Effect of Functional Groups in Pulp on the Colour Reversion

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• The effect of functional groups in pulp on the yellowing of paper has been investigated. Various oxypulps were prepared having different extents of both carboxyl and aldehyde groups and were subjected to two different accelerated ageing treatments, namely heating in oven and steaming under pressure for a specific time & were assessed for charges in functional groups, whiteness and yellowness index. During both heating and steaming, the yellowness developed seems to depend mainly on the extent of reducing groups, while carboxyl groups seem to have less pronounced effect. On heating, the oxypulps show decrease in copper number and increase in carboxyl, while samples with high carboxyl show decrease in carboxyl. However these samples on steaming show a decrease in carboxly and increase in copper number.

Factors which influence brightness reversion have been studied by various investigators, as the problem is of scientific as well as industrial interest[1-9]. Brightness reversion or yellowing has been attributed to nearly every constituent of pulp and paper. Highly purified pulp containing only small amounts of lignin, resin and hemicelluloses, still yellows on ageing, suggesting that degree of oxidation of the cellulose itself plays a role.

Giertz[3] has shown that oxidation leading to carboxyl or carbonyl groups was an important factor of yellowing. Sihtola[7] has shown that carboxyl groups also promote yellowing. Rapson and Hakin[9] have established that carbonyl groups contribute to a greater degree than carboxyl groups. Removal of carbonyl groups either by reduction with Sodium borohydride or oxidation with chlorous acid reduces yellowing[10,11]. Virkola[10] has reported that oxidation with chlorous acid resulted in a decrease in yellowing but not to the same extent as after sodium borohydride treatment. The present study relates to further assessment of the role of carboxyl and carbonyl groups during yellowing of pulp.

EXPERIMENTAL

Preparation of Oxidised Pulps

Oxidation was carried out in the dark by treating 100g of bleached bamboo pulp with the oxidising agents at 30°C at a liquor ratio of 50:1. Table-1 After the required time of oxidation, the pulp was washed with distilled water, air dried and conditioned. Part of each oxypulp was further given sodium borohydride[12] and chlorous acid treatment[13].

TABLE-1

CONDITIONS OF PREPARATION OF OXYPULPS

Oxy Pulp Sample	Oxidising Agent	Concentration of Reagent	Time (hr)
Oxycellulose	$K_2Cr_2O_7$+	0.2 M	4
Op_1	$(COOH)_2$	1.0 M	
OP_2	$NaIO_4$+	0.1 M	4
	H_2SO_4	0.1 M	

Preparation of Laboratory Brightness Sheets

Sheets for pulp, each oxypulp and their modified forms were then prepared in a laboratory paper making assembly and placed between smooth steel sheet and filter paper, preassed at 70kg/cm² for 3 min., air dried and conditioned.

Accelerated Ageing

(i) Sample pieces were heated in an oven at 150 ± 0.5°C for 4hr by suitably hanging the sheets, from hooks to have uniform exposure.

(ii) Sample pieces were steamed at 25 p.s.i. for 1/2hr in a laboratory steaming machine by Electronic and Engineering Company.

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Whiteness and Yellowness Measurement

Diffuse reflectance at various wave lengths between 400—700 nm was measured for all paper sheets on a Pye Unichem Ltd. Sp—8 400 UV/Vis. Spectrophotometer.

The whiteness and yellowness values calculated using the two equations[14],

$$W_1 = R\ 550$$

$$Y_1 = \frac{R\ 600 - R450}{R\ 550}$$

where R_{450}, R_{500} and R_{600} are the diffuse reflectance at these particular wavelengths.

A visual assessment of yellowness was done assigning the following yellowing grades.

White	Pale Yellow	Yellow	Light Brown	Brown	Dark Brown
0	1	2	3	4	5

Determination of Acid Content and Copper Number

The acid content was determined by indirect Iodometric method[15] aud copper number by Heyes method[16].

Qualitative Test for Lactones[17]

The test involves treatment of sample with hydroxylamine hydrochloride followed by ferric chloride when brown or pink colour development takes place. The intensities of colours developed during the test were graded as follows :

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

EXPERIMENTAL RESULTS AND DISCUSSION

Far a detailed study of correlation between functional groups and tendency of yellowing, bleached pulp (p) was oxidised by potassium dichromate + oxalic acid (OP_1) and sodium periodate + sulfuric acid (OP_2). A part of the pulp and oxypulps were then given sodium borohydride treatment (B) and chlorous acid treatment (Cl) seoarately. They were then analysed for copper number and carboxyl content Table-2. Table also gives the whiteness and yellowness index for these samples.

TABLE–2

FUNCTIONAL GROUPS AND YELLOWNESS INDEX OF OXYPULP SAMPLES

Designation Pulp	Carboxyl content meg./100g	Cu. No.	Lactone test Grade	Yellowness Iudex	Whiteness Index	Visual Assessment
P	1.9	1.5	1	0.17	81.3	0–1
OP_1	6.0	4.5	3	0.16	81.3	0–1
OP_2	1.7	29.5	6	0.15	80.0	0
Chlorous Acid Treated						
PC1	8.4	0.4	1	.05	88.3	0
OP_1 C1	12.4	0 5	4	.05	90.2	0
OP_2 C1	96.0	0.5	3	.03	93.2	0
Borohydride Treated						
PB	2.18	0.6	0	0.14	82 4	0
OP_1 B	6 4	0.8	2	0.11	84 5	0
OP_2 B	2.4	2.0	1	0.12	87.3	0

On oxidation with $K_2Cr_2O_7/(COOH)_2$, there is an increase of both carboxyl content and copper number and no change in the whitness. On periodate oxidation there is a drastic increase in Cu. No. and visually the samples become whiter. The carboxyl eontent was estimated by Methylene Blue method[18] for this particular sample, since samples of high copper number give anamalous high values of high copper number give anamalous high values of carboxyl content by iodometric method. Chlorous acid oxidation is known to oxidise the carbonyl to carboxyl groups, hence, after this treatment all samples show very low copper number and high value of carboxyl. After this treatment extremely whitesamples with very low Y-Index are obtained due to bleaching effect of chlorous acid. Borohydride treatment reduces the aldehyde groups, hence after this treatment the copper number decreases and the carboxyl content remains unchanged, while visually samples become whiter. However, the decrease in Y-index is much less as compared to the chlorous acid treated samples.

Accelerated Ageing Test

Because of the slow rate of natural ageing, it is usually acccelerated in laboratory investigations by controlling the important variables of time, temperature, humidity, availability of oxygen, exposure to visible or UV light and moisture. Giertz[3] has shown that yellowing took place faster in the presence of moisture. Richter and Wells[19] developed an incubation test which provided a high but unknown humidity.

All the above samples were aged both by heating in oven and by steaming. They were then studied for their carboxyl content, coppei number, Whitness and yellowness Index. (Table-3, Table-4).

TABLE-3

FUNCTIONAL GROUPS AND YELLOWNESS INDEX OF OXYPULP SAMPLES AFTER HEATING

Designation pulp	Carboxly content meg./100g.	Cu. No.	Lactone test Grade	Yellowness Index	Whiteness Index	Visual Assessment
P	3 14	1.9	0	0 41	64 8	1–2
OP_1	7.38	2.25	2	0 43	55.2	2
OP_2	0 2	22.0	5	0.79	32.9	4
Chlorous Acid Treated						
PC1	6.0	0.4	0	0.15	80.1	0–1
OP_1 C1	6 4	0.5	3	0 12	86.5	0–1
OP_2 C1	82 0	0.9	2	0 07	93.3	0
Borohydride Treated						
PB	3.2	0.4	0	0.17	81.2	0–1
OP_1 B	7.0	0.4	1	0.13	82.2	0–1
OP_2 B	2 8	0.5	1	0.13	86.3	0

TABLE-4

FUNCTIONAL GROUPS AND YFLLOWNESS INDEX OF OXYPULP SAMPLES AFTFR STEAMING

Designation Pulp	Carboxyl content Mcq/100g	Cu. No.	Lactone test Grade	Yellowness Index	Whiteness Index	Visual Assessment
P	3 5	1 1	0	0.43	62.5	1
OP_1	6.6	2.0	2	0.53	56 6	2
OP_2	3.2	27.0	3	0.92	18 2	3
Chlorous Acid Treated						
PCI	6.8	0 6	0	0.19	78.9	1
OP_1 Cl	6.8	0.7	3	0 22	76.7	1
OP_2 Cl	64.8	3.3	1	0.39	58.4	2
Borohydride Treated						
PB	3.2	0.5	0	0.18	80.2	0–1
OP_1 B	6.8	0.7	1	0.18	78.5	0–1
OP_2 B	4.0	0.6	1	0 13	82 2	0

Evaluation of Yellowing

Evaluation of yellowing index for sheets made from oxypulp, as also after both the ageing treatment is done by visual grading as well as calculation of Y-Index. For various oxypulps having different amount of aldehyde and carboxyl groups, the dry ageing treatment was found to give lower yellowness index as compared to steaming, but the trend for any particular sample is of similar nature.

As seen from Fig. 1, the Y–Index is found to be inversely related to whiteness Index throughout the entire range and the visual assessment follows definite steps in these changes as shown by dark lines in the graph. The Y–Index which is commonly employed in evaluation of yellowness of textile substrates is thus found to be quite useful for evaluation of pulp samples as well.

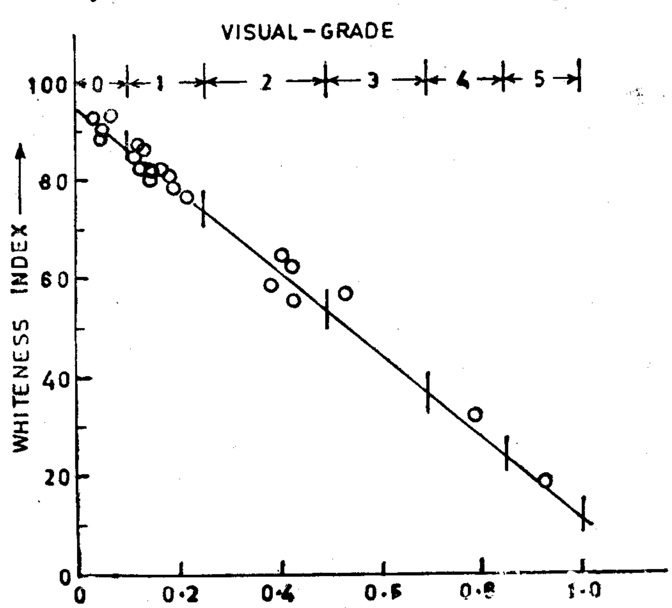

FIG.—1 YELLOWNESS INDEX ASSESSMENT OF YELLOWNESS

Effect of Functional Groups on Yellowing Index on Ageing

On comparison of yellowing induced on ageing for different samples it can be seen that higher extent of yellowing is observed for samples of higher copper number as in the case of oxycelluloses and the extent of yellowing increases with copper number. Borohydride treated samples having low copper number show insignificant amount of yellowing. The chlorous acid treated samples, which have a high carboxyl and low copper number, show intermediate levels of yellowing. The amount of reducing groups in the sample seems to play a major role in the yellowing.

Changes in Functional Groups on Ageing

For samples of higher copper number, heating produces a decrease in copper number due to their conversion to carboxyl as indicated by an increase in these values.

However for chlorous acid treated samples of high carboxyl, the ageing produces decrease in carboxyl, possibly due to either lactone formation or decarboxylation reaction. The result of lactone test (Table 2,3,4) however, show decrease in coloration test for lactones suggesting a lesser probability of lactone formation.

Opening up of lactones will lead to formation of carboxyl groups. Hence decarboxylation predominates over the formation of new carboxyl groups by oxidation of aldehydic groups or opening up of lactone.

Changes in Functional Groups on Steaming

The presence of moisture accelerates the yellowing process, as is observed from the Y-Index and the changes in functional groups accompanying steam ageing shows a different pattern as compared to heat ageing.

For samples of very low copper number and high carboyxl, namely the chlorous acid treated samples, there is an increase of copper number. Hence the decarboxylation is accompanied by formation of reducing groups when ageing takes place in the presence of moisture.

For samples of higher copper number steam ageing causes a greater increase in carboxyl as compared to the heated samples.

Conclusion

The aldehyic groups is oxypulp contribute more to yellowing as is evident from the fact that yellowing is drastically reduced when these groups are reduced or oxidised. The yellowing is accompanied by both decarboxylation and the oxidation of aldehydic groups to carboxyl. The former reaction is more prominent in high carboxyl materials and the latter reaction in low carboxyl materials with simultaneous decrease of copper number.

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