The action of strong acids on brightness and yellowness of paper

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SUMMARY

The addition of common strong acids like hydrochloric acid phosphoric acid, chlorosulfonic acid and perchloric acid to paper size improves the brightness and decreases yellowness of the paper. Phosphoric acid is the most effective The results clearly underline the importance of hydration of C-2 C-3 Ketonic functions of cellulose as one of the major contributing factor controlling the optical properties.

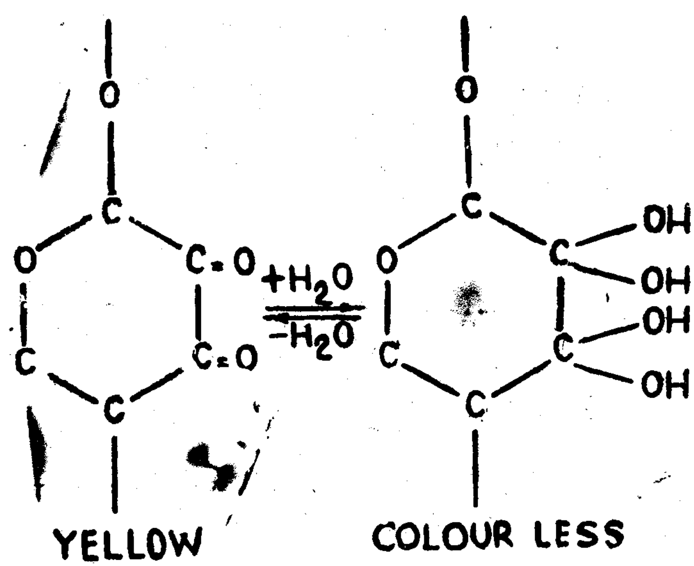
In our earlier paper[1] we had demonstrated that the replacement of alum by sulfuric acid in the alum blend used for sizing resulted in the improvement in brightness, reduction in "yellowness" and decrease in the dosage of more expensive optical whiteners. It was found out by us that replacement of alum by sulfuric acid upto 20% can be done without affecting either sizing or strength properties.

The "Yellowness" of the pulp is to be attributed to the presence of carbonyl functions in the C–2 and C–3 carbon atoms of glucose moiety of cellulose and a hydration of ketonic functions would result in the colourless form as shown in the figure[2].

It will be pertinent to refer here to the fact that many of the diketones such as glyoxal, diacetyl or benzil are yellow in colour, while the corresponding alcohols are colourless.

It is well established that the hydration of ketones is general acid catalysed[3]. The mechanism of hydration of carbonyl compounds, especially acetaldehyde[4] and dichloroacetone[5] has been investigated in detail. Excellent correlations were obtained in the Bronsted plots, with significant alpha value af 0.54 and 0.27 for these two compounds respectively.

Therefore on the basis of the results presented in our paper, it was suggested by us that the mechanism of action of optical whiteners, involved partly at least the hydration of the C-2, C-3, ketonic fuctions of cellulose catalysed by the sulfonic acid groups present in the optical whitener molecule.



FIGURE

In order to confirm this existence of such an effect we had also investigated the effect of added

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sulfamic acid (an acid commonly used in paper, and the results of this study was reported in a recent communication[6]. It was seen from the perusal of the data presented in the paper that no doubt the addition of sulfamic acid improved the optical properties of the paper but only to a marginal extent which can also be explained due to the less efficient catalysis by sulfamic acid (because of higher pka) as compared to sulfuric acid in promoting the hydration of the ketonic functions of cellulose.

We present in this paper the results of our studies on the effect of addition of common strong acids like hydrochloric acid, phosphoric acid, perchloric acid, chlorosulfonic acid on the optical properties of papaer.

We have been prompted to undertake this study for the following reasons:

1. Any improvement in optical proerties of paper especially increase in brightness and decrease in yellowness, will mean less use of expensive optical whiteners, which will improve the overall economy of paper manufacture as these acids are much less expensive and easily available.
2. The results will also throw more light on the importance of hydration of ketonic functions of cellulose in controlling the important optical properties of paper.

RESULTS AND DISCUSSIONS

As was observed in the case of addition of ulfuric acid as well as sulfamic acids, the addition of the acids results in the lowering of stock pH with increasing quantities of added acids the pH of the stock dropped. And to maintain the same stock pH, alum dosage was decreased. The alum dosages in our experiments were monitereo to maintain the same stock pH of 5.

The results of the study on the effect of addition of acids are presented in Tables 1 to 4.

From the perusal of the results it is evident that the addition of all acids improves the optical properties of the paper, the effect being maximum with phosphoric acid, and to a smaller magnitude with other acids.

It is interesting to note that during perchloric acid addition, even though the alum dosage was reduced from 5.5% to 4.8% in the presence of 1% perchloric acid, the improvement in the optical properties were only marginal, while in the case of phosphoric acid and sulfuric acid, the effect was much more pronounced (i. e.) – higher increments in brightness and sharper drop in yellowness.

These results like the ones observed by us earlier in the studies on the addition of sulfamic acid, point out to the fact quenching effect of

TABLE—1 EFFECT OF ADDITION OF CHLOROSULFONIC ACID ON OPTICAL PROPERTIES OF PAPER

Sample	Acid %	Alum %	Brightness % I	Brightness % II	Yellowness % I	Yellowness % II
1. Raw pulp			79.0	76.0	11.42	13.9
2. Beaten pulp			75.8	73.6	11.8	14.3
3. Beaten pulp + Rosin		6.5	75.7	70.6	12.4	17.3
4. Beaten pulp + Rosin + OWA		6.5	76.3	72.4	8.7	14.1
,, ,,	0.05	6.5	76.6	73.5	8.5	13.5
,, ,,	0.10	6.25	77.7	73.3	7.6	13.2
,, ,,	0.20	6.25	77.8	73.3	7.3	13.1
,, ,,	0.30	6.0	77.9	73.4	7.1	12.9

Rosin 0.8% : OWA 0.3%; Stock pH 5.0 ± 0.1

TABLE—2 EFFECT OF ADDITION OF PERCHLORIC ACID ON OPTICAL PROPERTIES OF PAPER

Sample	Acid %	Alum %	Brightness % I	Brightness % II	Yellowness % I	Yellowness % II
1. Raw pulp			72.2	74.6	15.1	14.2
2. Beaten pulp			69.5	71.8	15.5	14.8
3. Beaten pulp + Rosin		6.5	65.8	66.7	19.4	18.6
4. Beaten pulp + Rosin + OWA		6.5	67.9	68.9	15.4	13.5
,,	0.25	6.0	68.1	69.2	14.2	13.2
,,	0.50	5.5	69.0	70.1	13.9	13.0
,,	1.0	4.8	69.9	70.5	13.1	12.3

Rosin 0.8%; OWA 0.3%; Stock pH 5.0 ± 0.1

TABLE—3 EFFECT OF ADDITION OF HYDROCHLORIC ACID ON OPTICAL PROPERTIES OF PAPER

Sample	Acid %	Alum %	Brightness % I	Brightness % II	Yellowness % I	Yellowness % II
1. Raw pulp			75.5	78.5	15.2	13.8
2. Beaten pulp			71.6	75.3	15.5	12.1
3. Beaten pulp + Rosin		6.5	65.7	68.7	20.1	18.8
4. Beaten pulp + Rosin + OWA		6.5	69.5	71.7	15.3	13.3
,,	0.10	6.0	69.9	73.0	14.7	12.7
,,	0,20	5.5	70.5	73.7	14.2	12.2
,,	0.30	5.0	71.3	73.9	13.2	12.0

Kosin 0.8%; OWA 0.3%; Stock pH 5.0 ± 0.1

TABLE—4 EFFECT OF ADDITION OF PHOSPHORIC ACID ON OPTICAL PROPERTIES OF PAPER

Sample	Acid %	Alum %	Brightness % I	Brightness % II	Yellowness % I	Yellowness % II
1. Raw pulp			74.2	78.3	14.6	11.7
2. Beaten pulp			71.9	75.1	15.5	12.1
3. Beaten pulp + Rosin		6.5	65.6	68.7	19.1	18.8
4. Beaten pulp + Rosin + OWA		6.5	68.2	71.7	13.4	13.2
,,	0.1	6.5	71.6	74 3	12.6	11.3
,,	0.2	5.75	12.2	75.4	12.0	10.6
,,	0.3	5.0	72.9	76.2	11.1	9.9

Rosin 0.8%; OWA 0.3%; Stock pH 5.0 ± 0.1

aluminium ions on the optical properties of paper may be relatively of lesser importance. We do not contend that aluminium ions do not have a dulling effect. It is quite possible that the aluminium ions concentration has already attained the optimum level, above which it does not have any more further effect on the optical properties of the paper. The observation that sizing was not affected much by the decrease in alum dosage indicates this. Theoretically only 0.35 parts of alum are needed per part of rosin size but in practice 3-5 times this amount is needed.

Thus replacement of alum by phosphoric acid partly results in the considerable improvement in optical properties of the paper and this could bring down the dosage of optical whiteners. However we have found that when the dosage of phosphoric acid exceeds 0.5% even though further addition contribute to the improvement on sizing and sizing is reduced to almost zero.

It will also be pertinent to point out here that the effect of phosphoric acid on optical properties is much more significant than those of phosphates, the results of which we have reported in our earlier paper[8].

We had also tried both the modes and order of addition of the acids. In one set the acids were added prior to the addition of alum and in the other set the acids were added after the addition of major portion of alum. For perchloric acid this doesn't have any significant effect on sizing, but in the case of phosporic acid, sizing was dependent on the order of addition. It was found out by us that the phosphoric acid should be added after the alume dosage, in order to maintain sizing and it should not be added prior to the addition of alum. When it was added prior to the addition of alum, even small amounts of phosphoric acid, affected sizing advarsely.

Nevertheless at the same level of alum addition and when stock pH and other conditions were kept constant it was found that added phosphloric acid have much more effect than the hydrochloric acid or perchloric acid, with phosphoric acid being most effective, as evident from the result presented in Table–5.

TABLE–5 EFFECT OF ADDITION OF HYDROCHLORIC ACID (I), SULFURIC ACID (II) AND PHOSPHORIC ACID (III) ON THE OPTICAL PROPERTIES OF PAPER

Sample	Alum	ACIDS			Brightness %	Yellowness %
		I	II	III		
1. Raw pulp	—	—	—	—	78.3	11.7
2. Beaten pulp	—	—	—	—	75.3	12.1
3. Beaten pulp + Rosin	6.5	—	—	—	68.7	18.8
4. Beaten pulp + Rosin + OWA	6.5	—	—	—	71.7	13.2
,,	6.0	0.1	—	—	73.0	12.7
,,	5.75	0.2	—	—	73.7	12.2
,,	5.3	0.3	—	—	73.9	12.0
,,	6.0	—	0.1	—	73.6	12.5
,,	5.75	—	0.2	—	74.4	11.8
,,	5.5	—	0.3	—	74.5	11.7
,,	6.0	—	—	0.1	74.3	11.3
,,	5.75	—	—	0.2	75.4	10.6
,,	5.5	—	—	0.3	76.2	9.9

Rosin 0.8%; OWA 0.3%; Stock pH 5.0 ± 0.1

Thus it is evident from the results presented in Table—5, that the addition of phosphoric acid io the size after the addition of alum, considerably improves the optical properties of paper. The results also underline the importance of hydration of ketonic functions in controlling the optical properties of paper.

EXPERIMENTAL

In our investigations, kraft pulp of bamboo and mixed tropical hardwoods blended in the ratio of 60:40 was used. The pulp was bleached by CEHH sequence to get the desired brightness level. Handsheets of 120 gsm/sq m were prepared in a laboratory sheet maker as per the TAPPI standard method after beating and then adding rosin, optical whitening agent (OWA) acid and alum. The addition of alum was monitered to get a final stock pH of 5.0±0.1. A reference sheet was also made from the same pulp without whitening agent.

Yellowness was determined by measuring the reflectance with three different tristimulus filters FMx/c, FMy/c and FMz/c which are amber (A), green (G) and blue (B) filters respectively. The "Yellowness" was then calculated by using the standard farmula given in the TAPPI information sheet "Indices for whiteness, Yellowness, Blue Reflector and Luminous Reflectance Factor" 1972.

$$\% \text{ yellowness} = \frac{A-B}{G} \times 100$$

The Elrepho refectance photometer was calebrated with cleaned opal glass working standards. The caliberation was also counterchecked with a tablet made from analytically pure MgO having a brightness of 99.2%, as determined by comparison with standard MgO with an assumed brightness of 100% (TAPPI standard T6330S-50)

The paper maker's brightness of reflectance at 457 nm was determined using R457 filter.

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