2-2.

(b) Methods

(1) Treatments for nondurable (7 kinds) and durable(3 kinds) flame retardant finishes were carried out in the same manners as mentioned also in 2-2-2

(2) Determination of smoke concentration

Transmittance of generated smoke of each sample was observed by a burning apparatus for LOI test method, of which a top board was removed and attached with a smoke tester, together with a hood. Smoke concentration was calculated according to the following equation and obtained down to three places of decimals on the basis of JIS Z-8401.

$$C_{s\text{-}max} = (2.303/L)\log 100/T_{min}$$

where $C_{s\text{-}max}$: maximum extinction coefficient, L : light path(500 mm by this standard), T_{min} : minimum transmittance at the time of maximum smoke generation.

(3) Measurement of CO and CO_2

The instrument was constituted by a burning chamber and a gas measuring apparatus. Standard gases and peak areas for CO and CO_2 from each sample and standard CO and CO_2 were measured by the gravimetric method.

(4) Evaluation of flame retardance

Flame retardance of each sample was evaluated by LOI method described in 2-1-2.

2) Results and Discussion

(a) Effect of flame retardant finishes on smoke generation

Fig.6-54 shows Cs-max versus LOI value curves, in which broken line indicates a level of unfinished cotton. This explains that almost all finished samples showed increase in smoke with rise of LOI value,i.e.,with increase in add-on of flame retardants(Fig. 6-55) which means that such increase in smoke is attributed to flame retardant itself in each case. This figure obviously discloses that organic flame retardants generate extremely high level of smoke rising with increase in LOI value elevating with the amount of any flame retardant contained in each sample, whereas inorganic compounds showed much lower level, especially boric acid and borax gave the lowest level at a vicinity of unfinished level, a little difference observed between unfinished level and $C_{s\text{-}}$

max versus LOI curve of boric acid and borax is supposed to be steam which came out of water of crystallization of borax($Na_2B_4O_7$ 10 H_2O) because of colorless visual appearance.

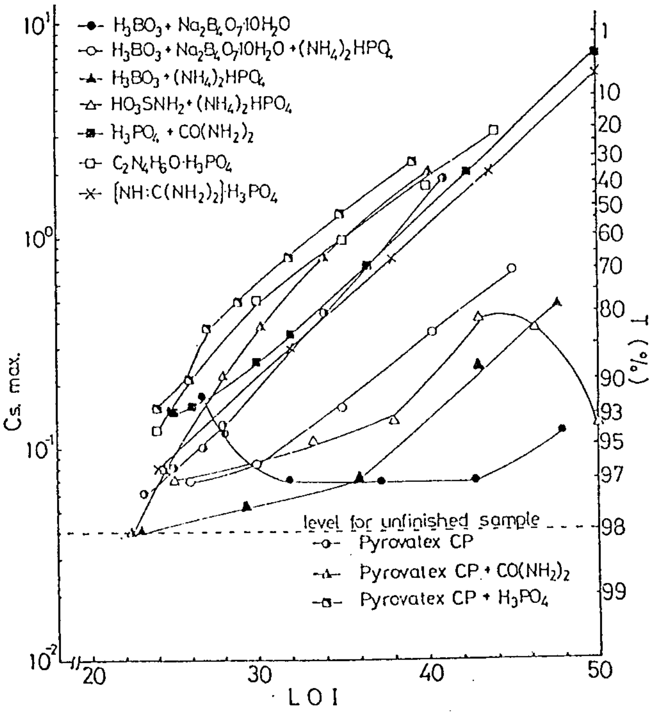


Fig. 6-54 Relation between LOI and smoke concentration.

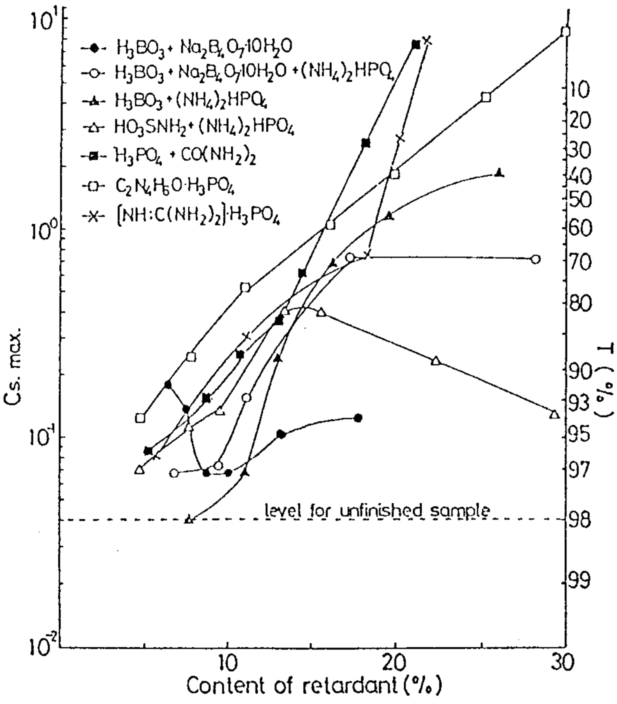


Fig. 6-55 Relation between content of retardant and smoke concentration.

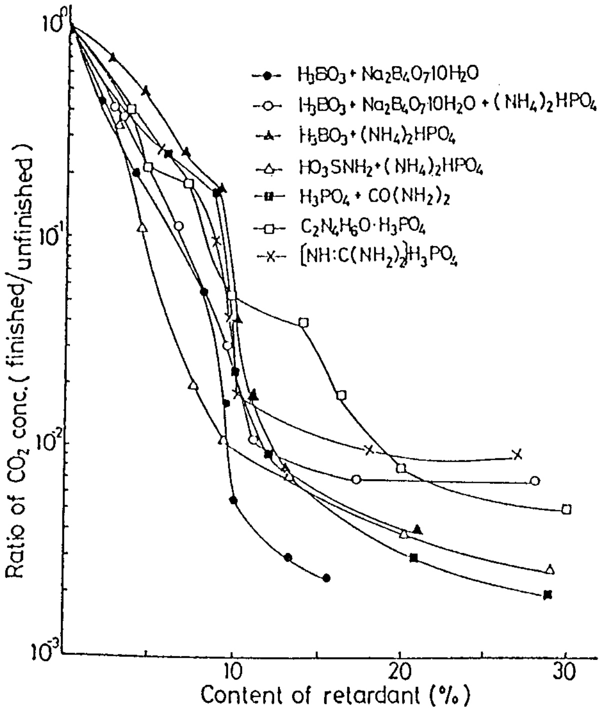


Fig. 6-56 Relation between contents of retardants and CO_2 concentrations (expressed by CO_2 from finished sample / CO_2 from unfinished sample).

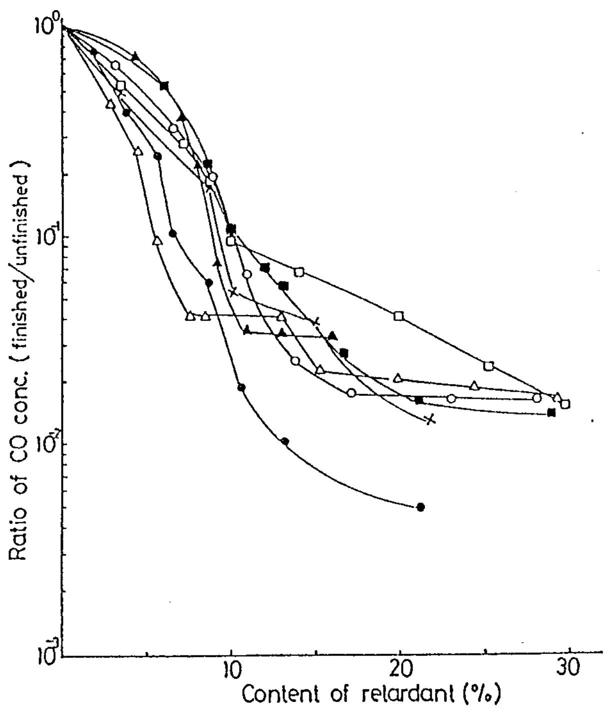


Fig. 6-57 Relation between contents of retardants and CO concentrations (expressed by CO from finished sample / CO from unfinished sample).

(b) Effect of flame retardant finishes on production of CO and CO_2

Fig. 6-56 and 57 illustrate ratios of CO and CO_2 concentrations(finished /unfinished) versus contents of retardant curve for each sample. Attention is drawn to that boric acid and borax showed remarkable reduction far apart from those of other fame retardant samples,i.e., CO was reduced down to 1/100 by finishing with 10% solution and even to 1/200 with 20% solution, and in the case of CO_2, 10% solution gave reduction down to 1/200 and 15% solution reduced even down to approximately 1/500 compared with the unfinished level.

3) Conclusion

Attention should be paid to the fact that inorganic nondurable flame retardants showed much less gas generation, particularly boric acid and borax the most reduction in generation of smoke, CO and CO_2, down to 1/200-1/500.

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Chapter 7

Chapter 7 Final Overall Conclusion

The purpose of a series of the studies on flame retardant finishes was to secure the safety of our individual lives as well as of the public living environments not only by extinguishing fire after its outbreak but rather by defending fire outbreak itself by converting any flammable material to flame retardant resisting against ignition and flame propagation.

1. Establishment of most Favorable Finishing Conditions for Flame Retardant Finishes

The establishment of the adequate finishing conditions is indispensable to obtain any flame retardant materials with sufficient performances. In this sense, the investigations were first carried out to establish most favorable finishing conditions for durable and non durable flame retardant finishes for cellulosic fibers, PET fibers and cotton/PET blended fabrics most widely used, and succeeded in finding sufficiently favorable finishing condition for each finish as well as in improving finishing conditions.

From the standpoint of level of flame retardance, cotton fabric treated with sufficient amounts of nondurable inorganic compounds showed significantly higher flame retardances compared with those shown by durable flame retardant finished cotton fabric.

2. Influences of Flame Retardant Finishes on Dyestuffs (Comparison between Nondurable and Durable Flame Retardant Finishes)

From the practical standpoint, influences of flame retardant finishes on dyed fabrics were investigated and it was found that durable flame retardant finishes caused much larger discoloration compared with that caused by nondurable flame retardant finishes.

3. Effects of Flame Retardant Finishes on Discoloration of Dyed Fabrics by UV Irradiation

Taking a more practical case, i. e., exposure to sunshine into consideration, investigations were attempted to see how flame retardant finishes influence on the discoloration of dyed fabrics to be caused by UV irradiation, the results of which showed a tendency that durable flame retardant finishes gave much larger discoloration compared with that by nondurable finishes. It was surprising fact that boric acid and borax remarkably suppressed discoloration by UV irradiation.

4. Effect of Flame Retardant Finishs on Propagation of Smoldering in Fiber Assemblies from Burning Cigarette and on Heat of Combustion

Attention was also paid to the heat propagation behavior in fiber assemblies from burning cigarettes which can be a heat source of fire outbreak in most major cases as well as to the heat of combustion related to danger of burning materials in contact with the body skin.

Flame retardant fiber assemblies also extremely depressed propagation of heat from burning cigarette by self-extinguishing. Nondurable inorganic compounds also reduced the heat of combustion of celluloses. Boric acid and borax were the most effective also in this case.

5. Characteristic Thermal Degradation Behavior of Nondurable Flame Retardant Cellulosic Fibers

The results of thermogravimetric observations for thermal degradation behavior showed that TDOP, MDRP and FP of nondurable flame retardant cotton samples shifted to much lower temperatures compared with those observed in the cases of flammable cotton samples and durable flame retardant samples. Particularly, attention should be paid to the fact that FP of nondurable flame retardant cotton samples treated with inorganic compound come far after TDOP and MDRP showing much retardation of ignition, whereas flammable samples and durable flame retardant finished cotton was ignited before MDRP soon after TDOP. In the case of PET fiber, FP came the last showing difficulty of ignition irrespective of flammable or flame retardant because of melting properly of this fiber.

6. Apparent Activation Energy (Ea) and Effect of Flame Retardation on Ea

Thermal degradation behavior observed in the case of nondurable flame retardant cotton samples mentioned above was reflected well on Ea distribution at different stages in the process of thermal degradation. Moreover, the structural modification observed by IR spectroscopy with the progress of thermal degradation of celllulose revealed that the destruction of cellulose typical structure was observed at much lower temperature in the case of nondurable flame retardant samples compared with flammable samples, which agrees well with the thermogravimetric observations.

7. Pyrolytic Gas Generation from Textile Fibers and Effects of Flame Retardant Finishes with the Synergistic Effects of N and P and N and Halogens on the Pyrolytic Gas Production Behavior

Comparison between flammable and flame retardant cotton samples treated with nondurable inorganic compounds revealed that flame retardant cotton samples treated with inorganic compounds containing P or halogens in combination with N extremely reduced production of not only smoke, CO and CO_2 but also pyrolytic gases including toxic gas, acrolein, and in contrast, acetonitrile, an effective radical scavenger, appeared significantly only in the case of cotton samples containing N and P and also from those containing N and Br.

8. Special Attention to Boric Acid and Borax as a Nondurable Flame Retardant for Cellulosic Materials

Special attention should be paid to boric acid and borax for flame retardant finish of cellulosic fiber products since this mixture gives remarkable flame retardance, strong inhibition of discoloration of dyed fabric to be caused by UV irradiation and significantly large reduction of pyrolytic gas production. It is nondurable against laundry but durable against dry cleaning. Although nondurable against laundry, it can be applicable to paper products or interior materials in buildings and even to any clothing materials which require frequent laundry since retreatment after washing is very easy and simple just pad-and-dry after daily home laundry.