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PRE-TREATMENT OF CELLULOSIC FIBRES WITH SOME CHEMICALS FOR EFFECTIVE SIZING

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ABSTRACT

There are a number of problems experienced during internal sizing of papers. Poor size retention and back water contamination are just two of them. The method which supports the maximum attachment of sizing agents specifically to cellulose fibres is needed to solve some problems encountered with sizing operations. In this work, handsheets were produced from bleached long fibres with the blend of pretreated fibres with various sizing chemicals. The fibre pretreatments were achieved by mixing unbeaten fibres with rosin, paraffin and alkyl ketene dimer (AKD) emulsions at quite higher proportions, followed by filtration and drying. Strongly sized fibres then were beaten and mixed with untreated fibres in making a number of handsheets. Pre-treatments were discussed in respect to paper sizing, recycling and some suggestions were made.

INTRODUCTION

Papermakers like higher first pass retention, but fast drainage also needs to be maintained, which allows paper machine to run at a higher speed. Stock ingredients in small sizes, such as fines, fillers and chemicals are more likely to be lost to back water more that those having bigger particle sizes such as fibres. Poor retention causes many problems, especially in recycling papermills (IMAMOGLU *et al.*, 2005). It is reported that even higher retention of sizing chemicals does not actually guarantee the higher water resistance of resultant paper. Sizing chemicals should protect the hydroxyl groups of fibres from approaching liquids by developing chemical bonds and/or wrapping them up physically. Homogenous distribution of retained sizing chemicals in paper mat and controlled drying are important for good sizing (ROBERTS, 1991; KARADEMIR *et al.*, 2004; HUBBE, 2006).

Many papermills have witnessed a rapid conversion from acid to neutral/alkali system due to many advantages discussed elsewhere in details (HUBBE, 2006; WILEY, 1989; ROBERTS, 1992; ABELL, 1985). Alkyl ketene dimer (AKD) is the main sizing agent extensively used in the pH range of 7 to 10 (Wiley, 1989; Abell, 1985; Crouse and Wimer, 1990). It is a waxy material and insoluble in water with a melting point around 50^{0}C depending on chain length. Commercial AKD's are prepared from naturally fatty acid sources and mainly stearic acid is used for this purpose (ROBERTS, 1996).

Relatively low level of AKD (0.1% to 0.5% on oven dry furnish) compared to the traditional rosin sizing (2% to 4% on oven dry furnish) is added to the mixing box of the paper machine during internal sizing application. It is known that AKD retention is quite sensitive to stock pH and reported to be better at pH 8 (ROBERTS, 1985; BOTTORF and SULLIVAN, 1993; RAVNJACK, 2007). The second important step in AKD sizing is the reaction mechanism with furnishes. In general, it is believed that AKD reacts with cellulose fibre and forms a beta-keto ester bond, hence makes paper hydrophobic (ROBERTS, 1996; EKLUND and LINSTROM, 1991). AKD also reacts with water molecules producing an unstable beta-keto acid which, then, decarboxylates to form a ketone (BOTTORF and SULLIVAN, 1993; KARADEMIR *et al.*, 2007). Calcium carbonate loading is reported to increase the AKD demand in paper (KARADEMIR *et al.*, 2007; KARADEMIR and HOYLAND, 2003). Paraffin is also used, especially in corrugated board production for imparting water repellent properties to cartonboards. It is a long aliphatic hydrocarbon chain which is physically attached to fibres without any chemical bond formation. Some paraffin molecules may also have branches and aromatic rings (cycloparaffin). There have been some recent reports on the use of AKD on particle modification to improve hydrophobicity with mixing commercial resins. Some good findings were reported (HUNDHAUSEN *et al.*, 2009a; HUNDHAUSEN *et al.*, 2009b).

It is aimed to highlight the effects of hard sized cellulose fibres on paper's water resistance. Sizing chemicals may be added to the stock as attached to some fibres, rather than in the form of an emulsion. It may help internal sizing operation if conditions are optimised.

Authors' references:

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MATERIALS AND METHODS

Fibres and chemicals

Bleached long fibres were used as virgin wood pulps and beaten in a PFI mill in accordance with Tappi T 248 sp-08 method until 37 °SR values are reached.

Three commercial sizing emulsions were used. AKD and rosin emulsions were obtained from Kahramanmaraş Papermill (Kahramanmaras, Turkey) and paraffin emulsion was obtained from Caran Chemical (Izmir, Turkey). The solid content of AKD was 25%, while rosin and paraffin emulsions were at 40%.

Pretreatment of fibres and handsheets making

Calculated sizing emulsions were added to unbeaten pulp slurries prepared at 0,5% consistency in a Dynamic Drainage System (DDS) (**Figure 1**). Mixture was initially stirred at 500 rpm for 3 minutes, then at 200 rpm for 1 minute. And then the suspension was filtered on 200 mesh wire just after 10 seconds waiting without mixing. Filtered fibre mats were oven dried at 100ºC for four hours. Dried filtrates, then, were soaked in water overnight, blended with untreated fibres and then beaten in a PFI mill. This oversized beaten pulp was mixed at calculated amounts with untreated beaten pulps, and a number of handsheets at a grammage of 75 g/m^2 were made in a Rapid Köten sheet former, according to Tappi 205 sp-95 method.

Handsheets were conditioned in accordance with Tappi T 402 om-88 method at 23±2°C and 65±2% relative humidity for at least 24 hours before testing. Tensile index and water absorption capacity were determined according to TAPPI T 494 om-88 and Cobb methods respectively.

RESULTS AND DISCUSSION

Effects of pretreated fibres on paper strength

Adsorbed amounts of sizing emulsions in pretreated fibres were calculated after 4 hours drying at 100ºC and noted to be in the range of 1 to 10 percent of the handsheets weights. It was noted that overall, pretreated fibres dramatically reduced the tensile index values of papers in which they were added (**Figure 2**). Sharp and dramatic drop in tensile index was caused by AKD treated fibres while rosin treated fibres created around 25% reduction. It is, in a sense, a reflection of bonding strength developed between sizing chemicals and pretreated fibres. One might say, from this figure, that AKD developed the strongest bond with pretreated fibres. Paraffin is known to be attached physically, which allows it's molecules to move between and around fibres. It was believed to interfere the fibre bonding in paper, reducing tensile index.

Results plotted in **Figure 3** were not so different than what was seen in Figure 2. Burst index values of all handsheets produced with the addition of pretreated fibres were dramatically affected. Pretreated fibres were found to have just destroyed papers strengths. It suggests that pretreated fibres had no bonding ability at all. They must not have developed any bonds between themselves and with untreated fibres. It is obvious that oversizing (pretreatment) made fibres inaccessible to water. This was actually witnessed while processing overnight soaked fibres. Oversized fibres could not, in fact, properly swell and be beaten as good as untreated fibres were. In such case, pretreated fibres would have a quite rigid structure, behaving like nodes in pulps compared to untreated fibres. Sized fibres were also thought to have no available hydroxyl groups on them to develop some kinds of bonds with ad-

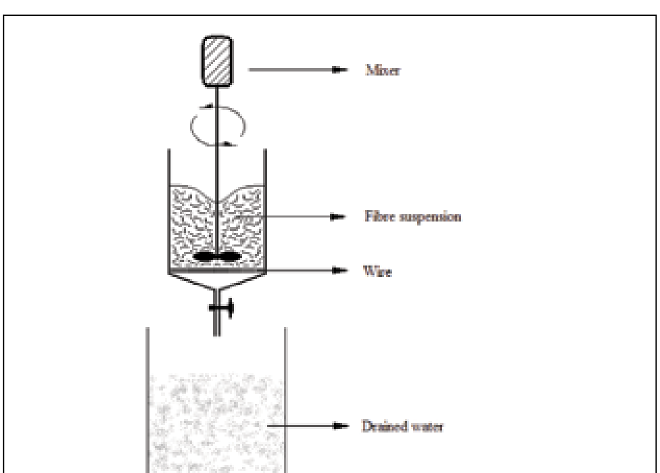

Figure 1. Fibre suspension mixed with sizing emulsions at high proportion

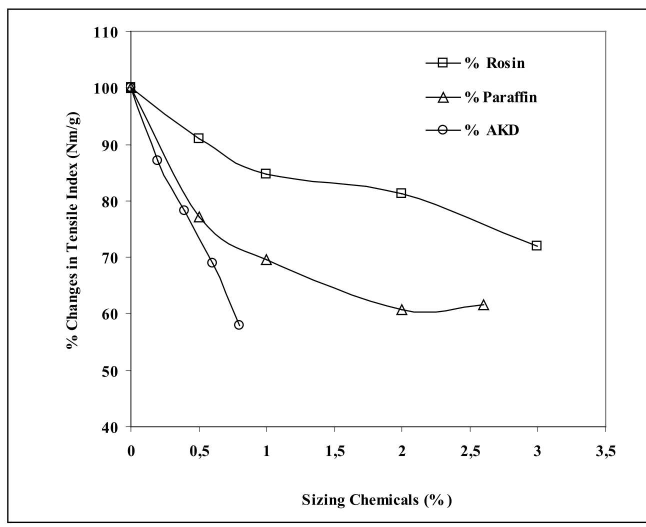

Figure 2. Pretreated fibres reduced tensile indexes

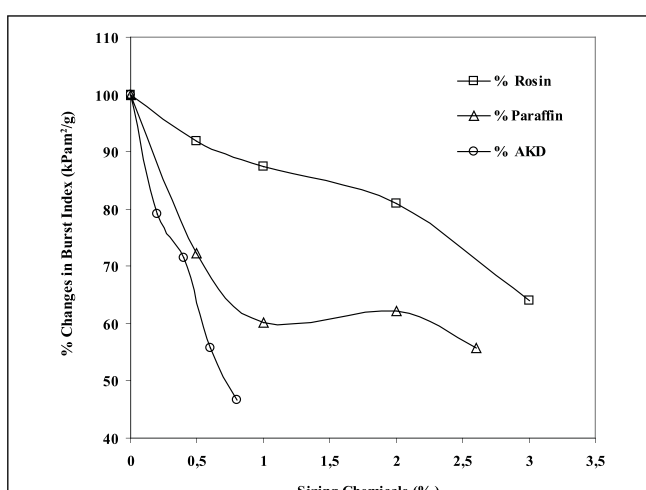

Figure 3. Pretreated fibres reduced burst indexes

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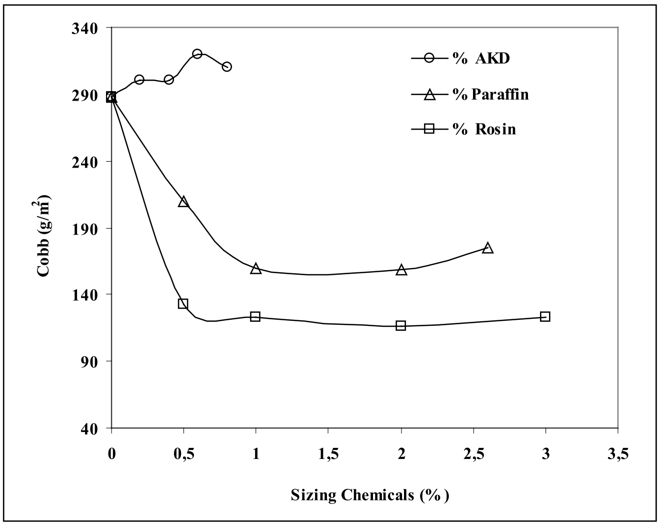

Figure 4. Fibres having adsorbed AKD molecules showed no improvements on paper sizing

jacent components. Furthermore, after beating some kinds of broken and hydrolysed sizing chemicals were believed to be generated which were not expected to have positive effects on interfibre bonding.

Pretreated fibres were believed to have hindered interfibre bonds in paper structure. They probably made fibres separated and blocked any potential fibre-fibre bonds around them, destroying interfacial contact.

Effects of pretreated fibres on Cobb value

The Cobb values seem to be developed as a result of fibre additions treated with both paraffin and rosin emulsions (**Figure 4**). Fibres treated with AKD emulsions, however, did not make any contributions to sheet's hydrophobicity (Figure 4). It is known that AKD develops strong chemical bonds (ester bonds) with hydroxyl groups of cellulose fibres and quite effective in improving paper resistance against liquids (KARADEMIR *et al.*, 2004; HUBBE 2006; ROBERTS 1992). Rosin molecules too develop some chemical bonds with cellulose fibres during drying stages. Paraffin is, however, just physically attached to fibres and weakly stayed in paper structure. Some heating over it's melting points may cause paraffin molecules to move in paper matrix. It is, therefore, believed that the beating processes had destructive effects on treated fibres in general. Fibres treated with AKD emulsions were probably experienced the most severe mechanical damage, and transformed into a small rigid fibre broke rather than becoming flexible and fibrillated fibres. It is also most likely that any AKD molecules stayed as unreacted form over treated fibres were hydrolyzed giving ketone. Ketone is reported to have no sizing effects and may increase water take up in sheets (KARADEMIR *et al.*, 2004; KARADEMIR *et al.*, 2007; JIANG and DENG, 2000).

CONCLUSIONS

It is showed that the using of some oversized cellulose fibres in pulp slurry did not offer any good, but actually caused great losses in the strength properties of handsheets. The sizing chemicals adsorbed on treated fibres changed the way in which fibres behave during beating. Such fibres could not be beaten properly and could not develop any bond in the paper structure. It may be said from these findings that the recycling of unsized or poorly sized papers can be achieved with less problems than that of hard sized sheets. Fibres having lots of sizing chemicals would likely to give some problems experienced during paper recycling.

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