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# DEVELOPMENT AND EVALUATION OF FIRE RETARDANT COTTON FABRICS

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## ABSTRACT

A few compositions based on monoammonium phosphate, diammonium phosphate, orthophosphoric acid, urea and M-80 (a melamine formaldehyde resin) have been studied in order to impart durable fire retardancy to cotton fabrics. The treated specimens are tested for their burning and smoke generation characteristics, as well as strength and washability. The treatments may prove quite effective in reducing the hazards in case of cotton fabrics.

## 1. INTRODUCTION

Fire hazards cause tremendous loss of life and property. The furnishing materials like curtains, carpets, cushions etc. often are used in buildings for various purposes. These materials are intrinsically combustible due to their cellulosic nature. To retard the burning characteristics of cotton fabrics, various chemical treatments have been suggested from time to time. A large number of fire retardant treatments based on organophosphorous and halogenated compounds [1-3]are reported for cellulosic materials. However, they have not been widely accepted due to their high cost and toxicity. Other fire retardants are water soluble inorganic salts [1&3] which are comparativ ly cheaper, non-toxic and readily available are w dely used. Since the protection afforded by t ese chemicals is temporary in nature, attempts are made to bind these compounds directly to the cellulosic fabrics in order to achieve a durable effect.

The present communicaton concerns with the development and efficacy of fire retardant treatment for cotton fabrics.

## 2. EXPERIMENTAL

### 2.1 Materials

Chemicals namely monoammonium phosphate (MAP), diammonium phosphate (DAP), orthophosphoric acid and urea used were of Laboratory Reagent grade. M-80 (a melamine formaldehyde resin) obtained from synthetic and polymer industries, Ahmedabad. Fabrics : 100 percent cotton, undyed of average weight 335 gm/$m^2$ and coloured cotton carpet of average weight 1605 gm/$m^2$ obtained from local market.

### 2.2 Method

Aqueous solutions of 1-50 percent concentrations containing mixrures of MAP-urea, DAP-urea, orthophosphoric acid-urea of ' 1-1:10, w/w ratios and DAP-urea-M-80 of 1:2.2: .8, w/w ratio were prepared. The specimens c: fabrics were immersed in the solution for one hour to obtain maximum chemical retention. The specimens were dried and then cured at 130℃ to 180℃ ± 2℃ for 1 to 100 minutes. They were washed with water to remove unreacted chemicals and then

dried. Effect of weight ratios, dry chemcal retentions, curing temperature and time on fire performance and strength of fabrics were determined.

## 3. EVALUATION OF FIRE PERFORMANCE AND PHYSICAL CHARACTERISTICS OF FABRICS

### 3.1 Fire Performance

Six specimens of the size 318 × 51mm were cut from each fabric and were hang vertically in the test chamber. A standard flame was applied for a period of 12 seconds and then withdrawn. The afterflame and the afterglow times were determined according to British Standard (BS) 3119 method [4]. The average char length and char area were also measured in case of various treatments at different weight ratios, dry chemical retentions, curing temperatures and time. The results are represented graphically[Figs. 1-5].

The fire performance of carpet was evaluated by British Standard 4790 method [5]. The specimens were placed at the bottom of the test chamber and were ignited with a hexagonal nut which was previously heated to a temperature of 900 ± 2℃. The afterflame afterglow times and char areas were noted with specimens treated with various treatments. The results are given in Tabel 1.

### 3.2 Smoke Emission Test

Tests were carried out in the NBS (National Bureau of Standards) smoke density chmber. Specimens of 76 × 76mm each were cut from treated and untreated samples. Test specimens were affixed to 6 mm asbestos board and were arranged to face the electrically heated radiant energy source which is mounted within an insulated ceramic tube and positioned so as to produce an irradiance level of 2.5 W/cm² averaged over the central 38.1 mm diameter area of vertically mounted specimen. Generation of smoke was determined following ASTM E 662 method [6].

The follwing parameters were determined:

$D_m$ = maximum specific optical density

$t_{90\%}$ = moment where upon 90 percent of Dm is reached (min.).

$D_{90S}$ = optical density at 90 sec.

SON = sum of the specific optical densities at 1,2,3 & 4 min a measure for the rate of smoke development.

$V_{max}$ = maximum rate of smoke development estimated every 30 sec and expressed in $D_s$/min.

SOI (Smoke Obscuration Index) calculated as:

$$\frac{Dm^2}{2000t_{16}}\left(\frac{1}{t_{0.9}-t_{0.7}}+\frac{1}{t_{0.7}-t_{0.5}}+\frac{1}{t_{0.5}-t_{0.3}}+\frac{1}{t_{0.3}-t_{0.1}}\right)$$

Table 1. Fire performance of carpet.*

| Sr. No. | Composition | Dry Chemical Retention (%) | Curing Temp. and time | After flame time (sec) | After glow time (sec) | Char Area ($cm^2$) | Remarks |
|---|---|---|---|---|---|---|---|
| 1. | MAP-urea | 15.2 | 160 ± 2℃ and 18 min | 0 | 0 | 2 | No heat penetrated Self extinguished |
| 2. | DAP-urea | 15.8 | –do– | 0 | 0 | 2 | –do– |
| 3. | Phosphoric acid-urea | 13.6 | –do– | 0 | 0 | 2 | –do– |
| 4. | DAP-urea-resin | 14.8 | –do– | 0 | 0 | 2 | –do– |
| | UNTREATED | – | – | 8 | 48 | 6.5 | Heat penetrated |

* As per BS 4790 Method

Table 2. Results of smoke generation test.

| Sr. No. | Composition | Values of * | | | | | |
|---|---|---|---|---|---|---|---|
| | | $D_m$ | $t_{90\%}$ (min.) | $D_{90s}$ | SON | $V_{max}$ (min.$^{-1}$) | SOI (min.$^{-2}$) |
| 1. | MAP-urea | 3.4 | 11.2 | 1.4 | 6.9 | 1.1 | 00 |
| 2. | DAP-urea | 3.4 | 12.6 | 1.4 | 6.3 | 1.0 | 00 |
| 3. | Phosphoric acid-urea | 4.1 | 10.5 | 2.1 | 9.5 | 1.8 | 00 |
| 4. | DAP-urea-resin | 3.8 | 11.8 | 1.8 | 7.9 | 1.4 | 00 |
| | CONTROL FABRIC | | | | | | |
| | 335 gm/m$^2$ | 44.80 | 12.0 | 12.0 | 68.0 | 17.8 | 5.36 |
| | 1605 gm/m$^2$ | 202.40 | 12.4 | 11.5 | 166.0 | 29.6 | 23.45 |

$D_m$, $D_{90s}$ and SON are max. specific optical density, optical density at 90 Sec. and sum of specific optical densities at 1, 2, 3, & 4 minutes respectively and are dimensionless quantities.

$V_{max}$ is the rate of smoke development.

$t_{90\%}$ is the time to reach 90% of the max. specific optical density.

SOI is the smoke obscuration Index which incorporates the effect of total smoke generation rate and time to reach Ds value of 16.

* Lower value of $D_m$, $D_{90s}$, SON, $V_{max}$, SOI and higher value of $t_{90\%}$ better the performance of a material.

Where $t_{16}$ = time to reach $D_m = 16$
$t_{0.9}$, $t_{0.7} \cdots\cdots t_{0.1}$ = time to reach 90 %, 70%……10% of maximum $D_m$.
The results are reported in Table 2.

### 3.3 Strength of The Fabrics

Strength of the fabrics 150 × 350 mm size was determined by a tensometer Model W. Monsanto, London at different curing temperatures and times. The results are represented graphically [Figs. 6-8]. The effect of melamine formaldehyde resin [M-80] on the strength and fire performance was also studied. For this, a 40 percent aqueous solution of diammonium phosphate and urea (1:2.2, w/w) was used. M-80 resin along with one percent catalyst by weight of resin was added in different amounts to the above solution. Fabrics were immersed in this solution for one hour. They were taken out and dried completely. These were then cured at 160℃ ± 2℃ for 18 minutes followd by washings with water and drying. The fire performance and strength of fabrics were determined by standard methods. The results on the fire performance and decrease in strength (percent) are represented graphically [Fig. 9].

### 3.4 Effect of Laundering on Fire Performance

The treated specimens were washed with soft water and with water containing 112 mg/lit, 156 mg/lit and 208 mg/lit of hardness and 0.5 percent surf.* Specimens were also drycleaned with mineral turpentine oil (M.T. oil) in order to determine the durability of the treatments against launderings. Fire performance after each washing and drycleaning evaluated employing B.S. 3119 method is given in Table 3.

### 3.5 Weathering Effects on The Fabrics

The specimens were placed in a chamber at 96-98 percent relative humidity for 28 days. They were dried completely either in the sun or in the

*Trade name of a detergent manufactured by M/s HINDUSTAN LEVER LTD. BOMBAY.

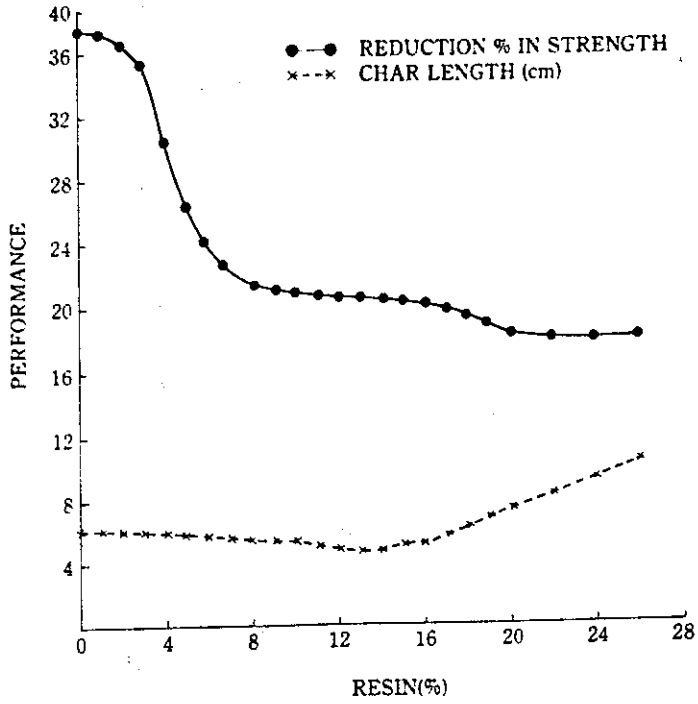



Figure 9. Effect of resin on strength and fire performance.

Table 3. Effect of launderings on the fire performance.

| Composition | No. of washings /Dry cleaning | Exposure Time (sec) | Washings with soft water containing 0.5% surf | | | Dry cleanings with M.T oil | | |
|---|---|---|---|---|---|---|---|---|
| | | | After flame Time (sec) | After glow Time (sec) | Char length (cm) | After flame Time (sec) | After glow Time (sec) | Char length (cm) |
| 1 | 5 | 12 | 0 | 0 | 5.40 | 0 | 0 | 5.50 |
| | 10 | 12 | 0 | 0 | 5.50 | 0 | 0 | 5.50 |
| | 15 | 12 | 2 | 0 | 19.80 | 0 | 0 | 5.40 |
| | 20 | 12 | 6 | 10 | 26.80 | 0 | 0 | 5.50 |
| 2 | 5 | 12 | 0 | 0 | 6.00 | 0 | 0 | 6.00 |
| | 10 | 12 | 0 | 0 | 6.00 | 0 | 0 | 6.00 |
| | 15 | 12 | 3 | 0 | 21.30 | 0 | 0 | 5.90 |
| | 20 | 12 | 7 | 12 | 28.60 | 0 | 0 | 6.00 |
| 3 | 5 | 12 | 0 | 0 | 4.50 | 0 | 0 | 4.40 |
| | 10 | 12 | 0 | 0 | 4.50 | 0 | 0 | 4.50 |
| | 15 | 12 | 0 | 0 | 8.80 | 0 | 0 | 4.50 |
| | 20 | 12 | 2 | 0 | 17.20 | 0 | 0 | 4.50 |
| 4 | 5 | 12 | 0 | 0 | 5.50 | 0 | 0 | 5.50 |
| | 10 | 12 | 0 | 0 | 5.50 | 0 | 0 | 5.50 |
| | 15 | 12 | 3 | 0 | 17.60 | 0 | 0 | 5.50 |
| | 20 | 12 | 5 | 8 | 24.90 | 0 | 0 | 5.50 |

Table 3 (contd). Washings with hard water containing 0.5% surf.

| Composition | No. of washings | Exposure Time (sec) | Hardness 112 mg/lit | | | Hardness 156 mg/lit | | | Hardness 208 mg/lit | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | After flame Time (sec) | After glow Time (sec) | Char length (cm) | After flame Time (sec) | After glow Time (sec) | Char length (cm) | After flame Time (sec) | After glow Time (sec) | Char length (cm) |
| 1 | 10 | 12 | 0 | 0 | 5.50 | 0 | 0 | 8.80 | 8 | 5 | 28.40 |
| | 12 | 12 | 0 | 0 | 6.80 | 5 | 1 | 15.80 | 8 | 8 | 31.80 |
| | 14 | 12 | 0 | 0 | 15.40 | 8 | 5 | 21.70 | – | – | – |
| | 16 | 12 | 3 | 0 | 29.80 | 8 | 8 | 29.80 | – | – | – |
| 2 | 10 | 12 | 0 | 0 | 6.10 | 0 | 0 | 9.60 | 9 | 5 | 30.00 |
| | 12 | 12 | 0 | 0 | 7.80 | 6 | 5 | 18.70 | – | – | – |
| | 14 | 12 | 8 | 5 | 21.40 | 9 | 5 | 24.60 | – | – | – |
| | 16 | 12 | 8 | 8 | 30.20 | 9 | 8 | 31.80 | – | – | – |
| 3 | 10 | 12 | 0 | 0 | 4.60 | 0 | 0 | 6.40 | 5 | 3 | 19.40 |
| | 12 | 12 | 0 | 0 | 5.30 | 0 | 0 | 9.30 | 6 | 8 | 27.00 |
| | 14 | 12 | 1 | 0 | 14.80 | 7 | 3 | 19.20 | 8 | 8 | 31.80 |
| | 16 | 12 | 6 | 2 | 28.20 | 8 | 8 | 27.80 | – | – | – |
| 4 | 10 | 12 | 0 | 0 | 5.50 | 0 | 0 | 5.40 | 8 | 5 | 26.50 |
| | 12 | 12 | 0 | 0 | 5.50 | 0 | 0 | 8.60 | 8 | 6 | 31.80 |
| | 14 | 12 | 0 | 0 | 10.80 | 0 | 0 | 17.80 | – | – | – |
| | 16 | 12 | 3 | 6 | 17.60 | 0 | 0 | 26.90 | – | – | – |

___ indicates that the performance could not be measured as the specimen was burnt completely.

oven or over fused calcium, chloride in order to determine the effect of humidity on the fire performance and strength of fabric. Results are recorded in Table 4.

## 4. RESULTS AND DISCUSSION

From the burning test, it is evident that the fire retardant compositions studied are quite effective in reducing the flammable chracteristics of the fabrics. The fire performance and physical properties are very much dependent on the stoichiometric ratios of ingredients, chemical retentions, curing time and temperature of the reactions. Combinations of MAP-urea and DAP-urea are quite effective in reducing the flammable chracteristics at 1:2 – 1:2.5, w/w ratios and 15-17 percent dry chemical retention. The combination of orthophosphoric acid-urea in ratio 1:2·5-1:3 by weight is adequate to obtain effective fire retardancy. It is also established that 13-16 percent dry chemical retention is required to achieve maximum fire retardancy [Fig. 1&2].

In the reaction of cellulose with acidic phosphate or phosphoric acid in the presence of urea, the formation of monosubstituted esters predominate. However, the formation of disubstituted products by esterification of two hydroxyl groups on the same anhydroglucose unit or on

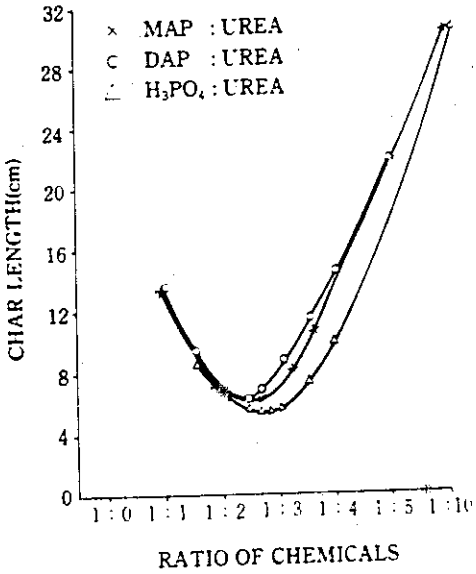



Figure 1. Effect of chemicals on char length.

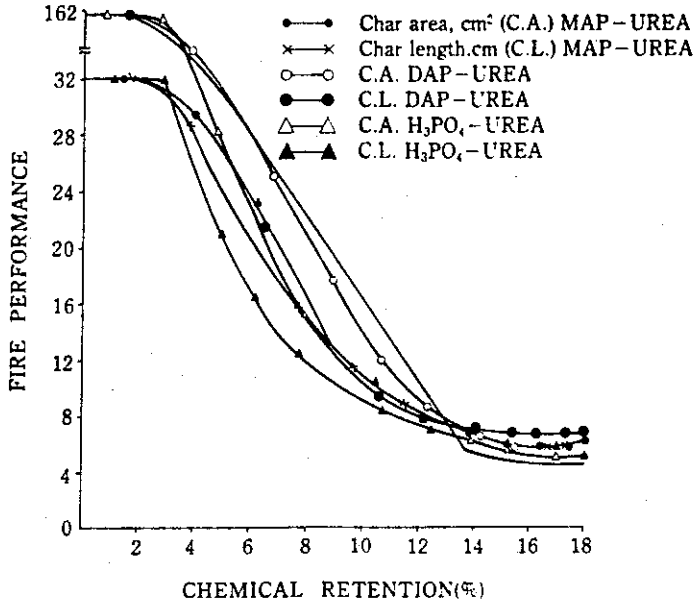
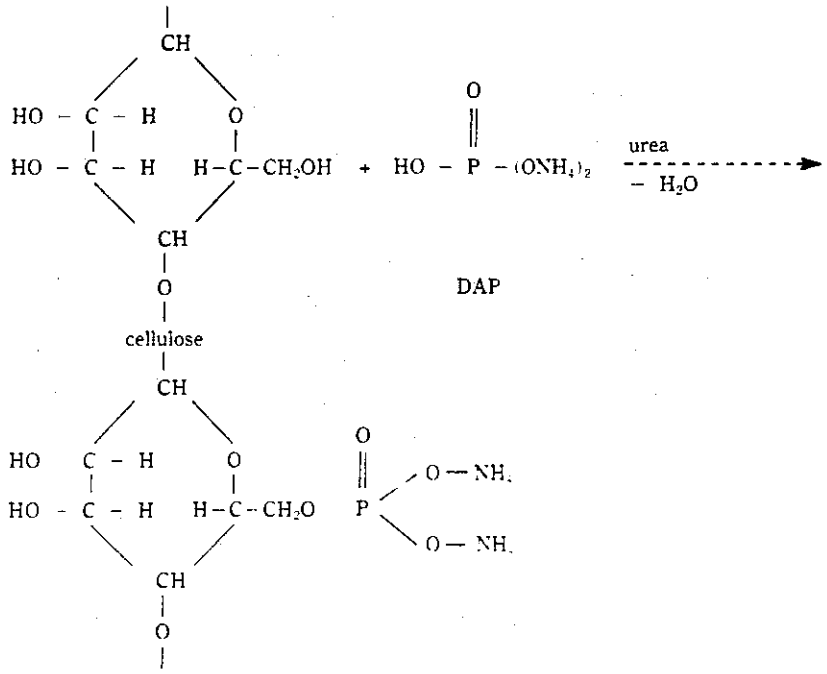



Figure 2. Effect of chemical retention on fire performance.




neighbouring cellulose chains can not be excluded. Mono substitution may take place any of the three hydroxyl groups available in the anhydroglucose unit but the primary hydroxyl group is most readily esterified [7]. In this reaction urea is probably serving as a dehydrating agent [8].

The function of phosphorus containing fire retardants is to alter the course of decomposition of the cellulosic material so that lower amounts of flammable volatiles and large quantities of char are formed. Consequently the flammable characteristics of cellulosic materials are reduced [9-11].

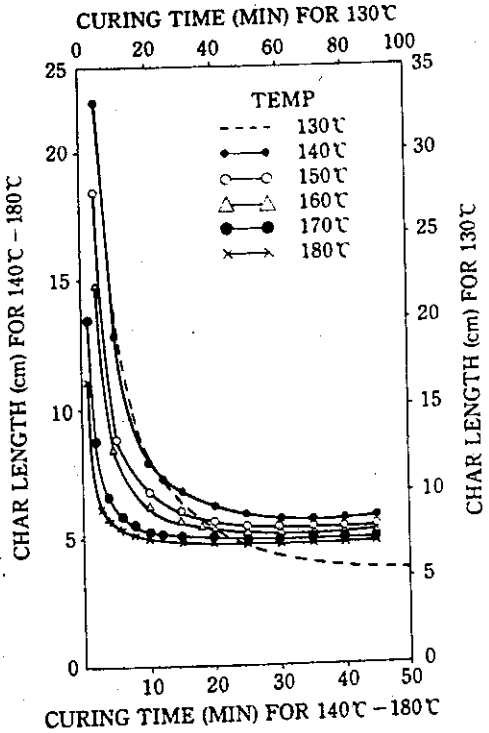



Figure 3. Effect of curing temp. & Time on char length with MAP-urea.

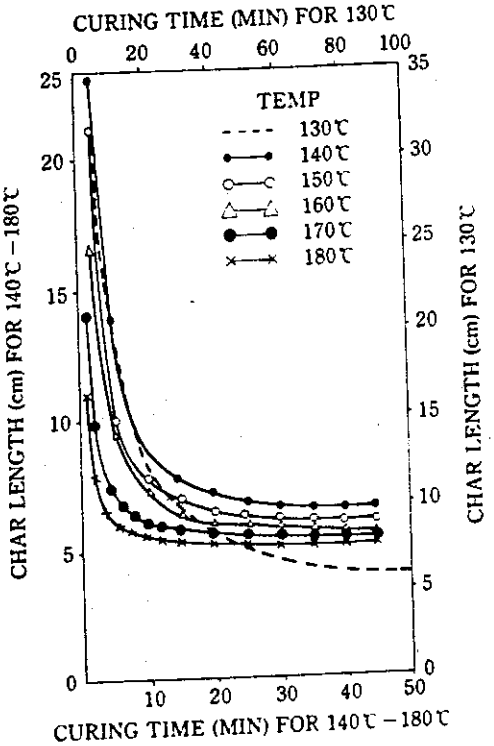



Figure 4. Effect of curing temp. & Time on char length with DAP-urea.

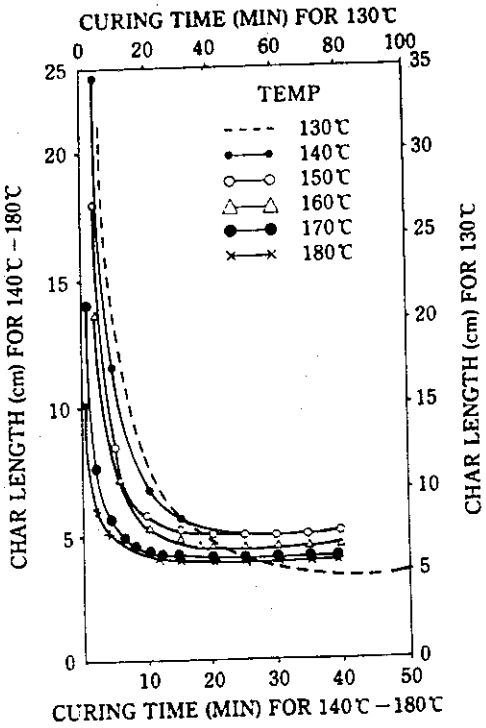



Figure 5. Effect of curing temp. & Time on char length with $H_3PO_4$-urea.

Fire performance of the fabrics is very much dependent on the curing temperatures and duration of the reaction. It is observed that phosphorylation of cotton fabrics takes place at 130℃ in about 80 minutes although about 6-8 minutes are required at 180 ℃ for effective fire retardancy [Figs. 3-5]. Loss in strength has been found to be dependent on the curing temperature and time. From Figs. 6-8, it is noted that at 160℃ only 18 minutes are required for obtaining effective fire retardancy and minimum loss in strength for which MAP-urea, DAP-urea (1:2.2, w/w) and orthophosphoric acid-urea (1:2.6, w/w) treatment have been used. The above treatments caused 42, 37.50 and 49 percent loss in strength respectively.

The phosphorylation reaction in the presence of M-80 (Melamine formaldehyde resin) has also been studied and it is noted that the loss in strength is 21 percent instead of 37.5 percent on the addition of about 8 percent resin in DAP-urea treatment [Fig. 9]. In such a system the cross linking of resin to cellulose may take place. When

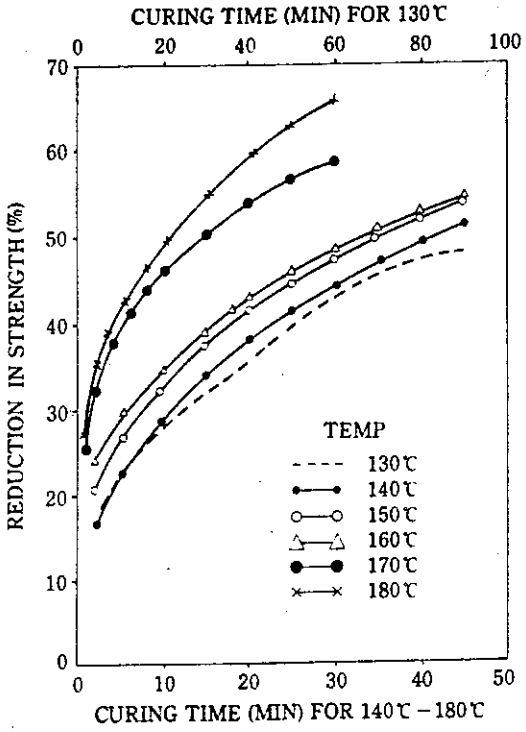



Figure 6. Effect of curing temp. & Time on the strength with MAP-urea.

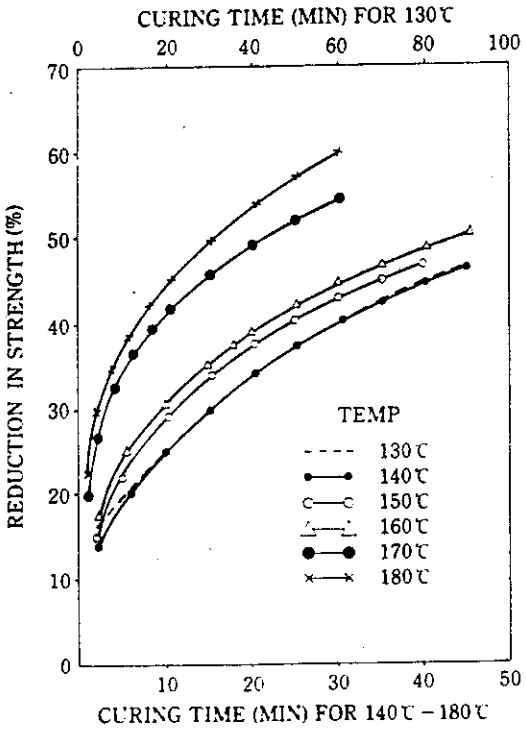



Figure 7. Effect of curing temp. & Time on the strength with DAP-urea.

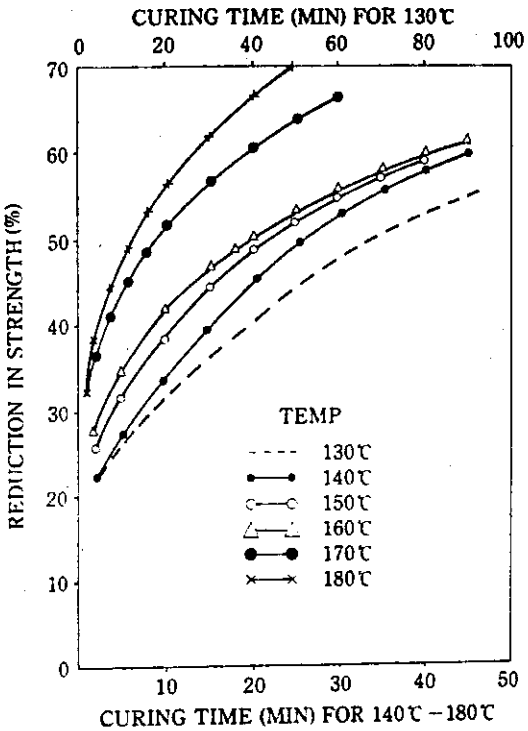


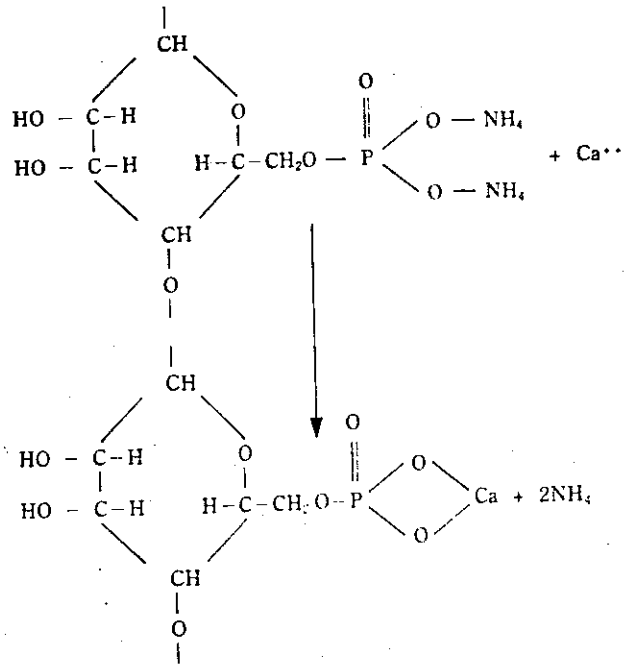

Figure 8. Effect of curing temp. & Time on the strength with $H_3PO_4$-urea.

higher amounts of resin are used specimens became very stiff although the loss in strength was 18 percent instead of 37.5 percent.

Fire performance data show that there is no change on repeated drycleanings. The fire performance is, however, affected by washings with hardwater and detergents [Table 3]. It is established that phosphate esters obtained by the esterification of cellulose have ionic character, the free acid groups being neutralized by nitrogen base. The ionic salts are capable of exchange with metallic ions. On immersion in hard water the calcium salt of the cellulose phosphate may be formed [7].

Such a replacement of the ammonium groups with metal ions to form salts which do not decompose to release free acid at the combustion temperature reduces or even entirely destroys the flame retarding effectiveness.

The treated specimens of fabics tested as per BS 3119 show no flame spread and afterglow combustion. The specimens remain self extin-



guished while the untreated specimens completely burn within 20 seconds. The samples of carpets tested according to BS 4790 method show no afterflaming, no afterglow and no heat penetration. The char area is found to be only 2cm$^2$ while untreated specimens show flame spread upto 8 seconds and afterglow upto 48 seconds. The heat penetration also takes place. The char area is 6.5c m$^2$ [Table 1].

It is evident from Table 2, that emission of smoke is very much dependent upon the material as well as types of fire retardant used. Maximum specific optical density ($D_m$) of cotton fabrics of two different weights i.e. 335gm/m$^2$ and 1605gm/m$^2$ was found to be 44.80 and 202.40 respectively. The both materials used in the study are cellulosic in nature, however, difference in the values seems to be due to different weights. The compositions employed to reduce the flammability of materials were also found effective in reducing the smoke generation.

The data of fire performance and strength of

Table 4. Weathering effect on fire performance and strength.

| Composition | Fire Performance | | | | Tensile Load Warp Direction(kg) | |
|---|---|---|---|---|---|---|
| | Exposure Time (sec) | After flame time (sec) | After glow time (sec) | Char length (cm) | Before ageing | After ageing |
| 1 | 12 | 0 | 0 | 5.50 | 14.80 | 14.58 |
| 2 | 12 | 0 | 0 | 6.00 | 15.35 | 15.10 |
| 3 | 12 | 0 | 0 | 4.60 | 10.36 | 10.18 |
| 4 | 12 | 0 | 0 | 5.50 | 18.96 | 18.70 |
| CONTROL | 12 | 8 | contd. till complete burning | Burnt completely | 24.00 | 23.60 |

the fabrics before and after ageing for 28 days at 96-98 percent relative humidity show that there is no change in fire performance and in the strength of the fabrics [Table 4]. The treated specimens which are subjected to the natural climatic changes inside a room for a period of 8 months, are unchanged with regard to their physical appearance as well as their fire performance.

It is concluded that the fire retardant treatment proposed under the present study are not only cheap but quite effective in the case of cotton fabrics.

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