Characterization of Acidic Groups in Oxycelluloses IV. Effect of Accelerated Aging on Yellowing as Well as Carboxyl Groups and Lactones in Pulp

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Synopsis

Bleached bamboo pulp as well as two oxypulps were subjected to accelerated aging by heating as well as steaming, and the yellowing or color reversion was studied. The yellowing is increased by the presence of free carboxyl and the reducing groups in oxycelluloses. The aging treatments were found to cause an increase in free carboxyl groups accompanied by a reduction in copper number. A differentiation between free carboxyl and various lactone groups in oxidized and also aged samples was carried out based on the variation in their reaction rates with KI/KIO_3 solution, and the characteristic acidic group spectrum showed that on steam aging the fast-reacting lactones are lost.

INTRODUCTION

Brightness reversion or yellowing has been attributed to nearly every constituent of pulp and paper. Giertz and McPherson[1] showed that oxidation leading to carboxyl or carbonyl groups was an important factor for yellowing. The role of acidic groups and the carboxyl groups in particular have been studied by various investigators.[2,3] Different accelerated aging tests have been suggested in the literature to assess yellowing on prolonged storage. In the present work both hot air and steam aging have been studied on two types of oxycelluloses to obtain further insight into the role of functional groups on aging. The nature and amount of acidic groups present both before and after aging were estimated by the differential kinetic rate analysis of the indirect iodometric method.[4]

EXPERIMENTAL

Preparation of Oxypulps

Oxypulp O_1 was prepared by oxidizing with potassium dichromate (0.20 M)-oxalic acid (1.00 M) for 4 h. Oxypulp O_2 was prepared by oxidizing with potassium dichromate (0.10 M)-sulfuric acid (0.20 M) for 15 h. Oxidation of bleached bamboo pulp (P) was carried out in the dark by treating 100 g with the oxidizing agents at 30°C at a liquor ratio of 50:1. After the required time of oxidation, the pulp was washed with distilled water, air dried, and conditioned at 65% RH.

Journal of Applied Polymer Science, Vol. 32, 3913–3917 (1986)

CCC 0021-8995/86/033913–05$04.00

PREPARATION OF LABORATORY BRIGHTNESS SHEETS[5]

Sheets of 7.5 cm diameter for pulp and oxypulps (having weight 1.5 ± 0.1 g each) were prepared in a laboratory sheet-making assembly.

ACCELERATED AGING

Heat Aging. Sheets were heated (H) in a thermostatistically controlled oven at 150 ± 0.5°C for 4 h by suitably hanging from hooks.

Steam Aging

Sheets were steamed (s) at 25 psi for ½ h in a laboratory steaming machine (Electronic and Engineering Company).

WHITENESS AND YELLOWNESS MEASUREMENT

Diffuse reflectance at various wavelengths between 400 and 700 nm was measured for all paper sheets on Pye Unichem Ltd. Sp-8 400 UV Visible Spectrophotometer. Since optical properties may change with time, reflectance was measured at least 2 h but not more than 24 h after forming the sheets or after the aging.

DETERMINATING OF ACID CONTENT AND COPPER NUMBER

The acid content was determined by the indirect iodometric method[6] and copper number by the Heyes method.[7]

QUALITATIVE TEST FOR LACTONES

A qualitative test for lactones was carried out as suggested by Kaverzneva and Salova[8] and coloration graded.[9]

	No color	Tinge	Pale	Light	Medium	Dark	Intense
Grade	0	1	2	3	4	5	6

RESULTS AND DISCUSSION

General

In order to study the effect of functional groups, two oxypulps having different contents of functional groups were prepared by oxidizing bleached bamboo pulp (P) using dichromate with oxalic acid (O_1) as well as sulfuric acid (O_2).

Laboratory brightness sheets were prepared from these samples, which were aged by heating in oven and by steaming. All the sheets were assessed for carboxyl content, copper number, whiteness, and yellowness index.

In order to assess whiteness-yellowness index, various formulas have been suggested for pulp as well as cotton fabrics.[10] After correlation between whiteness and yellowness measurements by different formulas for the pulp and oxypulp and aged samples, better correlation was observed between values calculated by the following two formulas:

$$W = R_{550} \qquad Y = \frac{R_{600} - R_{450}}{R_{550}}$$

where R_{450}, R_{550}, and R_{600} are the diffuse reflectance values at these particular wavelengths.[11]

ROLE OF FUNCTIONAL GROUPS ON YELLOWING

The values for carboxyl content, copper number, whiteness, yellowness index, and lactone color reaction grades are given in Table I. It is observed that both these oxidation treatments lead to a slight improvement in whiteness index with a corresponding decrease in yellowness index. Both oxycelluloses have a high extent of reducing groups and carboxyl groups and show considerable yellowing. The steam aging causes a greater extent of yellowing than heat aging. Thus in general the presence of carboxyl as well as reducing groups promotes yellowing after aging.

EFFECT OF AGING ON FUNCTIONAL GROUPS

Aging is found to cause an increase in carboxyl content for both oxypulps and a decrease in copper number. The decrease in copper number is greater in the case of steam aging. The lactone color reaction shows that oxidation introduces an appreciable amount of lactone groups. However, the lactone color reaction shows a decrease in color intensity on aging; hence the oxypulp samples have been thoroughly studied for characterization of acidic groups by the differential kinetic rate analysis of the indirect iodometric reaction. The details of the differential kinetic rate analysis method to differentiate

TABLE I
Changes in Functional Groups and Whiteness on Aging

Sample	Carboxyl content (mEq per 100 g)	Copper number	Lactone grade	Whiteness index	Yellowness index
P	1.9	1.5	1	81.0	0.17
PH	3.1	1.9	0	65.0	0.41
PS	3.5	1.1	0	62.5	0.43
O_1	6.0	4.5	3	81.5	0.16
O_1H	7.4	2.3	2	55.0	0.43
O_1S	6.6	2.0	2	56.0	0.53
O_2	7.6	6.5	3	82.0	0.15
O_2H	10.0	4.6	2	33.0	0.79
O_2S	8.8	3.2	1	18.0	0.90

TABLE II
Characterization of Acidic Groups in Pulps Before and After Aging

		Acid group 1		Acid group 2		Acid group 3	
Sample	Conditions	Rate k[a]	Content[b]	Rate k	Content	Rate k	Content
P		1.4	0.7	—	—	208	1.6
O_1	$K_2Cr_2O_7/(COOH)_2$	0.8	2.7	31.0	1.20	288	4.7
O_1H		0.6	2.5	17.0	1.0	95	5.4
O_1S		0.9	2.2	—	—	80	5.8
O_2	$K_2Cr_2O_7/H_2SO_4$	1.3	6.0	19.8	3.0	573	2.1
O_2H		0.9	6.2	10.0	5.0	256	2.7
O_2S		2.3	11.1	—	—	133	3.0

[a] Rate k in units of $[(mEq/L)^{-1}\ min^{-1}] \times 10^6$.
[b] Acid content in units of mEq per 100 g.

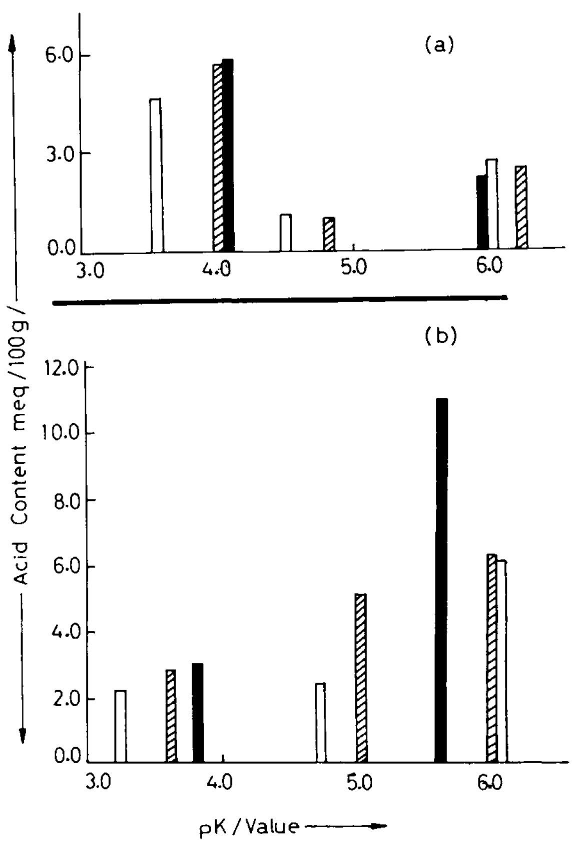

Fig. 1. Acidic group spectra: clear blocks, before aging; lined blocks, after accelerated heat aging; dark blocks, after accelerated steam aging; (a) O_1; (b) O_2.

between free carboxyl and lactone groups in oxycelluloses have been discussed in earlier work.[4] The results of the kinetic rate analysis are given in Table II and Fig. 1. There is an increase in the amount of fast-reacting free carboxyl groups on aging. In oxypulp O_2 there is an appreciable increase in the amount of the slow-reacting lactones. The fast-reacting lactones or type 2 acid groups are lost on steam aging.

For the fast- and medium-reacting acidic groups, the value of rate constant k decreased on aging, as shown by the shift in pK value, which is likely to be caused by the changes in physical structure brought about by aging.

CONCLUSION

Yellowing of pulp is caused by the presence of both aldehydic and carboxyl groups in pulp. Both heat and steam aging are accompanied by an increase in the total acid content. However, the faster reacting lactones seem to be destroyed on steam aging. The shift in the pK values in possibly due to the changes in the physical structure induced during aging.

References

1. H. W. Giertz and J. McPherson, *Svensk Papperstidn.*, **59,** 93 (1956).
2. J. S. Arney and A. H. Chapdelaine Kinetic Study of Influence of Acidity on Accelerated Ageing of Paper, Adv. in Chem. Ser. (ACS) No. 193, 189 (1981).
3. Anon, *Papier Cellulosa,* **73,** (11), 35 (1980).
4. W. B. Achwal and G. Shanker, *J. Appl. Polym. Sci.,* **16,** 1873 (1972).
5. TAPPI Standard Test Methods T-218 (1982).
6. W. B. Achwal and G. Shankar, *Svensk Papperstidn.*, **75,** 131 (1972).
7. T. F. Heyes, *J. Soc. Chem. Ind.*, **47,** 90 (1928).
8. E. D. S. Kaverzneva and A. S. Salova, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk,* 782 (1951); *C.A.*, **46,** 5833 (1951).
9. W. B. Achwal and G. Shankar, *J. Appl. Polym. Soc.,* **16,** 1791 (1972).
10. A. S. Divatia and R. H. Shah, *Text. Dyer Printer,* **10**(19), 35 (1977).
11. W. B. Achwal and R. Murali, IPPTA, *22* (3), 1 (1985).