Effect of Short Thermal Treatment on Cotton Degradation

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Synopsis

Cotton fabric was subjected to thermal treatment for durations ranging from 0.5 to 5 min at a temperature range of 160° to 220°C. In comparison with the untreated cotton, the copper number (measure of the aldehyde content) decreased after heating cotton for up to 3 min at 160°, 180°, and 190°C but increased when heating was prolonged to 5 min. Thermal treatment at 200°C or above caused an appreciable increase in the copper number. The carboxyl content increased with time of heating, attained a maximum, and then fell down to reach values which in some cases were lower than that of untreated cotton. Thermal treatment at 180°C caused a substantial reduction in the D.P.; this reduction increased with time of treatment. At the other temperatures there was no significant decrease in D.P. when cotton was heated up to 3 min. The D.P. decreased in these cases only when the thermal treatment was conducted for 5 min. The tensile strength remained practically unimpaired after thermal treatment of the cotton for up to 2 min, regardless of the temperature used within the range studied. A loss in tensile strength of ca. 9% and 13% was observed with fabrics treated for 5 min at 160° and 180°C, respectively. This contrasts with a loss of ca. 4% at 190°C, 7% at 200°C, and 8% at 220°C. The highest dye exhaustion was obtained on cotton which was thermally treated at 180°C prior to dyeing, while the lowest dye exhaustion was obtained on cotton heated at 220°C. Thermal treatment at 160°C left the susceptibility of cotton toward the dyestuff practically unaltered.

INTRODUCTION

A number of modern dyeing and finishing processes involve high-temperature (100–250°C) treatment for varying lengths of time, depending upon the process. By way of example, mention is made of the following: thermosol dyeing, high-temperature steaming, permanent press, curing, vapor-phase dyeing, and the classical process of singeing. Contact heating or thermal treatment by heat convection or radiation can be applied in these processes.

Although thermal degradation of cellulose brought about by long thermal or pyrolytic treatment has been studied by many workers,[1–5] very few studies[6,7] have dealt with the effect of short thermal treatments on cotton and the resulting changes in its structure. The aim of this work is to investigate the changes in the structure of cotton cellulose brought about by heat treatment. The latter was conducted for short duration over a range of temperatures which are of particular importance in textile chemical technology.

EXPERIMENTAL

Mill-scoured and bleached cotton (plain weave construction, 69 warps per inch, 69 wefts per inch) was used without further purification. The fabric acquires a weight of 158.36 g/m^2, a D.P. of 2220, a copper number of 0.077, a carboxyl content of 1.04 meq/100 g cellulose, a tensile strength of 64.3 and 65.1 kg for the

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warp and weft directions, respectively, and a moisture regain of 6.38%. Samples of this fabric were thermally treated for various periods of time (0.5–5 min) over a temperature range of 160–220°C. Thermal treatment was carried out through convective heating on a laboratory-scale tenter frame using an oven with circulating air.

The tensile strength of the fabric before and after thermal treatment was measured according to the ASTM strip test,[8] using an A.V.K. (Budapest, Hungary) apparatus; the copper number was determined using the procedure of Heyes[9]; and the carboxyl content was estimated according to Lüdtke et al.[10] Viscometric determination of the degree of polymerization (D.P.) was carried out on samples previously nitrated according to a method described elsewhere.[11] Moisture content was determined as per a reported method.[12]

Dyeing of cotton samples before and after being subjected to thermal treatment was performed under similar conditions using Cuprophenyl Red FGL. This dye belongs to the class of direct dyes and was kindly supplied by Ciba-Geigy, Switzerland. It was used without further purification. The dyeing bath was prepared containing 1% of the dyestuff. The sample was then introduced in the dyeing bath maintained at 70°C using a liquor ratio of 1:100. Dyeing was carried out for different periods of time ranging from 5 to 60 min. Dye exhaustion on the sample was measured spectrophotometrically[13] for each duration. Percent dye exhaustion was calculated by dividing the weight of the dye exhausted on the fiber by the weight of original dye used and then multiplying by 100.

RESULTS AND DISCUSSION

Since the aim of this work is to study the physical and/or chemical changes in the cellulose structure brought about by thermal treatment, cotton cellulose in fabric form was subjected to different heat treatments for various periods. The fabric before and after such treatment was then analyzed for copper number, carboxyl content, D.P., dye uptake, and tensile strength. Presented below are the results obtained along with their appropriate discussion.

Copper Number

Figure 1 shows the copper number as a function of heating temperature at various durations of thermal treatment. The data indicate (a) that samples thermally treated at 160, 180, and 190°C for a duration ranging from 0.5 to 3 min acquire lower copper numbers than untreated samples; (b) that these samples possess a higher copper number than the untreated sample when the duration of treatment was prolonged to 5 min; (c) that samples heated at 200°C or above show a much higher copper number than the untreated sample regardless of the duration of treatment; and (d) that the increase in copper number is largely dependent on the duration of treatment: the longer the duration, the higher the copper number.

During thermal treatment of cellulose, the following reactions would be expected to occur: (a) oxidation of the functional end reducing groups to carboxyl groups, (b) oxidation of the cellulose hydroxyls to aldehydic groups, (c) hydrolysis of the glucosidic bond of the cellulose chains with resultant increase in the aldehydic groups, (d) oxidation of the newly introduced aldehydic group to carboxyl group, and (e) decarboxylation The magnitude of these reactions would

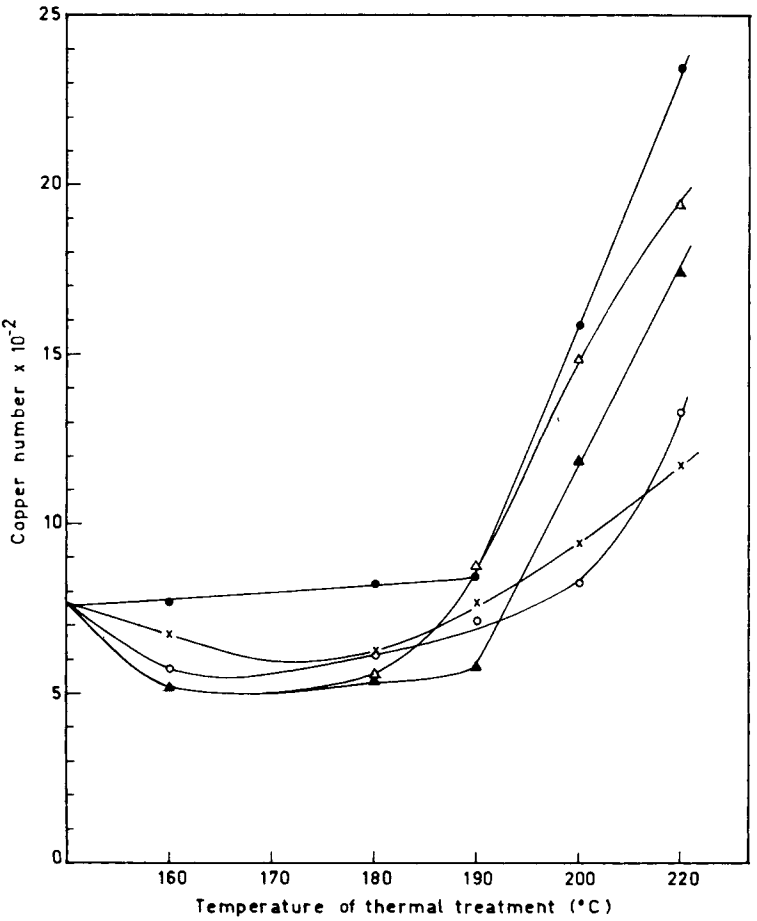

Fig. 1. Copper number vs. temperature of thermal treatment. Duration of heating: (×) 0.5 min; (⊙) 1 min; (▲) 2 min; (△) 3 min; (●) 5 min.

certainly be dependent on the temperature and duration of the treatment provided that the condition of treatment is kept constant, which is the case in the present work.

Thus, a decrease in copper number observed in the first 3 min of treatment at a temperature range of 160–190°C is unequivocally due to conversion of the aldehydic endgroup to carboxyl group via oxidation. This decrease is overbalanced by creation of more aldehyde groups via hydrolysis of cellulose glucosidic bonds and/or oxidation of cellulose hydroxyls when the duration of the treatment was prolonged to 5 min or a higher range of temperature was used.

Carboxyl Content

Figure 2 shows the variation of the carboxyl content of cotton cellulose with duration of thermal treatment over the temperature range of 160–220°C. As is evident, thermal treatment of cotton cellulose causes an increase in carboxyl content. This increase becomes enhanced with time, attains a maximum, and then falls to reach values which are, in a few cases, lower than that of the untreated cotton.

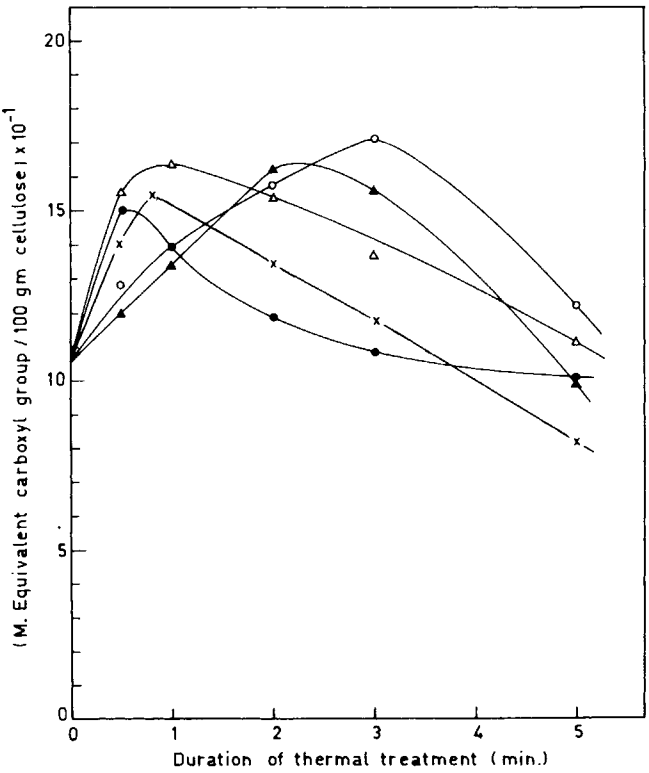

Fig. 2. Effect of heating time on carboxyl content of cotton cellulose at various temperatures: (⊙) 160°C; (▲) 180°C; (△) 190°C; (×) 200°C; (●) 220°C.

The maximum carboxyl content decreases as the temperature of the treatment increases. The duration is also shorter with higher than with lower temperature. For instance, maximum carboxyl content is obtained at 160°C in 3 min while the lowest carboxyl content is obtained at 220°C in 0.5 min. This is, indeed, direct evidence for the point that during thermal treatment of cellulose two reactions take place simultaneously. The first is oxidation of the aldehyde and/or hydroxyl groups to carboxyl groups, and the second is decarboxylation. Which of the two prevails would be reflected by the carboxyl content of the cellulose. Furthermore, the rate of oxidation of aldehyde groups to carboxyl groups is essentially dependent on the availability of the aldehyde groups in the cellulose molecule, which, in turn, depends on hydrolytic scission of glucosidic bonds of cellulose and/or oxidation of cellulose hydroxyls. Bearing this in mind, the present data would imply that the rate of oxidation prevails over the rate of decarboxylation at a temperature range of 160–180°C, presumably owing to the higher rate of hydrolysis of cellulose molecules with resultant aldehyde groups susceptible to oxidation. This state seems to be invalid at higher temperatures (i.e., above 190°C), presumably owing to the higher rate of water evaporation. That is, the rate of water evaporation is so fast at higher temperatures that the contribution of water to cellulose hydrolysis is not great. In addition, the rate of decarboxylation would be expected to proceed at a fast rate at higher temperature.

Degree of Polymerization (D.P.)

The effect of thermal treatment on the D.P. of cotton cellulose is shown in Table I. Treatment of the cotton fabric at 160°C for a period ranging from 0.5 to 3 min leaves the D.P. of cotton cellulose practically unaltered. A decrease in the D.P. could only be observed when the treatment was performed for 5 min at this temperature. The same situation was encountered with the corresponding treatments at 190°, 200°, and 220°C. Upon treatment at 180°C, on the other hand, the D.P. reduces substantially, and the reduction is greater the longer the duration of the treatment becomes. This indicates that within the range of temperatures studied, maximum hydrolysis of cellulose occurs at 180°C.

It is interesting to point out that in a few cases, particularly at 190°C, the thermally treated cotton cellulose acquires a higher D.P. than the untreated cotton. Extension of the cellulose chains resulting from heating the cellulosic material at elevated temperatures[14,15] would account for this.

Tensile Strength

Table II shows the tensile strength of the cotton fabric before and after thermal treatment. As can be seen, the tensile strength remains practically intact after the fabric is thermally treated from 0.5 to 2 min, regardless of the temperature employed within the range studied. A loss in tensile strength of ca. 9% and 13% could be observed with fabrics thermally treated for 5 min at 160° and 180°C, respectively. This contrasts with ca. 4%, 7%, and 8% for fabrics heated for the same duration at 190°, 200°, and 220°C, respectively. Similar to the D.P., it is clear that the highest loss in tensile strength occurs at 180°C.

TABLE I
Effect of Thermal Treatment on the Degree of Polymerization (D.P.) of Cotton Cellulose[a]

Temperature of treatment, °C	D.P. after the thermal treatment				
	0.5 min	1 min	2 min	3 min	5 min
160	2340	2290	2275	2210	2000
180	2070	2020	1800	1650	1450
190	2105	2410	2520	2320	2100
200	2290	2135	2190	2160	1950
220	2305	2215	2180	2120	2000

[a] D.P. of cotton cellulose before thermal treatment = 2220.

TABLE II
Effect of Thermal Treatment on Tensile Strength[a] of Cotton Cellulose

Temperature of treatment, °C	Warp tensile strength, kg, after thermal treatment					Weft tensile strength, kg, after thermal treatment				
	0.5 mm	1 mm	2 mm	3 mm	5 mm	0.5 min	1 min	2 min	3 min	5 min
160	63.1	62.6	62.2	58.7	58.5	65.0	63.8	63.6	59.1	58.9
180	62.8	62.0	62.0	56.0	56.3	64.4	64.1	63.6	58.9	57.1
190	65.6	62.4	62.3	62.0	62.0	66.0	64.2	62.0	62.0	60.8
200	65.5	64.5	63.4	62.7	59.7	66.9	66.2	63.8	62.0	60.8
220	65.8	62.1	62.0	61.5	58.9	66.0	64.8	64.5	62.6	60.7

[a] Tensile strength of cotton before thermal treatment = 64.3 and 65.1 for the warp and weft directions, respectively.

Besides the drop in the D.P., the higher loss in tensile strength observed at 180°C could be associated with changes in the fine physical structure of cotton cellulose. During the thermal treatment it seems likely that cellulose undergoes decrystallization and recrystallization. Loosening of the cellulose structure, which may alter surface friction, stresses, and the like on interaction of the fibers and yarns that make up the structure, is also possible under the influence of heat and water present in the vicinity of the cellulose. The magnitude of such changes is presumably dependent upon the temperature of the treatment. Data of current work suggest that decrystallization and loosening of the cellulose structure occur to an appreciable extent at 180°C (see also below).

Dyeability

It has been postulated above that thermal treatments of cotton cellulose may be accompanied by a substantial change in its fine physical structure. Once crystalline domains are adversely affected and/or the cellulose structure is loosened under the influence of heat and water present in the proximity of the cellulose, one would expect increased accessibility. On the contrary, if part of the amorphous domain is somehow converted to crystalline regions and/or if better orientation of the cellulose chains is brought about by the thermal treatment, one would expect decreased accessibility. A decrease in accessibility may also result through oxidation of aldehyde and/or hydroxyl groups along the cellulose chains to carboxyl groups, provided that decarboxylation takes place, a process that causes disappearance of some of the cellulose hydroxyls.

To check the validity of the presumed changes in accessibility, dyeing of the cotton cellulose with only one direct dye, i.e., Cuprophenyl Red FGL, before and

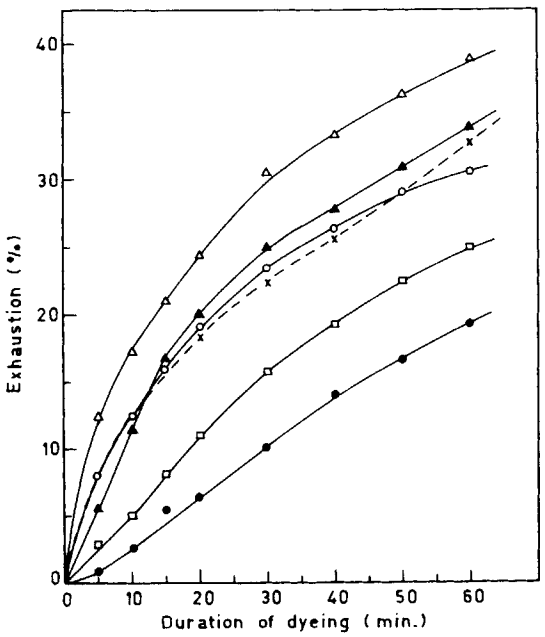

Fig. 3. Dyeing rate curves for cotton samples heated at different temperatures for 0.5 min prior to dyeing. Samples heated at: (⊙) 160°C; (△) 180°C; (▲) 190°C; (⊡) 200°C; (●) 220°C. Dotted curve represents the dyeing rate curve for cotton before thermal treatment.

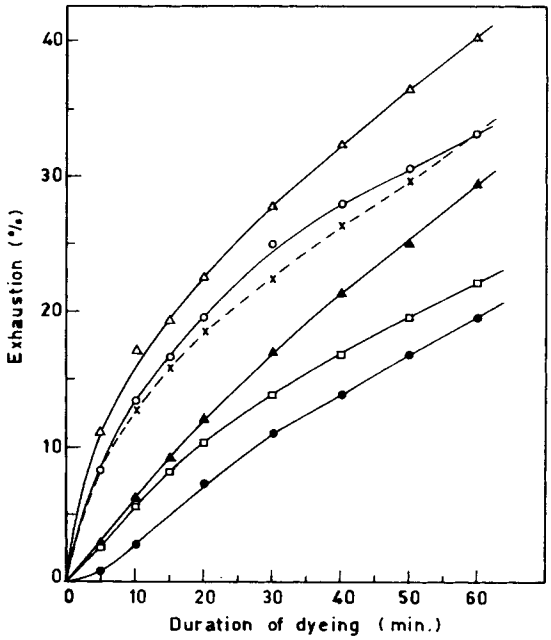

Fig. 4. Dyeing rate curves for cotton samples heated at different temperatures for 2 min prior to dyeing. Samples heated at: (⊙) 160°C; (△) 180°C; (▲) 190°C; (⊡) 200°C; (●) 220°C. Dotted curve represents the dyeing rate curve for cotton before thermal treatment.

after being thermally treated was carried out. Only one dye was used just to avoid the role of dye molecule size, which is an important factor particularly in dyeing celluloses having different accessibility.[16–18] Dyeing rate curves for each substrate were produced by plotting the amount of dye exhausted in the fiber versus time of dyeing. Typical examples of the results obtained are given in Figures 3, 4, and 5.

Figure 3 shows the dyeing rate curves for substrates heated for 0.5 min at temperatures ranging from 160 to 220°C. The dyeing rate curves for cotton cellulose before the thermal treatment are given in the same figure for comparison. As is evident, subjecting cotton cellulose for 0.5 min to the range of temperatures in question causes a considerable change in its accessibility as evidenced by the great difference in its behavior toward dyeing. Heating cotton cellulose for 0.5 min at 180°C prior to dyeing improves substantially its accessibility to the direct dye. The opposite holds true for substrates heated at 200° and 220°C for the same duration, whereas heating at 160° or 190°C leaves the affinity of the substrate for the dye practically unaltered.

Figure 4 shows the dyeing rate curves for cotton cellulose before and after subjecting it for 2 min to different temperatures. Here, too, heating cotton cellulose at 180°C proved to increase the accessibility of cotton cellulose since the dye exhaustion of the substrate is much greater than that of the untreated cotton. Substrates obtained by subjecting cotton cellulose to temperatures higher than 180°C acquire lower dye exhaustion than the untreated cotton, indicating lower accessibility to dye. The accessibility seems to remain intact upon heating cotton cellulose at 160°C because the exhaustion rate curve for the substrate obtained at this temperature nearly coincides with that of the untreated cotton.

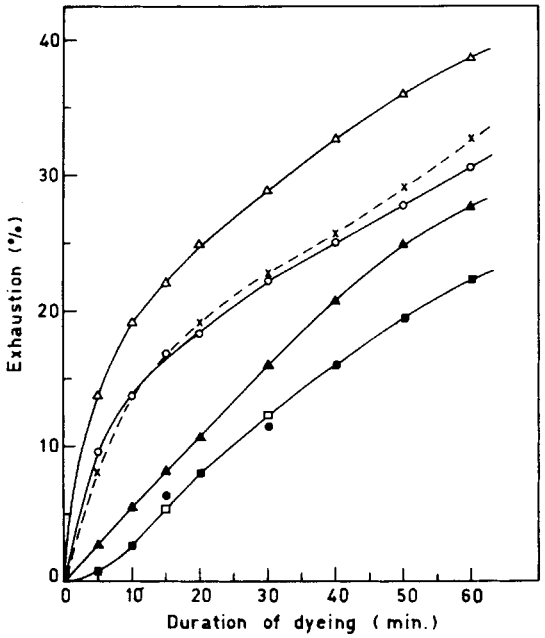

Fig. 5. Dyeing rate curves for cotton samples heated at different temperatures for 5 min prior to dyeing. Samples heated at: (⊙) 160°C; (△) 180°C; (▲) 190°C; (⊡) 200°C; (●) 220°C. Dotted curve represents the dyeing rate curve for cotton before thermal treatment.

Dyeing rate curves for cotton celluloses thermally treated for 5 min at different temperatures prior to dyeing along with the dyeing rate curve of untreated cotton are shown in Figure 5. It is obvious that dye exhaustion is obtained with substrates heated at 180°C while the lowest exhaustion is obtained with substrates heated at 200 and 220°C. Dye examination of untreated cotton is nearly equal to that obtained with substrate heated at 160°C but higher than that obtained with substrates heated at 190°C.

Thus, regardless of duration of the thermal treatment, substrates heated at 180°C, prior to dyeing, possess greater susceptibility to the dyestuff than the untreated substrate. In contrast, substrates heated at temperatures higher than 180°C are less amenable to the dye than the untreated cotton, particularly if the thermal treatment lasted longer within the range studied. Furthermore, a comparison of Figures 3, 4, and 5 (see also Fig. 6) reveals that prolongation of the thermal treatment lessens the difference in dye exhaustion of substrates heated at 190, 200, and 220°C prior to dyeing. For instance, there is a marked difference between the dyeing rate curve of substrate heated for 0.5 min at 200° and 220°C. This difference becomes smaller when the duration of the treatment at these two temperatures was 3 min and vanishes completely at 5 min.

A more clarified picture of the effect of temperature and duration of thermal treatment of cotton prior to dyeing on its dyeing behavior is shown in Figure 7. Results of this figure reveal that (a) cotton cellulose thermally treated at 180°C prior to dyeing has the highest exhaustion regardless of the duration of dyeing, as already indicated; (b) the dye exhaustion decreases significantly as the temperature of the thermal treatment increases from 180 to 220°C; and (c) thermal treatments prior to dyeing at 200 and 220°C inhibits the affinity of cellulose toward the dyestuff in the first 5 min of dyeing, particularly when thermal treatments were conducted for 5 min.

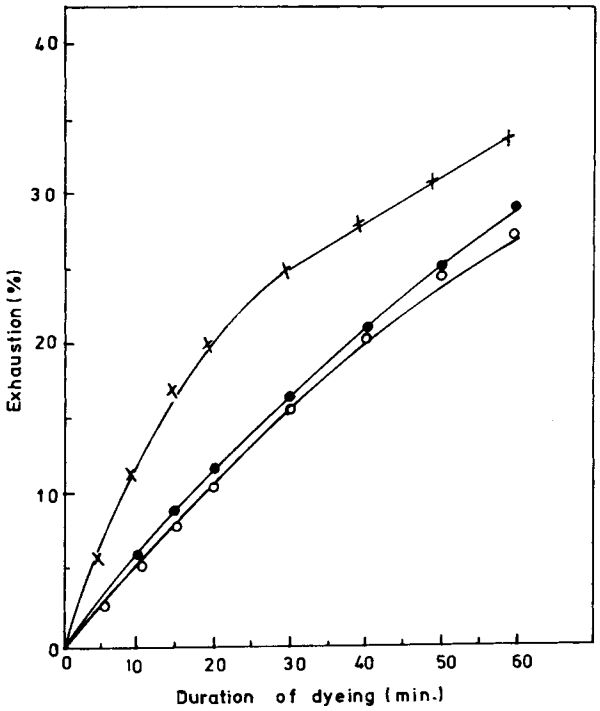

Fig. 6. Dyeing rate curves for cotton samples heated at 190°C for different periods prior to dyeing. Duration of thermal treatment: (×) 0.5 min; (●) 2 min; (○) 5 min.

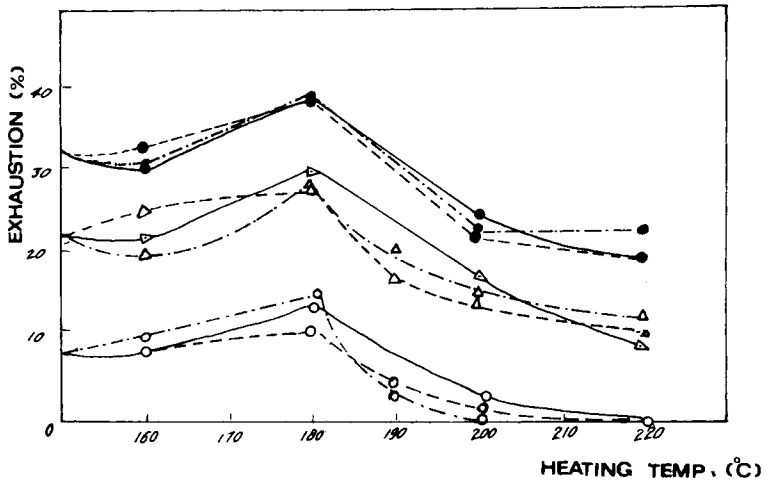

Fig. 7. Effect of heating cotton at different temperatures on percent dye exhaustion. Dye exhaustion after: (○) 5 min; (△) 30 min; (●) 60 min. Duration of thermal treatment: (—) 0.5 min; (- - -) 2 min; (------) 5 min.

The higher exhaustion of the dyestuff obtained with cotton previously heated at 180°C substantiates the assumption that thermal treatment at this particular temperature causes an increase in cellulose accessibility via decarboxylation and/or loosening of the cellulose structure. The onset of this effect prevails over the adverse effect which would be expected from the carboxyl groups created during thermal treatment. On the other hand, the lower dye exhaustion ob-

served with substrates subjected to thermal treatment at temperatures higher than 180°C supports the assumption that decarboxylation decreases significantly the reactivity and therefore the accessibility of cellulose. That is why the carboxyl contents of these substrates are relatively lower than those of substrates treated at 180°C or below. However, the adverse effect of blocking of hydroxyl groups at higher temperatures on the accessibility to dye cannot be ruled out.

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