

## COST REDUCTION AND UPGRADING OF BASIC PROPERTIES OF ABSORBENT-GRADE PAPER

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Absorbent-grade paper is a highly specialized product due to introduction of certain special characteristics, namely high water absorbency, castor oil penetration (COP), and porosity. Water absorbency is affected by the radius of capillaries within the paper. Likewise the COP is affected by pulp beating and by the degree of collapse of the paper structure during sheet pressing. Using 4% NaHCO<sub>3</sub> solution during manufacturing of absorbent grade paper not only improves all the three basic properties, but it also mitigates the cost of absorbent grade paper by US\$ 4.07 per metric tonne. Fibers come closer to each other during sheet making as a result of increased surface tension forces due to mixing of NaHCO<sub>3</sub> in tap water.

*Keywords:* Absorbent grade paper; Surface tension; Castor oil penetration; Water absorbency

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### INTRODUCTION

Inexorably, the rising costs of pulpable wood, energy, non-fibrous additives, and labor in paper industries mitigate the profit margin. The profit margin can be improved in two ways: (a) manufacture of value-added papers in place of commodity grades of paper, and (b) change in the manufacturing process through in-house research and development without adversely affecting the quality of the end product. Absorbent paper typically is made from kraft fiber; it is hydrophilic in nature with a porous structure and a high degree of water absorption. The most important properties for absorbent grade paper are water absorbency, maximal unbound fiber surface area, oil absorbency as measured by castor oil penetration (COP), porosity, bulk, and wet strength (Dutt *et al.* 2003a). Water absorbency in a paper depends upon the length and diameter of capillaries, while COP depends on the pulp beating level. Introduction of certain special properties above and beyond basic properties of absorbent grade papers make them specialty papers, as in the delineation of top and bottom sides in padding paper (Dutt *et al.* 2003b), laying of 25 µm thin copper film as a top layer in pictorial circuit board (Dutt *et al.* 2003c), toxicity test in seed germination paper (Dutt *et al.* 2005a), pore size and filtering rate in automobile and industrial filter paper (Dutt *et al.* 2005b), and resistance to flow, filtration efficiency, and dust holding capacity in beer, coffee, beverage, and tea bag filter paper (Dutt *et al.* 2007). The present investigation aims at improving three basic properties of absorbent grade paper, namely the water absorbency (Klemm test), COP, and porosity by increasing the surface tension force of water with NaHCO<sub>3</sub>. The impact on cost of the absorbent grade paper is also studied.

## EXPERIMENTAL

### Raw Materials

Screened chips of veneer waste of poplar and eucalyptus mixed in the ratio of 80:20 were digested at 20.0% active alkali (as Na<sub>2</sub>O), sulphidity 20%, bath ratio 1:2.8, maximum cooking temp 162°C, time to temp 120 min, and time at temp 90 min in a batch digester of capacity 85 m<sup>3</sup>. The cooked material was passed through a knoter screen and washed in Dorr-Oliver brown stock washers. The pulp was bleached by CEopHH bleaching sequence. The viscosity and brightness of pulp are 9.2 cps and 84% (ISO), respectively. Softwood pulp of brightness 88% (ISO) was collected from Star Paper Mills Ltd., Saharanpur (India).

### Surface Tension Determination

Surface tension values of tap water (hardness 340 ppm), double-distilled water, and solutions of NaHCO<sub>3</sub> in tap water and double-distilled water at different concentrations were determined at a temperature of 30°C. The dissolution of NaHCO<sub>3</sub> stopped at concentrations of 4 and 6% for tap and double-distilled water, respectively. The surface tension was compared with that of the pure liquid by use of a stalagmometer of capacity 2.5 mL, which operated on the drop weight principle. We took a fixed volume (that between the marks) of the liquid flow through the capillary, and counted the drops; knowing liquid densities, the drops, weight and surface tensions might be compared (Chichkanov 2002).

$$\gamma_1 / \gamma_2 = n_2 \rho_2 / n_1 \rho_1 \quad (1)$$

In Eq. 1,  $\gamma_1$  and  $\gamma_2$  are the surface tensions of distilled water (72.5 dyne/cm) and sodium carbohydrate solution (90.5 dyne/cm),  $\rho_1$  (distilled water 1.01 g/cm<sup>3</sup>) and  $\rho_2$  (1.0117) are the densities, and  $n_1$  and  $n_2$  are number of drops of water and liquid, respectively.

### Pulp Beating, Blending, and Stock Preparation

Both mixed hardwoods and softwood pulps were beaten by valley beater method (TAPPI T 200 sp 01 “Laboratory beating of pulp [Valley beater method]”) in two sets (a) beating at different beating levels (b) beating at fixed °SR (30±1) in a valley beater. A consistency of 1.57% in the valley beater was maintained with 4% NaHCO<sub>3</sub> solution. Hardwood and softwood pulps were blended in various ratios by oven-dry weight. A pulp suspension of 0.8% consistency was prepared for each blend. 1% melamine formaldehyde to develop crosslinking (Geobel *et al.* 1997), and 0.1 % sodium hexametaphosphate for uniform mixing of non-fibrous additives (Kleeman *et al.* 2003) were added. Non-ferric alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> • 14-18 H<sub>2</sub>O) was also added to maintain a pH of 6.5 and to enhance interlinking with melamine formaldehyde resin with fibers.

Laboratory handsheets (80 g/m<sup>2</sup>) were prepared on a British sheet former (TAPPI T205 sp-02 “Forming handsheets for physical tests of pulp”) using 4% NaHCO<sub>3</sub> solution. Back water was collected and re-used during sheet-forming as follows: 4% NaHCO<sub>3</sub> solution and back water were mixed in the ratio of 1:1 and used for each subsequent sheet. Laboratory-made handsheets were conditioned at a relative humidity of 65±2% and temperature 27±1°C (TAPPI T 402 sp-03 “Standard conditioning and testing atmospheres

for paper, board, pulp handsheets and related products”) and evaluated for wet strength (TAPPI T 456 om-03 “Wet tensile breaking strength of paper and paperboard [Wet tensile strength]”), castor oil penetration (COP) (TAPPI T 462 om-01 “Castor-oil penetration test for Paper”), and water absorbency as measured by the Klemm test (TAPPI T 492 pm-76 “Water absorption of paperboard [Non-Bibulous]”, see also ASTM D3285) (TAPPI Test Methods 2007), and porosity (IS: 9894-1981 “Method of test for smoothness/roughness of paper”) (BIS 1997).

## RESULTS AND DISCUSSION

Figure 1 shows that surface tension forces increase with increasing  $\text{NaHCO}_3$  concentrations in tap water and double-distilled water, respectively at a temperature of  $30^\circ\text{C}$ . The dissolution of  $\text{NaHCO}_3$  stopped beyond concentrations of 4 and 6% in case of tap water and double distilled water, respectively. We did not go beyond concentrations of 4 and 6% because excess of  $\text{NaHCO}_3$  will act as a filler and would affect the water absorbance properties at  $30^\circ\text{C}$ . Addition of  $\text{NaHCO}_3$  beyond these limits causes a slight drop in surface tension forces.

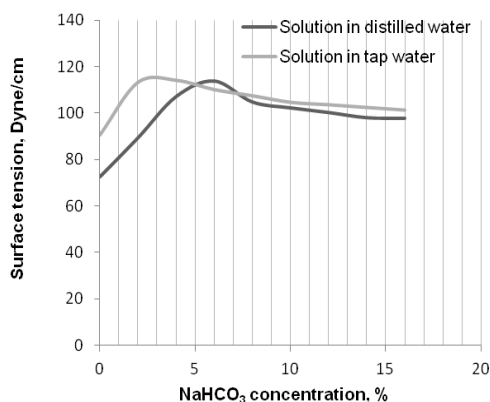


Fig. 1. Effect of  $\text{NaHCO}_3$  concentrations of surface tension

According to the Gibbs adsorption isotherm, there is a noticeable increase in the surface tension with an increase in the concentration of inorganic salts in a two-component system (Heald and Smith 1974, 1982). Addition of the electrolyte increases the surface tension. This can be expressed using the Gibbs adsorption isotherm, as given in Eq. 2. The increase in the surface tension ( $\gamma$ ) leads to an enhanced capillary effect, as expressed in Eq. 3. At the some critical concentration of the electrolyte, saturation limits for a given temperature. An increase in the temperature increases the saturation limits.

$$\Gamma_s = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln c} \right)_{T,P} \quad (2)$$

$$h = \frac{2\gamma \cos \theta}{\rho g r} \quad (3)$$

In these equations  $\Gamma_s$  is the surface excess,  $C$  is the concentration,  $R$  is the gas constant,  $T$  is the absolute temperature (in Kelvin),  $h$  is the height the liquid is lifted,  $\gamma$  is the liquid-air surface tension,  $\rho$  is the density of the liquid,  $r$  is the radius of the capillary,  $g$  is the acceleration due to gravity, and  $\theta$  is the angle of contact.

Inter-fibers spaces constitute capillaries in a paper sheet, and water lifts itself up through these capillaries to a certain height when the end of the paper strip is immersed in water. The characteristic pore radius tends to be greater in a paper sheet that is made up of softwood pulp fibers; hence water does not lift itself up to as great a height as in the case of a corresponding hardwood sheet. In the present study the softwood pulp fibers were optionally suspended in a solution of  $\text{NaHCO}_3$  (0.5 to 0.7% consistency), and pulp slurry was formed into sheets with a British sheet former. The pulp mat was pressed with the help of a stainless steel roller using blotter and steel plate. During drying it is known that surface tension forces bring the fibers closer to each other, resulting in a decrease in diameter of capillary spaces (Fig. 2). When the edge of this paper is placed in water during use, the water is lifted to its maximum height (relative to the water level in the container) according to Eq. 3.

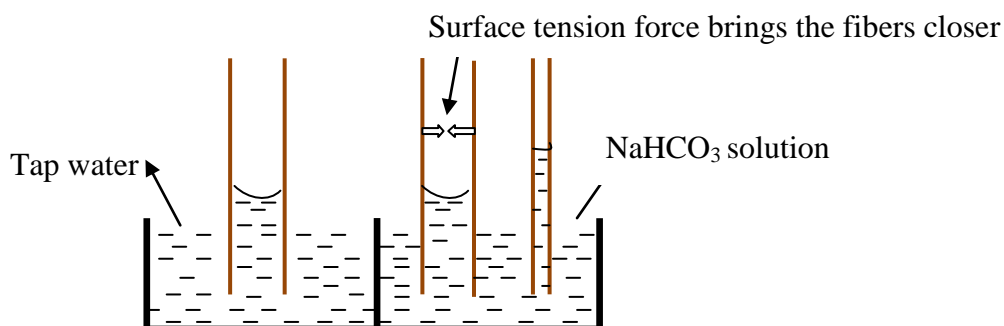


Fig. 2. Effect of surface tension on height of water in a capillary

**Table 1.** Effect of Blending of Softwood with Hardwood Pulp at  $30 \pm 1$  °SR on Water Absorbency (Klemm test), Oil Penetration (COP), and Porosity (Bendsten)

| Sl No | SW:HW ratio | Water absorbency (Klemm), mm/4min |                                | COP at $35 \pm 1$ °C, s |                                | Porosity (Bendsten), mL/min |                                |
|-------|-------------|-----------------------------------|--------------------------------|-------------------------|--------------------------------|-----------------------------|--------------------------------|
|       |             | With tap water                    | With $\text{NaHCO}_3$ solution | With tap water          | With $\text{NaHCO}_3$ solution | With tap water              | With $\text{NaHCO}_3$ solution |
| 1     | 00:100      | 50.00                             | 52.75                          | 9                       | 12                             | 2459.4                      | 2606                           |
| 2     | 20:80       | 47.75                             | 49.50                          | 13                      | 16                             | 1809.4                      | 2437                           |
| 3     | 30:70       | 43.75                             | 46.25                          | 17                      | 20                             | 1540.7                      | 2204                           |
| 4     | 40:60       | 39.00                             | 42.25                          | 22                      | 25                             | 993.8                       | 1850                           |
| 5     | 50:50       | 30.50                             | 33.50                          | 26                      | 30                             | 650.0                       | 1234                           |
| 6     | 60:40       | 28.75                             | 30.75                          | 31                      | 36                             | 487.5                       | 699                            |
| 7     | 70:30       | 24.75                             | 27.50                          | 37                      | 40                             | 396.9                       | 765                            |
| 8     | 100:00      | 19.50                             | 23.50                          | 41                      | 44                             | 175.0                       | 365                            |

Table 1 shows that water absorbency and porosity of laboratory-made handsheets prepared in tap water decreased with increasing softwood ratio. Beating of pulp at a beating level of 30 °SR removes the primary wall, exposes the secondary wall layers, and increases the fiber-water affinity. As the water drains in a British sheet former, followed by drying of the paper, fiber-water bonds are replaced by fiber-fiber bonds. Contraction of the web is due to surface tension of the water film between fibers and fiber shrinkage. The web contracts initially because of surface tension between fibers and then contracts further as drying proceeds because of intra-fiber shrinkage. Inter-fiber bonding starts at about the time the second effect takes over. Softwood fibers are flexible with low Runkel ratio and are easily converted to double-walled ribbons on pressing. This results in an increase in hydrogen bonding and reduction in water absorbency and porosity. Conversely, it shows an increase in COP. On the other hand, the Runkel ratio of most of the hardwood fibers is above 1.0 and such type of fibers is considered as thick-walled fibers which are stiffer, less flexible, and they form bulky paper sheet of lower bonded area (Dutt *et al.* 2009). This causes an increase in water absorbency and porosity of paper.

Addition of 4% NaHCO<sub>3</sub> in tap water increases the surface tension force which helps bring the fibers close to each other and also helps in decreasing the radius of the capillary. Therefore, capillary rise of water in a sheet prepared in 4% NaHCO<sub>3</sub> solution will be more comparable to a sheet prepared in tap water. Surface tension is important in contracting the fibers together during the drainage and drying of the sheets. As water is removed, surface tension creates a tremendous force which compacts and draws the fiber into more intimate contact. The contraction of the web in thickness begins at a very early stage in the manufacture of paper, long before drainages complete on the wire. Surface tension is so important in fiber bonding that the presence, either from poor washing or deliberate addition, of even a small amount of agents that reduce the surface tension will result in a sheet of low density. This lower density is probably the result of the reduction of contracting forces due to a reduction in surface tension; however, it may also be the result of the prevention of hydrogen bonding resulting from the adsorption of surfactant which masks the polar grouping on the surface of the fibers.

Surface tension is the principal factor in sheet consolidation in the early stages of drying up to a solid content of about 20 to 25% (Swanson 1961; Lyne and Gallay 1954). During this period there is a rapid decrease in the caliper of the wet web as water is removed, with increasing air intrusion into the web of fiber and water. In the cited studies it was concluded that up to 20 to 25% solids content, the fibers in a wet web of paper, are held together by surface tension forces. Surface tension forces decrease with increasing solids, but the hydrogen bonding begins and the strength increases as the water is removed (Swanson 1961; Lyne and Gallay 1954).

A question left unresolved by the present work is whether or not osmotic effects may contribute significantly to the speed of water sorption or the height to which water wicks into a strip of paper. In the present study, deionized water was used for the water uptake tests. By contrast, the paper had been formed in the presence of different levels of sodium bicarbonate ions. It is known that under suitable conditions, osmotic forces can provide an additional contribution favoring uptake of salt-free water into a polymeric material (such as a gel) that contains a higher concentration of ions (Adamson and Gast

1997). But because the paper strips are dry at the start of the water absorbency tests (Klemm method), further research is needed to fully understand the implications.

A paper sheet made from pulps having hardwood and softwood pulp in the ratio of 70:30 showed a water absorbency (Klemm test) value of 43.75 mm and a COP value of 17 s. Minimum values of water absorbency and COP are 25 mm and 15 s, respectively for pictorial circuit board (Dutt *et al.* 2003c). These values for pictorial circuit board can be achieved with hardwood and softwood pulp in the ratio of 80:20 using NaHCO<sub>3</sub> solution. Cost analysis by both methods is reported, as shown by the following values:

|   |                                |
|---|--------------------------------|
| Cost of hardwood pulp                       | = US\$ 569.68 per metric tonne |
| Cost of softwood pulp                       | = US\$ 813.83 per metric tonne |
| Cost of commercial grade NaHCO <sub>3</sub> | = US\$ 508.65                  |

The total cost of pulp when hardwood and softwood pulps mixed in the ratio of 70:30 using tap water is equal to US\$ 642.93 per metric tonne. The total cost of pulp when hardwood and softwood pulps mixed in the ratio of 80:20 using 4% NaHCO<sub>3</sub> solution equals US\$ 638.86 per metric tonne. The net saving in cost using NaHCO<sub>3</sub> solution equals US\$ 4.07 per metric tonne of paper.

## CONCLUSIONS

Surface tension forces have an important role for brining the fibers closer to each other. Three essential properties of absorbent grade paper *i.e.* water absorbency (Klemm test), oil penetration (COP), and porosity were found to improve when handsheets were prepared with a 4% solution of NaHCO<sub>3</sub> instead of using normal tap water. A paper sheet made from hardwood and softwood pulps in the ratio of 70:30 using tap water showed a water absorbency value of 43.75 mm and a COP value of 17 s. Against a water absorbency and COP values of 25 mm and 15 s, respectively for pictorial circuit board, a pulp blend of hardwood and softwood in the ratio of 80:20 gives water absorbency 49.50 mm and COP 16s. The change in blend ratio implies a net saving of US\$ 4.07 per metric tonne of paper.

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