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Reaction of Formaldehyde with Cellulose in the Presence of Sulfuric Acid

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Synopsis

The extent and rate of reaction between cotton yarn before and after slack mercerization and slack mercerization followed by stretching and formaldehyde, in the presence of various amounts of sulfuric acid (5–60% by weight) were studied. Beyond a concentration of 45% sulfuric acid, the reaction takes place very rapidly, and an explanation is put forward in terms of the extent of swelling of the fiber in sulfuric acid solutions. The reaction was also studied in the presence of glycerin, when the combined formaldehyde value is shown to decrease with an increasing concentration of glycerin.

INTRODUCTION

Treatment of cotton with sulfuric acid at certain concentrations is the basis of the well-established parchmentization process. The action of various concentrations of sulfuric acid is characterized by three stages.[1] The first effect occurs with sulfuric acid of 110° Tw (64.26% by weight), when a softening effect is obtained; the second effect is obtained at 114° Tw (65.9%), when considerable contraction takes place, making the cloth stiff; the third effect, of stiffness with transparency, is produced at 125° Tw (70.74%). The sulfuric acid finishes fall into two classes: those in which the fibers move freely and those in which fibers have been caused to cohere by more drastic treatment. The organdie finish belongs to the first type, where cotton fabric is treated with sulfuric acid of 119°–120° Tw (68.05–68.51%) for a few seconds. The treated fabric becomes thinner, finer, and more transparent. Formaldehyde modifies the action of sulfuric acid in a remarkable manner, when novel effects such as transparency with crepe-like handle are produced. Modification of cellulosic fibers by formaldehyde treatment is apparently dependent on chemical reaction, and permanent alteration of fabric properties is chiefly effected under acidic conditions.

The reaction of formaldehyde with cellulose under acidic conditions was studied for the first time by Eschalier.[2] Barrett and Foulds[3] claimed that addition of up to 10% of formalin to sulfuric acid permitted an increase in the time of safe exposure during creping or parchmentizing of cotton. Using paraformaldehyde and sulfuric acid, Wood[4] was able to introduce

7% formaldehyde into cellulose. Roff[5] classified the reaction between formaldehyde and cellulose under the following main heads: (a) interaction under substantially nonaqueous conditions, (b) interaction under fully aqueous conditions, and (c) interaction in aqueous system, followed by drying and/or baking.

The reaction may take place at room temperature and under substantially anhydrous conditions, by treating cellulose with formaldehyde in strong sulfuric acid solution. Roff[6] studied the sorption of formaldehyde from its aqueous solution and found that the sorption is reversible but proceeds to a state of equilibrium with the possible formation of methylol cellulose. As a result of the reaction, the number of accessible hydroxy groups was shown to decrease; and Schenk[7] demonstrated that methylene bridges are formed between two glucose units of adjacent chain molecules during the reaction.

Although the reaction of formaldehyde with cellulose in aqueous and nonaqueous media in the presence of dehydrants such as calcium chloride has been extensively studied, analytic data on the sorption of formaldehyde by cellulose in the presence of different amounts of sulfuric acid are not available. The present communication deals with this aspect. The effect of changing the accessibility of the cellulosic material by carrying out mercerization in the slack condition, with or without subsequent stretching, on the formaldehyde uptake is also discussed. The rate of the reaction was investigated up to a stage when equilibrium was attained. The effect on yarn properties of polyols present as additives during the reaction was also studied.

EXPERIMENTAL

Cotton

Carefully purified and bleached 2/20s cotton yarn and mercerized superfine mull were used. The cloth was desized with a solution of Rapidase (2 g/l.) at 70°C and pH 7.5 for 2 hr, followed by thorough washing and drying in air.

Mercerization of Cotton Yarn

Purified cotton yarn was treated with sodium hydroxide solution (25.5% wt/wt) at 15°C for 3 min in a slack condition during the treatment. The yarn was washed first with hot distilled water and then with cold distilled water. This was followed by treatment with dilute hydrochloric acid (0.5%) at 30°C for 5 min to neutralize residual alkali. The sample was washed free of acid and dried in air.

Cotton yarn was also mercerized by treating it with sodium hydroxide solution (25.5% wt/wt) at 15°C for 2 min and allowed to contract freely. It was then stretched to the original dimensions and washed free of alkali, as in the above case.

Formaldehyde

Paraformaldehyde (E. Merck) was used as source of formaldehyde. When analyzed iodometrically,[8] it had a purity of 95 ± 2%. All other chemicals used were of C.P. grade.

Preparation of Reaction Mixture

The required quantity of paraformaldehyde was weighed and added to the sulfuric acid solution of requisite concentration in a 250-ml volumetric flask and occasionally shaken. A clear solution was obtained in two days for 5–20% sulfuric acid solutions, while for higher concentrations, a clear solution was obtained after one day.

Reaction of Formaldehyde with Cotton Yarn

Two grams of the fiber substance was treated with 100 ml of the reaction mixture. At the end of the requisite period, the solution was filtered through a sintered glass funnel (G3). The formaldehyde content of the solution was determined iodometrically[8] before and after the treatment, and the total formaldehyde uptake was calculated from the difference in the formaldehyde contents of the solution. This includes physically adsorbed and chemically reacted formaldehyde.

Determination of Longitudinal Shrinkage in Sulfuric Acid Solutions

The extent of lateral swelling produced in cotton yarn by sulfuric acid solutions of different concentrations was estimated in terms of longitudinal contraction produced in the yarn, using a cathetometer by the method of Nabar and Achwal[9] for studying the swelling action of sodium hydroxide solutions on cotton yarn. Single yarn (18 cm long) was suspended by tying one end to a fixed glass ring and the other to another glass ring weighing 1.716 g. A measuring cylinder (500 ml capacity) containing sulfuric acid (30–60%) was placed in such a position that the yarn and both of the rings were completely immersed in the solution. A cathetometer was focused on the knot tied to the lower ring, and the longitudinal contraction undergone by the yarn was measured. A blank experiment in which only distilled water was used instead of sulfuric acid solution was performed. The contraction is expressed as a percentage of the original length.

RESULTS AND DISCUSSION

Reaction of Formaldehyde with Cellulose

Three purified cellulosic fiber substances, viz., standard cellulose, slack-mercerized and restretched cotton, and cotton mercerized in the slack condition were treated with formaldehyde in the presence of various amounts of sulfuric acid at 30° ± 2°C for 5 min by the method described above. The total formaldehyde uptake was calculated by determining

the formaldehyde content of the solution before and after the formaldehyde treatment. The results are given in Table I.

TABLE I
Uptake of Formaldehyde by Cellulosic Fiber Substances in the Presence of Sulfuric Acid at 30°C ± 2°C for 5 Min

Concentration of sulfuric acid, % by weight	Total formaldehyde uptake, g HCHO/kg fiber		
	Standard cellulose	Slack-mercerized and restretched cotton	Slack-mercerized cotton
5	6.38	6.77	8.72
10	9.57	9.80	11.59
15	12.77	11.08	13.52
20	13.99	16.74	14.09
25	16.15	18.42	17.68
30	19.16	18.98	18.91
35	20.54	21.82	20.74
40	20.82	22.43	21.41
45	21.23	23.03	22.52
50	26.09	27.38	30.39
55	28.92	32.04	31.00
60	30.08	42.52	37.72

It is seen from Table I that the reaction between formaldehyde and cellulose is influenced by the sulfuric acid concentration. As the concentration of sulfuric acid increases from 5% to 30%, the total formaldehyde uptake increases rapidly, reaches a more or less constant value over the range 30–45% sulfuric acid, and then increases rapidly with further increase in sulfuric acid concentration. This behavior is observed for all the three fiber substances studied.

When cotton is mercerized, some of the hydrogen bonds existing between the hydroxyl groups of adjacent chain molecules are severed. During the subsequent washing and drying operations, some of these bonds are reformed, but the original number of hydrogen bonds is not reached. The degree of orientation, which is characteristic of crystallites in native cellulose, could either be retained by the application of tension or increased by stretching the swollen fibers. The orientation of cellulose crystallites decreases if mercerization of cotton is carried out in the slack form. Since this type of mercerization decreases the amount of crystalline fraction and causes a decrease in the hydrogen bonding between cellulose chains, the resulting fiber substance has a greater absorptive capacity and hence is more reactive. Due to these factors, total formaldehyde uptake should be greater in the case of mercerized cotton than in unmercerized cotton. The results (Table I) obtained in the present investigation show that this is so. These values of the two cellulose samples mercerized under different conditions are more or less of the same order.

Abnormal Behavior of Sulfuric Acid

When the reaction of formaldehyde with cellulose in the presence of sulfuric acid was carried out, it was observed that, irrespective of the accessibility of the cellulosic fiber substance, the total formaldehyde uptake increased rapidly when the concentration of sulfuric acid was raised above 45% (Table I). The formaldehyde uptake behavior of the three cellulosic substances studied in the presence of 45% or more of sulfuric acid in the reaction mixture was found to be different from that studied in the presence of lower concentrations of sulfuric acid. This abnormal behavior of sulfuric acid may be due to the following reasons: (a) swelling action of sulfuric acid of higher concentrations (45%) and (b) the presence of sufficient amounts of hydrates of sulfuric acid in its solutions at higher concentrations (45%).

Swelling Action of Sulfuric Acid

It is known that cotton dissolves in concentrated sulfuric acid, accompanied by hydrolytic degradation, depending on the temperature of dissolution. Generally, swelling precedes dissolution. Although concentrated sulfuric acid dissolves cotton, solutions of the acid at lower concentrations do not do so at room temperature, but they exert a swelling action on cotton. This action may not be appreciable for low concentrations of

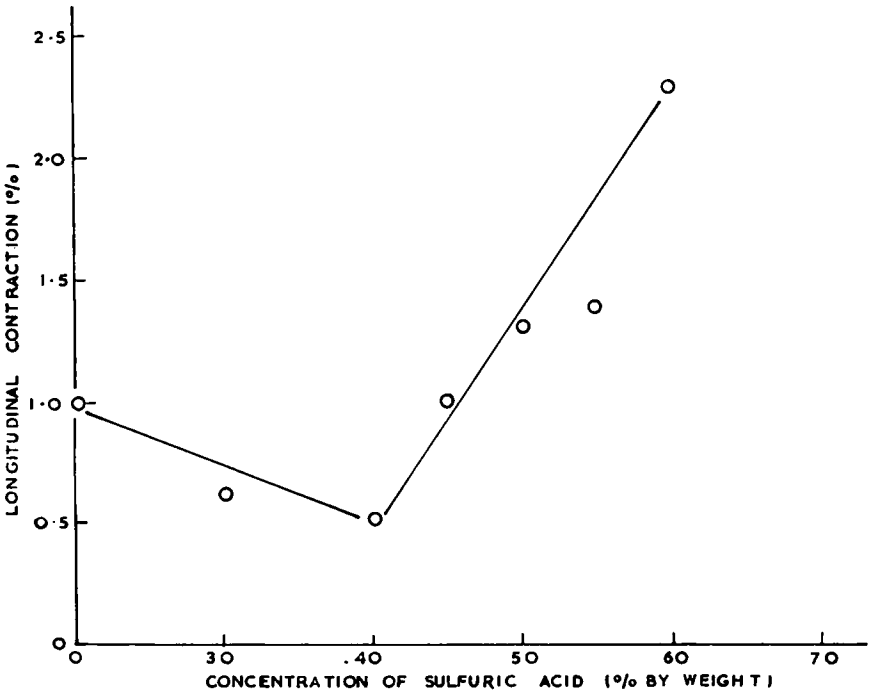

Fig. 1. Relation between longitudinal contraction and sulfuric acid concentration.

the acid. In order to study this aspect, cotton yarn was treated with sulfuric acid solutions of various concentrations (30–60%) by the method described earlier. The longitudinal contraction undergone by the yarn was measured, and the percentage longitudinal contraction, a measure of lateral swelling, was calculated. The results are shown in Figure 1.

It is seen that as the concentration of sulfuric acid increases from 0% to about 40%, the longitudinal contraction (and hence the lateral swelling) decreases; but after 40%, it increases upon further increase in concentration of sulfuric acid, reaching a value of about 1% longitudinal contraction at 45% sulfuric acid. This value is the same as that produced by distilled water alone. The value increases to 2.3% when the sulfuric acid concentration is raised to 60%. From this it may be said that 45% sulfuric acid solution or stronger solutions produce more swelling, thereby making more hydroxyl groups available for chemical reaction. From this it follows that if cellulose is treated with a chemical which reacts with the free hydroxyl groups, e.g., formaldehyde, in the presence of sulfuric acid, the extent of the reaction should increase considerably in the presence of sulfuric acid of concentrations of more than 45%. This has been found to be the case in the present investigation (Table I).

Rate of Reaction Between Formaldehyde and Cellulose

Slack-mercerized and restretched cotton cellulose was selected for this study. These samples (2 g) were treated with 100 ml of a solution containing formaldehyde (20 g) and different amounts of sulfuric acid (20–45%) for different periods (5 sec to 5 min). The total formaldehyde uptake values were determined, and the results are shown in Figure 2.

It is seen from Figure 2 that for all the concentrations of sulfuric acid studied, the reaction between formaldehyde and cellulose takes place very rapidly in the initial stages of the reaction and slowly in the later ones, tending to attain an equilibrium after about 3 min. It remains the same thereafter, even when the reaction time is increased to 5 min. It is also seen that the rate of reaction is increased by increasing the concentration of sulfuric acid in the treating liquor.

The reaction between formaldehyde and cellulose is complex in nature, and most probably the rate of the reaction is also governed by factors other than the concentration of the reactants. It is difficult to find out the exact order of reaction with respect to the concentration of hydroxyl groups in cotton cellulose, as its fine structure is complex in nature and it appears that only a fraction of the total number of hydroxyl groups is taking part in the reaction. The rate of reaction of formaldehyde with the hydroxyl groups in various cellulosic fiber substances depends on the proportion of the accessible hydroxyl groups. This observation leads one to expect that the reaction of formaldehyde with cellulose hydroxyl groups is of the first order if it is assumed that all the hydroxyl groups in the fiber substance are equally accessible for the reaction. It is very likely that the total accessible hydroxyl groups, viz., those situated in the interior of the fiber

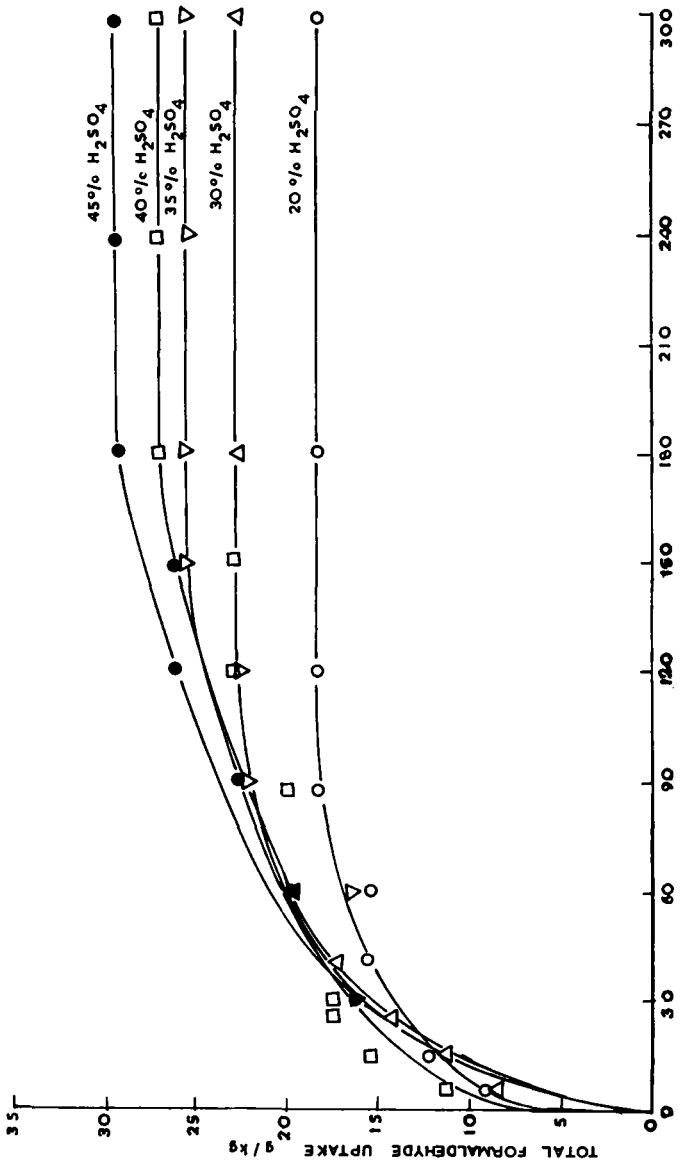

Fig. 2. Rate curves for the reaction of formaldehyde with cellulose in the presence of different amounts of sulfuric acid: (●) 45% H_2SO_4; (□) 40% H_2SO_4; (▽) 35% H_2SO_4; (△) 30% H_2SO_4; (○) 20% H_2SO_4.

substance, will not be accessible to formaldehyde during the various stages of the reaction. Most of the reactions of cellulose strongly depend on the internal order of the chain molecules in cellulose.

Reaction of Formaldehyde with Cellulose in the Presence of Polyhydroxy Compounds

When formaldehyde reacts with cellulose in the presence of sulfuric acid, either methylol compounds or methylene crosslinks are formed with hydroxyl groups of the same molecular chain or of adjacent chains, respectively. If another hydroxy compound is also present in the reaction mixture, the uptake of formaldehyde by cellulose should be hindered due to the competition offered by the additional hydroxy compound toward formaldehyde, with which it also can combine. Hence, the total formaldehyde uptake of the cellulosic material should be lower in the presence of the hydroxy compound than in its absence. In order to see whether this is so, the effect of the presence of glycerin on the combined formaldehyde value was studied. The reaction of formaldehyde with standard cellulose in the presence of sulfuric acid (35–50%) and glycerin (0–50 g/l.) at 30°C ± 2°C was carried out for 5 min. The total formaldehyde uptake values were determined as before. The results are given in Table II.

TABLE II
Effect of Glycerin on the Total Formaldehyde Uptake by Standard Cellulose in the Presence of Sulfuric Acid at 30°C ± 2°C for 5 Min

Concn. of H_2SO_4, %	Concn. of glycerin, g/l.	Total formaldehyde uptake g HCHO/kg fiber
	0	20.54
30	10	11.53
	30	8.14
	50	6.78
	0	20.82
40	10	13.56
	30	13.56
	50	10.85
	0	21.23
45	10	12.97
	30	12.97
	50	7.78
	0	26.09
50	10	19.45
	30	11.68
	50	11.68

It is seen that, as expected, the total formaldehyde uptake of standard cellulose, determined in the presence of glycerin, is lower than that obtained in the absence of glycerin at all the concentrations of sulfuric acid

studied. As the concentration of glycerin increases, the total formaldehyde uptake decreases for all the sulfuric acid concentrations.

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