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Reaction of Formaldehyde with Cellulose in the Presence of Phosphoric Acid

V. A. SHENAI and J. M. MANJESHWAR, *Department of Chemical Technology, University of Bombay, Bombay, India*

Synopsis

The extent and rate of reaction between cotton yarn before and after slack mercerization and slack mercerization followed by restretching and formaldehyde in the presence of various amounts of phosphoric acid (10–70% by weight) have been studied. The reaction is very rapid beyond a concentration of 45% phosphoric acid. The reaction has also been studied on mercerized cotton voile in the presence and absence of polyols and ammonium sulfate, and the effect of these substances on combined formaldehyde value and tensile strength of the fabric has been investigated.

INTRODUCTION

Recently, Nabar, Shenai, and Shenai[1] studied the extent and rate of reaction between cotton yarn before and after slack mercerization and slack mercerization followed by restretching and formaldehyde in the presence of various amounts of sulfuric acid (5–60% by weight). They determined the total formaldehyde uptake by cellulose by estimating the formaldehyde content (g CH_2O/kg cellulose) of the treating solution before and after treating the cellulose with formaldehyde. The total formaldehyde uptake values included physically adsorbed and chemically reacted formaldehyde. They found that beyond a concentration of 45% sulfuric acid, the reaction took place very rapidly, which was attributed to the increased swelling action of the sulfuric acid solutions exerted on the cellulosic fibers. The reaction was also studied in the presence of glycerin, when the total formaldehyde uptake was found to decrease with increasing glycerin concentration. The total formaldehyde uptake was found to increase with the increased accessibility of the cellulosic substrate brought about by mercerizing.

As a supplement to the above study, the present communication deals with the reaction of formaldehyde with unmercerized and mercerized cotton yarns, but in the presence of various amounts of phosphoric acid. The total formaldehyde uptake as well as the combined formaldehyde value were determined so as to determine the contribution of the physically adsorbed formaldehyde to the total formaldehyde uptake.

EXPERIMENTAL

Reaction of Formaldehyde with Cellulose. Two grams of the cellulosic fiber substances was treated with 100 ml of the reaction mixture at 25 ± 2°C. At the end of the requisite period, the solution was filtered through a sintered glass funnel (G 3). The formaldehyde content of the solution was determined iodometrically before and after the treatment, and the total formaldehyde uptake (g CH_2O/kg cellulose) was calculated from the difference in the formaldehyde contents of the solutions. The formaldehyde-treated sample was washed with cold water, boiled with distilled water for 5 min to remove the adsorbed formaldehyde, washed thoroughly with cold distilled water, and allowed to dry at 30°C. The combined formaldehyde value (g CH_2O/kg cellulose) was determined by the chromotropic acid method of Bricker and Johnson.[2]

Determination of Accessibility of Cellulosic Substrates. The accessibility of the differently mercerized and unmercerized cotton yarns was determined by the iodine absorption method of Hessler and Power.[3] These values were found to be 7.95%, 11.74%, and 13.83% for unmercerized cotton yarn, slack-mercerized and restretched cotton yarn, and slack-mercerized cotton yarn, respectively.

Determination of Moisture Regain. About 1 g formaldehyde-treated cotton yarn was kept over P_2O_5 for 4 hr under reduced pressure to reduce the moisture content below the regain value and then conditioned at 65% R.H. and 30°C until equilibrium was attained. It was accurately weighed, and dried in an oven at 110°C to constant weight, and the moisture regain was calculated from these weights.

The Reaction of Formaldehyde with Cotton Voile. The reaction mixture (100 ml) containing formaldehyde (2%) and phosphoric acid (85%) with or without the other additives was cooled to 25 ± 2°C and was added to a shallow porcelain tray. The cloth pieces (20 cm × 15 cm) were dipped in the solution, and after the required period, the cloth pieces were removed and, dipped in cold water, followed by washing with running tap water. The final traces of phosphoric acid were neutralized using a saturated solution of sodium carbonate, and then the samples were washed thoroughly and finally dried at 30°C. The dried samples were conditioned at 65% R.H. and 30°C. The copper number[4,5] and tensile strength were also determined.

RESULTS AND DISCUSSION

Reaction of Formaldehyde with Cellulose

The results of the total formaldehyde uptake and the combined formaldehyde value obtained with the different cellulosic fiber substances are given in Table I. It is seen that for all the fiber substances studied the relation between the total formaldehyde uptake and the duration of reaction in the presence of phosphoric acid is similar to that in the presence of sulfuric

TABLE I
Reaction of Formaldehyde (20 g/l.) with Cellulosic Fiber Substances in the Presence of Phosphoric Acid[a]

Concentration of phosphoric acid, wt-%	Moisture regain of treated unmercerized yarn, %	Total formaldehyde uptake, g CH_2O/kg fiber			Combined formaldehyde value, g CH_2O/kg fiber		
		Unmercerized yarn	Slack-mercerized and restretched yarn	Slack-mercerized yarn	Unmercerized yarn	Slack-mercerized and restretched yarn	Slack-mercerized yarn
0	6.645	—	—	—	—	—	—
15	6.334	9.00	10.39	10.39	8.80	9.25	9.62
20	6.292	10.50	10.50	10.39	9.42	9.95	10.20
25	6.250	10.71	12.00	12.00	10.35	10.75	10.95
30	6.039	12.12	12.00	13.50	11.00	11.20	11.52
35	6.024	13.64	13.50	13.50	11.25	11.88	12.30
40	6.099	15.00	15.00	15.00	12.00	12.38	12.75
45	5.903	16.67	15.00	15.00	12.18	13.00	13.30
50	5.841	17.64	16.50	16.50	14.40	15.00	15.38
55	5.828	17.64	18.00	18.00	15.50	16.00	16.45
60	5.781	17.82	18.00	19.50	16.12	16.45	17.38
65	5.589	21.00	21.00	21.00	18.75	19.60	20.15
70	5.527	21.00	22.50	22.50	20.25	21.75	22.18

[a] At 25 ± 2°C for 20 min.

acid in the earlier study.[1] It is also seen that a large amount of the total formaldehyde uptake is used up in the chemical reaction with cellulose. The extent of the reaction of formaldehyde in the presence of phosphoric acid depends on the state of the internal order of the cellulosic material and the combined formaldehyde values increase for the cellulosic materials in the order unmercerized cotton < cotton slack-mercerized and restretched cotton < slack-mercerized cotton, in accord with the order of their accessibility.

Further, it is seen from Table I that the moisture regain of formaldehyde-reacted unmercerized cotton yarn decreases with increasing phosphoric acid concentration in the treating solution, i.e., with increasing combined formaldehyde value, presumably because of the blocking of the increasing proportion of accessible hydroxyl groups by reaction with formaldehyde.

Pierce and Frick[6] studied the reaction of cotton print cloth with formaldehyde in the presence of 75% orthophosphoric acid and 3.7% hydrochloric acid and found that the bound formaldehyde increased with reaction time. The moisture regain of the crosslinked samples increased with increasing degree of crosslinkage. The high moisture regains have been attributed to the extensive fiber swelling occurring at the time of crosslinking. The crosslinks are predominantly intralamellar and are distributed throughout the fiber cross section.

Rate of Reaction Between Formaldehyde and Cellulose

The rate plots for the reaction of formaldehyde with cellulosic fiber substances of different accessibility in the presence of various concentrations of phosphoric acid are shown in Figure 1. It is seen that both the rate and the extent of reaction of formaldehyde with cellulose increase as the accessibility of the cellulosic samples increases or as the concentration of phosphoric acid in the treating solution increases, for the same fiber substance. It is also seen that the reaction tends to reach equilibrium after about 15 min. In the case of sulfuric acid swelling,[1] the equilibrium is reached in about 3 min.

Action of Formaldehyde on Cotton Voile in the Presence of Phosphoric Acid

The nature of the reaction of formaldehyde with cotton fabric is controlled by the amount of moisture present during the reaction, the presence of dehydrating agents, the nature and concentration of the acidic catalysts, and the temperature employed.[7] Hydroxy compounds, neutral inorganic salts, etc., were used to modify (moderate or enhance) the effect of formaldehyde on the fabric to prevent the tendering of the fiber substance. It has been reported[8] that the deleterious effect of the treatment of formaldehyde in the presence of sulfuric acid and other strong mineral acids on tensile strength and extensibility of cellulosic materials can be substantially reduced by replacing the acid by a water-soluble salt of magnesium, calcium, strontium, or barium.

TABLE II
Effect of Additives to the Treating Solution on the Properties of Cotton Voile[a]

Composition of treating solution, %			Combined formaldehyde value, g	Tensile strength,	Loss in tensile strength,	Copper
H_3PO_4	HCHO	Additive	CH_2O/kg	kg	%	number
—	—	—	0.00	18.6	—	0.026
85	—	—	0.00	16.6	10.75	0.039
85	2	—	4.50	15.1	18.82	0.043
85	2	2 (glucose)	3.80	13.4	27.96	0.065
85	2	2 (glycerin)	4.12	14.1	24.19	0.061
85	2	2 (ethylene glycol)	4.80	16.5	11.29	0.074
85	2	2 ($(NH_4)_2SO_4$)	6.90	17.1	8.07	0.052

[a] Duration of treatment 15 sec.

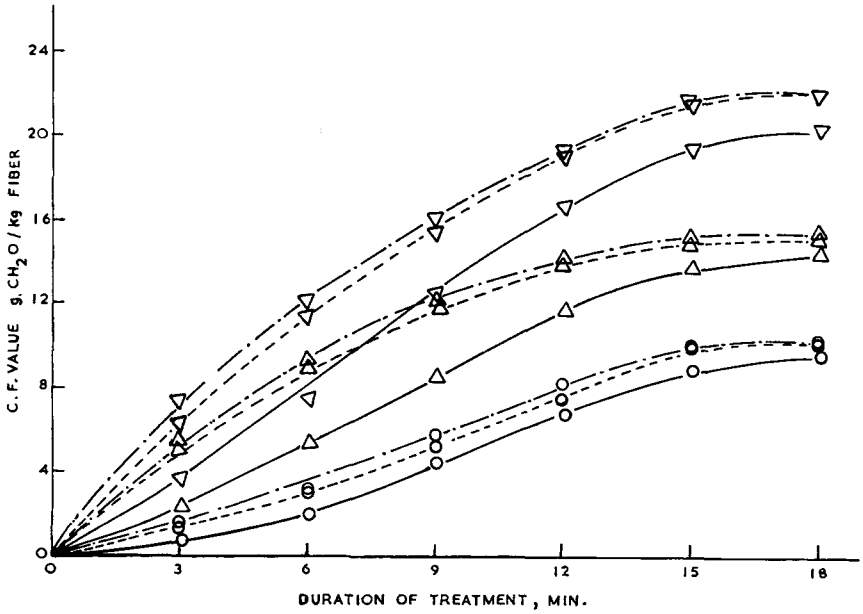

Fig. 1. Rate curves for the reaction of formaldehyde with cellulosic substrates in the presence of different amounts of phosphoric acid: (—) unmercerized cotton; (—) slack-mercerized and restretched cotton; (- - -) slack-mercerized cotton; (O) 20% H_3PO_4; (△) 50% H_3PO_4; (▽) 70% H_3PO_4.

When glucose or glycerin (polyol) is present in the treating solution, the reaction of formaldehyde with cellulose should be hindered owing to the competition offered by the additional hydroxy compound toward formaldehyde, with which it also can combine. Hence, the combined formaldehyde value should decrease in the presence of these polyols. In the present investigation, the reaction of formaldehyde (2%) in phosphoric acid (85%) in the presence of glucose, glycerin, or ammonium sulfate (2%) with

cotton voile at 25 ± 2°C for 15 sec was studied. Some of the properties of the treated samples are given in Table II. It is seen that, as expected, the combined formaldehyde value of the treated fabric is decreased when the reaction is carried out in the presence of glucose or glycerin. Increased extent of reaction (in terms of combined formaldehyde value) is seen in the presence of ammonium sulfate. Strength losses are found to be considerable when the formaldehyde reaction is carried out in the presence of glucose or glycerin, while ammonium sulfate seems to confer protection against strength loss. Similar behavior is seen when the degradation of the cellulosic substrate is assessed in terms of the copper number.

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