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# BORAX AS A STRENGTH ADDITIVE IN RECYCLING

by

Siva Krishnagopal Devisetti

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Science  
Department of Paper and Printing Science and Engineering

Western Michigan University  
Kalamazoo, Michigan  
June 1999

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1999

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Finally, my deepest gratitude and appreciation are extended to my family members and friends for their love and support to bring this study to completion.

Siva Krishnagopal Devisetti

## BORAX AS A STRENGTH ADDITIVE IN RECYCLING

Siva Krishnagopal Devisetti, M.S.

Western Michigan University, 1999

The effect of multiple recycling on strength properties and fiber properties like strength of fiber, weighted average fiber length, fines percentage and water retention values were investigated in this study. Borax was used as a strength aid and swelling agent to improve the flexibility of fiber and strength of recycled paper. Bleached softwood kraft pulp was used to make the hand sheets and recycled repeatedly for up to four cycles. The main objectives were to evaluate the chemically treated pulp and untreated pulp at each stage of recycling, to study the effect of multiple recycling on strength properties of paper and to find out whether the bonding ability of borax helps in improving the strength properties during recycling.

Recycling affects negatively the bonding potential and swelling properties of pulp. The loss in strength properties is related to the loss in bonding potential of fibers, as there was no evidence of major change in fiber length or intrinsic strength of fiber. Addition of 1% borax to the virgin stock and recycling further showed a significant improvement in tensile strength and retained the bonding or swelling potential of borax only up to first recycle. Addition of 1% borax to the secondary fibers showed a slight improvement in water retention values and not much improvement in strength properties in any of the four recycling stages.

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## CHAPTER I

### INTRODUCTION

Recycling will have to be increasingly relied upon to satisfy demand for papermaking fibers. Ecological demands are also creating pressure for the increased recycling. The Federal Government's Purchasing specifications are also changed to favor recycle products. A major reason for the government's interest in recycling is the problem of the disposal of solid wastes, a great deal, of which is a paper product. Recycling of waste paper can be used to help solve this problem and will be a profitable venture for the industry as well.

Drying damages the papermaking potential of cellulose fibers. The loss in strength properties due to multiple recycling is a limiting factor to use more recycled fiber in value added grades and in the utilization of lower quality waste paper in papermaking furnishes. It has been repeatedly said (1-4) that the hornification of fibers is one of the main causes for a reduction in fiber flexibility and resultant loss in bonding ability.

In the past, studies have been completed on how recycled fibers affect the strength properties of a sheet. But only limited work has been done in an effort to restore the papermaking potential of fiber. Thus, research work is still being suffered to determine ways to effectively improve the recycling potential of secondary fibers.

The papermaking potential of recycled pulp depends on original pulping process, the initial state of refining, and the initial papermaking process conditions. This study will concentrate on effect of recycling on the strength properties of chemical pulps. The main objective is to find whether borax will help to improve the bonding strength of recycled paper.

## CHAPTER II

### LITERATURE REVIEW

In this literature survey, the effect of recycling on the properties of fibers and on the properties of paper made from those fibers, is discussed. Detailed consideration is given to the causes and factors controlling the recycle potential. The influence of various aspects of the papermaking process on recyclability is examined. Lost potential in a recycled pulp can be recovered to some extent by refining, by chemical additives, by furnish blending and by separate treatment and recombination of pulp fractions (2). The possibilities in each of these areas are reviewed and methods for restoring some or all the inter-fiber bonding are emphasized.

Losses in strength properties due to multiple recycling can be related to two things, namely: (1) the number of times the fiber is recycled and (2) change in fiber surface morphology that takes place (1). It has been reported that the changes in the strength properties of paper are primarily due to variations in the bonding abilities of fibers and that the loss in the intrinsic strength of fibers has little or no effect (5). The reduced interfiber bonding capability and reduced conformability of are caused by the drying phase of the first papermaking cycle. Changes in the fiber result in stiffness. This effect is more pronounced in chemical pulps than in high lignin containing mechanical pulps (6).

## The General Effect of Recycling

### Bonding and Internal Fiber Stiffening

The most generally recognized property losses in paper recycling are those associated with interfiber bonding, such as tensile and burst strengths. Interfiber bonding consists primarily of hydrogen bonds between the surface carbohydrate macromolecules of neighboring fibers. The extent and magnitude of interfiber bonding depends on the exposure of polysaccharide molecules and the surface functional groups such as hydroxyl, carbonyl, and carboxyl that are on the surface (7). It also depends on the extent of surface contact between fibers.

The property that reflects the ease with which fibers are flattened and brought into contact with one another is known as fiber conformability. Surface contact may also be increased by fibrillation. Fibrillation is a disruption of the surface structure of the fiber, which produces strands or ribbons of cell wall polysaccharides (8). When the fibers are laid down in a paper mat, this fibril material overlaps adjacent fibers, creating strong interfiber bonds.

Loss in interfiber bonding is observed in fibers that have been thoroughly dried, as in the dryer section of most paper machines (2). The loss is attributed to the collapse of polysaccharide molecules onto each other as a result of dehydration, resulting in strong intermolecular hydrogen bonds. This general process has been termed as hornification. Such fibers are stiffer because of the internal collapse of the

fibers and are more resistant to fibrillation. Chemical pulps, particularly bleached chemical pulps, are more susceptible to hornification than are mechanical pulps because the removal of lignin provides the opportunity for greater intermolecular mobility and contact within the carbohydrate component (5).

Also, fibers with high lignin content are initially more rigid because of the three-dimensional structure and crosslinking characteristics of the lignin molecules, and hence their low initial strength. Under mild drying conditions, the flexibility of such fibers has been shown to increase upon repeated cycling; the greater flexibility results in increased conformability and interfiber bonding.

Internal fiber stiffening is interrelated with the surface effects that affect interfiber bonding (3). When hornification occurs with molecules internal to the fiber, the resultant stiffer fiber is not as conformable to other fibers and there is less opportunity to bond.

Although the exposure to drying is of relatively short duration during the papermaking cycle, it has been shown to be sufficient for some crystallization to occur because of the enhanced mobility of the cellulose when well saturated with water (4). When wet pressing is followed by dehydration, the enhanced crystallinity imparts greater stiffness to the fibers, not unlike that which might result from a limited amount of cross-linking. The crystallization may in fact be viewed as a physical cross-linking process. As mentioned earlier, the primary impact of this physical transformation is stiffening of the fibers, which results in reduced conformability during the papermaking process.



### Loss of Swelling Ability

As already mentioned the unit operation responsible for changes in fiber properties is drying. This is due to the fact that as the fiber cell wall losses water in the initial drying process, the lamellae of the fiber are brought together. These lamellae are bonded in planes that are so tight that some of these regions will not permit water molecules to penetrate when the fiber are re-wetted (9). The macroscopic effect of this would be that fibers never recover their original swollen diameter and, as a result, flexibility decreases.

This lack of ability to swell completely limits the strength of paper made from secondary fiber. Therefore, such recycled fibers are less flexible and less able to form fiber-to-fiber hydrogen bonds as the new sheet is formed. The reduction in hydrogen bonding reduces the strength of the newly formed sheet. Another impact that recycling has on fibers is a decrease in fiber length and an increase in total fines contents. The overall reduction in fiber length often decreases the strength properties of the sheet as well. The increase in fine content does not significantly impact the strength, but does significantly impact the drainage properties of the sheet on the wire.

A process that promotes fiber swelling should improve the strength potential of the pulp. The fibers should become more flexible as they swell and the development of fines during recycling should in turn be reduced due to a reduction in fiber cutting (10). Fiber swelling is known to be improved by the use of sodium

based chemicals, therefore such chemicals could enhance strength. As the swelling characteristics of a fiber seem to be very important for improving the strength properties of paper, chemicals which modify the surface of a fiber in order to preserve its swelling properties will help enhance the potential for recycle usage. As already stated, internal fiber stiffening is interrelated with the surface effects that affects interfiber bonding.

When hornification occur with molecules internal to the fiber, the resultant stiffer fiber is not as conformable to other fibers and there is a less opportunity to bond. Chemicals that modify swelling properties and or induce bonding between fibers are other means of restoring the papermaking potential for secondary fibers.

### Change in Strength Properties

The sheet properties, which are a direct function of fiber-to-fiber bonding decrease markedly with the number of times fibers are recycled. In contrast, those sheet properties such as tearing strength and flexural stiffness, which in one sense fibers are inversely related to bonding, increase with an increase in the number of times a fiber is recycled at the same freeness level.

The magnitude in the decrease of strength depends on the type of fiber and the processing it has undergone both in the initial papermaking and the recycling steps. For example low yield chemical pulps behave differently from high yield mechanical pulps when subjected to multiple recycling. In contrast, unbeaten Kraft pulps exhibit

an increase in tensile strength due to multiple recycling. This characteristic implies that not only the chemical nature but also the physical states of the pulp fibers determine the effect of hornification on paper properties. The findings of Boblek and Chaturvedi (1) proved that changes in strength could be attributed entirely to the effects of fiber drying and the concomitant loss in bonded area. The intrinsic fiber strength does not change during the initial processing of the fibers.

There is a general agreement that recycling causes a major reduction in breaking length and bursting strength, with a lesser reduction in apparent density and stretch. Increase in tear, stiffness, scattering coefficient, opacity, and air permeability are usually observed. The first recycle pass causes the greatest change in any property, and this appears to be true regardless of whether the virgin pulp was originally dry or moist (6). Figure 1, based on the work of Mckee (6), is representative of the general experience. With extended recycling i.e. in excess of four recycles, most physical properties have stabilized, though there is some evidence tear, in particular may go through a maximum before dropping a little.

#### Swelling and Water Retention Value

Reduced bonding ability is a widely recognized phenomenon, and has traditionally been described as "irreversible hornification", implying a stiffening and/or hardening of fiber. There is a general agreement among several researchers (1,5,6,9) that this loss of flexibility and plasticity is due to the reduced swelling

capacity of the fiber once it has been made into paper. Using water retention value (WRV) as a measure of internal fiber swelling, McKee(6) observed this trend for recycling, noting that the most rapid decrease occurred in the first two recycles. Lundndberg and de Ruvo (11), recycling a 50/50 bleached birch Kraft/Stone Ground Wood (SGW) mixture, found a direct relationship between WRV and tensile strength.

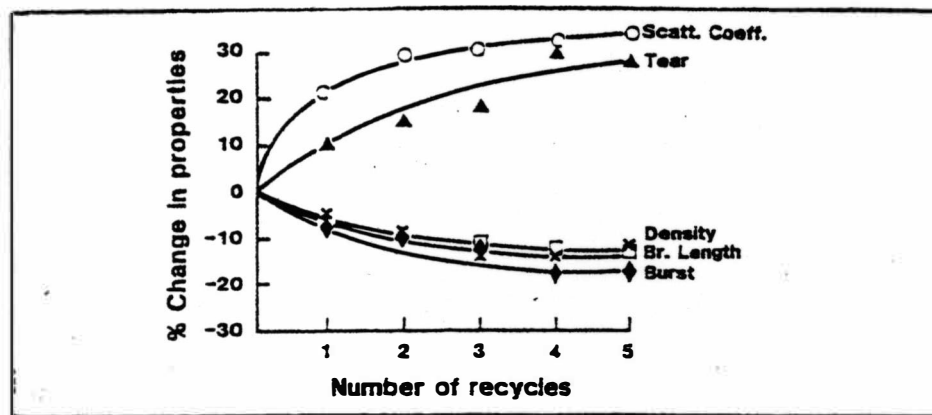


Figure 1. General Effects of Recycling With Chemical Pulp.

Scallar and Tigerstrom (12) have shown that high yield pulps such as thermomechanical (TMP) and chemithermomechanical pulp (CTMP) can recover the ability to take-up water following a drying treatment, while lower yield pulps can not. During their studies it was proved that, TMP was essentially unaffected by the recycling process, whereas the ultra high yield sulfite and kraft saw a 20% and 35% reduction in fiber saturation point, respectively after four recycles. They also observed a steadily decreasing flexibility for kraft fibers and a slight increase in the flexibility for TMP fibers. The loss in water absorbing ability in chemical pulps was

believed to be due to the reduction in the amount of lingo-hemicellulose during the pulping process.

## Factors Controlling the Recycling Potential

### Effect of Furnish

A decrease in the quality of paper with reuse might be intuitively expected, but the magnitude of the decrease/change depends on the type of fibers and processing history, both in the initial papermaking and the recycling steps (2). In addition to the changes in the fibers themselves, the effects of additives and contaminants on the recycle potential of paper must be considered. Not all pulps have the same recycle potential, and any individual pulp can have a different recycle potential, and any individual pulp can have a different recycle potential depending on its manufacturing history. Certain factors influencing the recycle potential of pulp have been identified in the literature and possible explanation has been advanced for that influence.

### Mechanical Pulps

All kinds of mechanical pulps behave essentially in the same manner during recycling. As shown in Figure 2, tensile strength, burst strength, and sheet density increase with recycling while scattering coefficient and tear decreases. However the magnitude in change will be different among different mechanical pulps depending

on their initial treatments. The mechanism behind the occurrence of an increased level of bonding in mechanical recycled paper could result from the flattening of fibers and the increased flexibility during the successive sheet making, pressing and drying cycles.

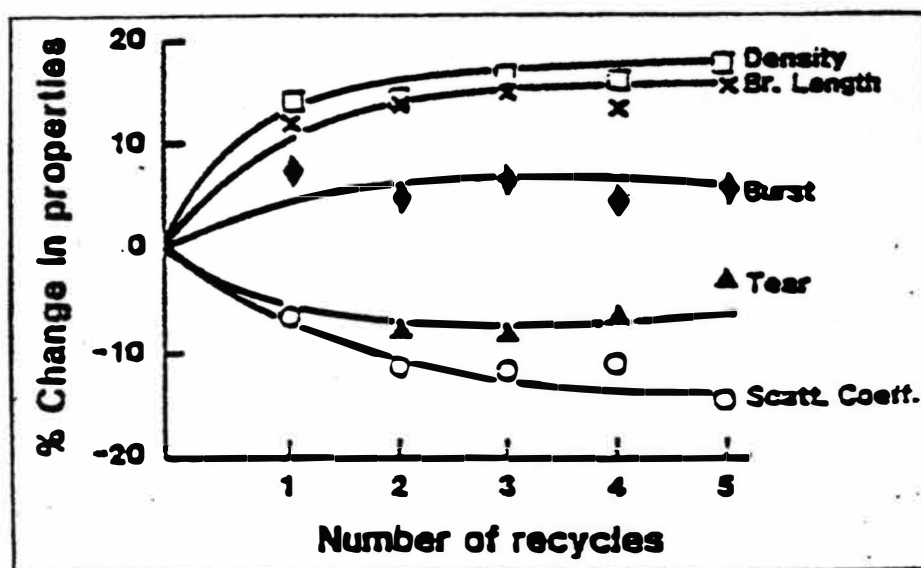


Figure 2. General Effects of Recycling With Mechanical Pulps.

#### Beaten and Unbeaten Chemical Pulps

Howard and coworkers (3) explained the difference in the response of different pulps to recycling. During this study, they reviewed the effect of recycling on beaten chemical pulps and unbeaten chemical pulps separately. They observed that beaten chemical pulps get homified with number of recycling due to repeated drying between cycles and results in a bulkier and weaker sheet. In contrast to this,

unbeaten chemical pulp fibers are initially curly in nature. Repeated recycling removes the curl in fibers and hence the tensile strength increases.

### Blend of Chemical and Mechanical Pulps

As already explained the trends displayed during the recycling of beaten chemical pulps were the exact opposite of those displayed by mechanical pulps. Studies conducted using blend of chemical and mechanical pulps (50/50 mix of beaten bleached kraft and TMP) have shown that breaking length and burst initially decrease during recycling, but then finally start to rise again (3). The tear strength values have shown an opposite trend. The explanation for these trends is that they represent the net result of two different events taking place at different rates. Initially, hornification of the chemical pulp fibers reduces the bonding potential, giving a weaker sheet. Then the flattening of the mechanical pulp fibers progressively take over, causing some strength recovery as shown in Figure 3.

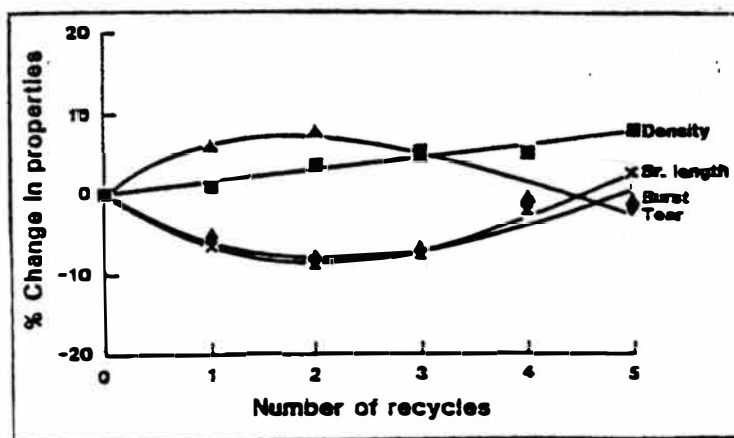


Figure 3. Effect of Recycling on Percentage Change in Properties for a Blend of TMP/Beaten Kraft Pulps.

### Effect of Initial Beating

There is a general agreement that greater the initial degree of refining, the greater the loss of pulp quality on recycling, and the lower the recovery potential of sheet properties that are a direct function of fiber bonding, e.g. burst strength and tensile strength. Recycling under minimal conditions of refining results in fiber network strength losses that are weakly related to the number of times the fiber is recycled. The decrease in strength is positively correlated to the extent of refining that the fibers undergo during their first use, particularly for softwood (13).

### Effect of Wet Pressing

Little has been published concerning the possible effect of the degree of wet pressing on the recycle potential of paper made at different levels of pressing. Carlson (14) measured the WRV of an unbleached kraft pulp after wet pressing and subsequent redisintegration. At moderate levels of PFI mill beating, there was only a slight decrease in WRV of approximately 5% up to a solids content of 60% after pressing. However, for a heavily beaten pulp, the corresponding fall was more pronounced at around 15%.

### Effect of Drying

It has been proved that high yield pulp (e.g. TMP) can recover the ability to take-up water following a drying treatment, while lower yield chemical pulps are



difficult to swell after being subjected to drying treatment (12). Chaterji and co-workers (15) examined the effect of four recycles on the fiber saturation point of TMP, ultra high yield sulfite and the kraft process. Multiple recycling involved repeated sheet formation, wet pressing, restrained high temperature drying and gently reslushing. They found that TMP was essentially, unaffected by the recycling process, whereas kraft saw a 30% reduction, respectively after four cycles.

As already mentioned, a fiber's ability to take-up water reduced due to recycling. This ability is measured by the water retention value, and is proven by the study conducted by Ruvo & Htun (16). Ruvo found that the pulp prepared from paper dried at a high temperature could not regain the WRV of the initial pulp even after prolonged beating. This is due to the fact that the larger pores in a fiber preferentially close up during drying (16,17).

In subsequent beating this part of the cell wall stays resistant to delamination, and indeed the whole fiber becomes stiffer and perhaps more brittle. An increase in cellulose crystallinity has been noted by Yamagishi (18) during the recycling of commercial hardwood and softwood bleached pulp, though the increase was small. Nissan (19) suggested that the "irreversible hornification" could indeed be a two component phenomenon, leading to both an overall stiffening of the fiber and a change to the fiber surface chemistry.

## Recovery of Papermaking Potential

Numerous studies have been conducted to examine how fibers are affected by the recycling process and what affects their response has on the paper properties of paper made from these fibers. Most of the work done is fundamental and only few researchers worked to improve the papermaking potential. Review of literature reveals that there are essentially four ways open to the papermaker to recover the lost potential of recycled fibers. These are (1) refining method, (2) blending with virgin pulp, (3) fractionation and (4) chemical treatment methods.

### Refining Method

G.V.Lavins (9) examined a method of reversing the hornification of commercially dried bleached kraft pulp. He found that, using a PFI Mill, the swelling of both fiber and fines could be restored towards their never dried levels with only a slight increase of fines. This approach has been successful both in lab and in full scale refining. Low intensity is generally recommended for such refining operations.

Fiber shortening and fines generation is more severe in recycled pulp than in virgin ones, and so there is a limit to the improvement that can be achieved. The basic problems are that (a) the fiber length distribution has already been decreased by the original refining and repulping, and (b) that the already hornified fines do not respond to beating (2). The already hornified recycled fibers are stiffer and tend to favor fines generation rather than fibrillation, and where as in a virgin pulp fines

generated by beating are beneficial to bonding, in a recycled pulp they may actually reduce strength.

Thus, the recycled fines simply act like inert filler, reducing drainage and contributing nothing to strength. An alternative approach to the development of strength properties without any undue fines generation and drainage rate reduction is to use high consistency refining (20).

### Blending Virgin Pulp and Recycled Pulp

Due to the fact that a virgin pulp contains not only more “active” (non-hornified) fibers, but also more “active” fines, the addition of refined virgin pulp produces a beneficial effect. This has been proved in the experiments carried out on chemical pulps (21). It suggests that a careful selection of furnish-components and their treatment may be the key to optimize quality.

### Fractionation Method

Fractionation is a method of choice in some board mills. After slushing the secondary fiber, the stock is separated carefully by screening. Then the long fiber fraction is beaten separately. The fiber fractions are then used according to one of the following schemes: (a) utilization of the two fractions in the production of two different grades on separate machines, (b) utilization of the two fractions in two or more plies in the same sheet of paper, and (c) mixing the beaten long fiber of virgin stock with unbeaten recycled short fraction.

### Chemical Treatment Methods

In the secondary fiber treatment process sodium hydroxide is used either to help in ink removal or help disintegration of heavily sized papers. It increases pH and causes fiber swelling. The beneficial effect of sodium hydroxide on strength is noticed. In recycling process the fibers should become more flexible as they imbibe water and the development of fines during recycling should in turn be reduced due to a reduction in fiber cutting (22). As mentioned already, fiber swelling is known to be improved by the use of sodium hydroxide and hence would possibly enhance strength. In more recent times, the use of sodium hydroxide as an upgrading treatment has been investigated for mixed waste paper, for recycled kraft pulp, for news print and for sized handsheets (23). In all the cases, breaking length improvement was found. Typically, less than 1.0% sodium hydroxide on bone dry fiber was used. None of the above researchers mentioned above has measured fiber-swelling properties.

Under the assumption of fiber swelling and paper strength are related, several researchers have used fiber swelling as an explanation of the strength improvement. Literature states that the degree of swelling in chemical pulp is related to the number of carboxylic acid groups on the cellulose chain (24).

Further studies proved that some of the acidic groups will be dissociated in water, thereby releasing mobile counter-ions to the fibers cell wall (25). As the concentration of these ions increase, osmotic pressure draws additional water into the

cell wall. The fibers swell as they gain water and will continue to swell until the pressure different is balanced. Therefore, if the number of acidic groups is increased, the swelling increases as well. Thus any treatment that effects the ionization characteristics of the fibers will effect the swelling potential. Addition of sodium hydroxide helps in improving fiber flexibility without reduction in freeness due to refining but some other undesirable effects, such as loss in brightness may be there (2).

Cationic starch increases the strength of virgin chemical pulp by improving bond strength/unit bonded area, and might be expected to do the same for recycled furnishes. Therefore, the addition of chemicals that can improve the swelling as well as bonding ability of secondary fibers is the best choice available.

Borates and other boron compounds have been tried as additives to papermaking stock suspensions to aid in wetting, swelling and to improve strength (26). Borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) is supposed to form covalent bonds with hydroxyl ion of cellulose and act as a bridge between two cellulose fibers as shown in Figure 4.

Boron compounds combine with certain sugars and form boric acid complexes. Equilibrium constants (27) for the formation of boric acid complexes from sugars are shown in Table 1.

During the internal studies conducted using borax as a strength additive, improvement in strength properties has been observed. During this study a bleached softwood pulp was treated with borax and an improvement in tear, tensile, burst and

stiffness was observed. A 1% borax is found to be suitable in improving the strength and any further addition has not shown considerable increase. Since borax is suitable in enhancing the strength of fiber networks, it can also be tried in recycled papers to improve strength properties through its bonding ability and this remains to be studied.

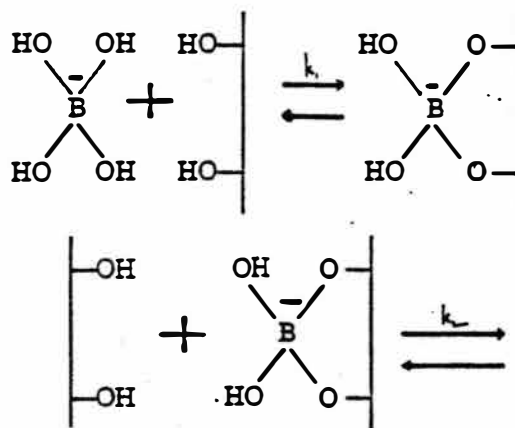


Figure 4. Mechanism of Covalent Bond Formation Between Borax and Hydroxyl Ion of Cellulose.

Table 1

Equilibrium Constants of Formation of Boric Acid Complexes

Sugar Compounds	Equilibrium Constants	
	$K_1$	$K_2$
D-Fructose	$3.00 \cdot 10^3$	$1.24 \cdot 10^5$
D-Galactose	$1.75 \cdot 10^2$	4.00.28
D-Glucose	$1.50 \cdot 10^2$	$7.60 \cdot 10^2$
D-Mannose	$1.02 \cdot 10^2$	$4.58 \cdot 10^2$

## CHAPTER III

### STATEMENT OF THE PROBLEM AND NEED FOR THE STUDY

Recycling, with each successive recycle causing further damage irreversibly damages the papermaking potential of cellulose fibers. However, recent studies show that a substantial change in the properties is being caused by the first cycle, with most of the physical properties stabilizing after four cycles (6). The loss in strength properties in recycled paper is attributed to the loss in bond strength and not to the loss in intrinsic fiber strength. This is particularly a problem in case of chemical bleached pulps. Hence a change in quality of paper takes place, but the magnitude and type depends on the type of fiber and the processing it had undergone both in the initial papermaking and the recycling stage. Mechanical pulp fibers are found to become flatter and more flexible giving a denser and strong sheet whereas chemical beaten pulps become stiffer and less flexible resulting in bulkier and weaker sheet.

This loss in strength properties due to multiple recycling is a limiting factor in using more recycled fiber in value added grades and utilizing lower waste paper qualities in papermaking furnish. The loss in strength properties with recycling is attributed mainly to the hornification of fibers that takes place during drying of paper. Hornification is the loss of swelling ability and this happens during the drying stage. The changes that take place in the structure of cellulosic fibers when they are recycled

needs to be more clearly understood. Possibly the changes in paper properties measured before and after each recycle could be explained by the changes in pulp/fiber properties.

The lost papermaking potential can be recovered possibly by refining at high consistency or by chemical treatment methods. As explained earlier, there is a limit to the improvement that can be achieved with refining.

Therefore, the addition of chemicals that can improve the water retaining and bonding ability is the best option. The bonding ability of borax might help in improving the strength properties of recycled paper. This study will mainly concentrate on effect of recycling on strength properties of chemical pulps. The main objective is to find whether borax improves the bonding strength of recycled paper.

### Objectives

1. To study the effect of multiple recycling on strength properties of paper.
2. To find out whether the bonding ability of borax helps in improving the strength properties of recycled paper.



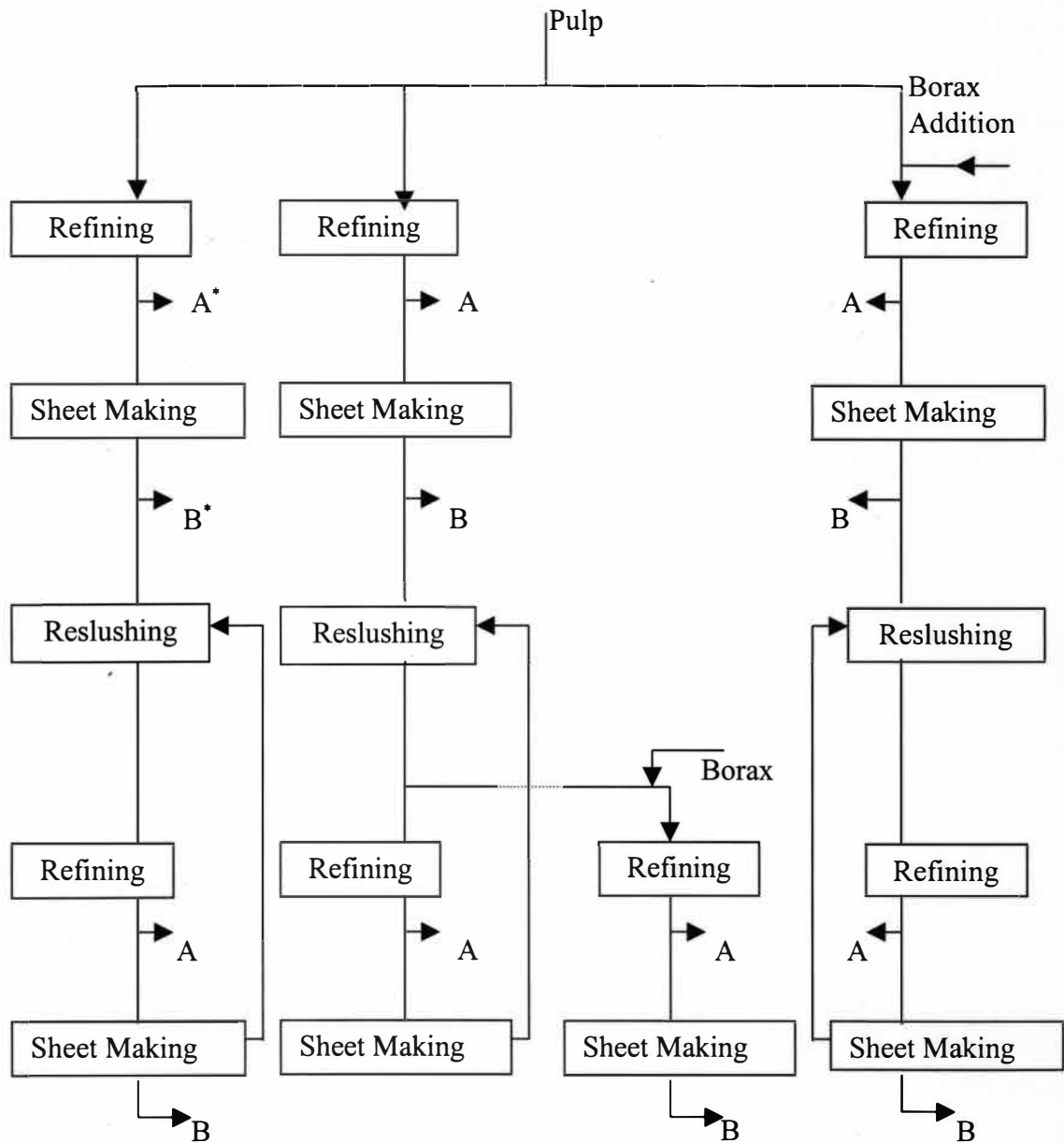
## CHAPTER IV

### Experimental Design and Methodology

#### Experimental Schematic

The experimental design used during this study was to investigate the effects of recycling on strength properties while using borax as a strength additive. It focuses on the characterization of chemical pulp at each stage of recycling. Experiments were conducted to measure the change in specific fiber characteristics such as fine percentage, fiber length, fiber strength and water retention values. Borax was used as a strength aid and swelling agent to improve the flexibility of fiber and strength of recycled paper. The main objective is to characterize the chemically treated pulp and untreated pulp at each stage of recycling and study its effect in restoring the recycle potential of papermaking fiber.

The schematic of the experimental design is shown in Figure 5. The schematic describes recycling experiments with and without addition of borax as a swelling agent and strength aid. In both control experiments and experiments conducted with the addition of borax, the pulp was recycled equal number of times and during each recycle samples of pulp and handsheets were retained for testing and analysis. The results thus obtained are analyzed and discussed further in Chapter V.



Control Experiments

Borax Addition to  
Recycled Stock

Borax Addition to  
Virgin Stock

\* A=Pulp Samples for Testing; B=Handsheets for Testing

Figure 5. Experimental Schematic Showing the Multiple Recycling Procedure and Point of Addition of Borax.

Initially, a sufficiently large number of handsheets were prepared so that a few handsheets can be used for testing strength properties between each recycle and the rest would be disintegrated for subsequent cycles. As shown in Figure 5, one set of recycling experiments were conducted without the addition of borax and designated as control experiments. Borax addition was conducted in two different ways. One set of recycling experiments with borax addition was conducted by adding borax only in the virgin stage. After adding borax in the initial stage, handsheets were made, disintegrated and recycled without any other addition in further stages. This is to determine whether recycling potential is enhanced by the borax treatment.

The other set of recycling experiments with borax contains its use on the recycled furnish in the respective stages. As depicted in Figure 5, during the control experiments, sufficient amount of pulp sample was retained between each recycle to make recycled handsheets with and without borax. The recycled furnish at each stage was treated with borax and handsheets were prepared to see the effect of borax on recycled fibers. This set of experiments was conducted to see whether the recycled fibers have their strength properties enhanced by borax similar to virgin fibers.

Treating the recycled furnish that was collected from control experiments after each stage helped to determine whether any modification of the multiple recycled fibers is possible in terms of swelling and strength. On the other side, use of borax in the virgin stage and recycling further helped in two ways. First, it is to confirm that it helps achieving better strength properties in the virgin stage compared to the virgin

stage of control experiments. Second, it is to see that the presence of borax as a strength additive in the virgin stage helps in restoring and/or retaining the swelling ability and papermaking potential of pulp in the further recycles.

## Experimental Procedure

### Recycling Procedure

Bleached softwood kraft pulp was used in the experiments. Dry pulp was initially slushed and centrifuged prior to storage in a clod room. Sheets were made without recirculation of backwater and addition of fillers or sizing materials. Refining was conducted between recycles to obtain a constant freeness. Pulp was refined in a PFI mill at 10% consistency. The PFI mill revolutions during interstage refining in control experiments are 1500, 1400, 1250 and 1650 in first, second, third and fourth recycle stages respectively. In the case of experiments with borax addition in virgin stage, the PFI mill revolutions were 1400, 1600, 1400 and 1500 in first, second, third and fourth recycles respectively. The PFI mill revolutions during this interstage refining showed no apparent pattern.

As explained earlier, sufficiently large amount of sheets – approximately 220 sheets without adding borax and 155 sheets with the addition of borax– were prepared in the virgin stage and after retaining six handsheets (in each stage) for testing, the rest were disintegrated for further recycling. The soaking time of handsheets before they are disintegrated was maintained at 24 hours in all cases. The time spent in

disintegrating the handsheets before each stage was kept constant at 10 minutes. The disintegrated pulp was then filtered on a 200 mesh screen prior to refining. The filtrate obtained was reused for dilution of the refined pulp prior to handsheet preparation. The refined stock was diluted with the filtrate from the disintegration stage as well as fresh water and was used to make 8 in by 8 in handsheets of 2.5 grams each ( $60 \text{ g/m}^2$ ).

Wet pressing was carried out in contact with a press felt on both sides and between steel rolls. Two pressings were done on each of the sheet. Handsheets were dried on a steam-heated dryer at around  $230^\circ\text{F}$ . The handsheets were dried once with the wire mesh contacting the dryer and then with the paper in contact with the dryer. The sheets were finally dried again with the wire side of paper contacting the dryer.

#### Fiber Characterization and Paper Testing

The freeness of pulp, average fiber length, fines percentage and water retention values were closely monitored by testing the pulp samples at each recycling stage. This helped to correlate the changes in fiber length and other stock conditions such as swelling ability with the strength properties of handsheets.

Pulp freeness was monitored during all the recycling stages to compare with the virgin stock and was maintained at relatively the same level with intermediate refining. Pulp was refined in a PFI refiner to an initial freeness range of 320 to 350 CSF by running the refiner up to 5500 revolutions. Between each stage, when the

handsheets were disintegrated for further recycling, freeness rose to about 450 to 500 mL CSF. This rise in freeness could be due to the loss of fines during handsheets preparation. In order to control the freeness values in a same range in all the stages, interstage refining was done and the freeness values obtained after refining are shown in Table 2.

Classification of fibers was carried out on the Clark classifier. Five grams of pulp was disintegrated in 1500 ml of tap water using a british disintegrator and mixed for five minutes. Weight percentages retained on four different mesh numbers of 14, 30, 50 and 100 were used to calculate the fines percentages lost through the 100-mesh screen.

Table 2  
Pulp Freeness (CSF)

Recycle #	Control Experiments	Borax Addition During Recycling to	
		Secondary Fiber	Virgin Fiber
1	340	-	360
2	360	380	350
3	360	360	375
4	365	375	360
5	340	375	350

Weighted average fiber length was determined on the kajaani fiber analyzers- Fiber Lab and FS-200. The fiber analyzer contains a microcomputer, measurement and control electronics, automatic sample handling, a measurement section with laser optics, and CRT display. A beaker containing the sample is inserted in the analyzer. After start command, the device mixes and dilutes the sample and sucks fibers from the dilution into a capillary funnel. In the capillary, the fibers pass through the optics section. A laser beam forms a light image of the fibers on the detector. This image is proportional to fiber length.

Water retention value is a measure of fiber flexibility. The dependence of fiber flexibility on the water holding capacity is well known. This property was tested on the pulp samples collected at the indicated stages of the recycling process for both control experiments and recycling experiments. Water retention value was evaluated by centrifuging at 900 g-force for 30 minutes on a bench top centrifuge for all the stages of the recycling process based on the TAPPI useful method. The results are reported as retained water in grams/gram of O.D fiber. This test was conducted on both control experiments and borax added stages to investigate whether there is any improvement in swelling ability of pulp, due to the addition of borax.

Zero span strength was tested as a measure of fiber strength. Tearing resistance was tested as a measure of fiber length and fiber strength. Tensile and burst strength was tested as a measure of bonding related properties.

All the test procedures were carried out as per standard TAPPI methods listed in Table 3.

Table 3  
Experimental Test Methods

Name of the Test	Test Equipment	TAPPI Test Methods
Fines Percentage	Clark Classifier	T-233 cm-82
Fiber Length	Kajjani (Fiber Lab/FS-200)	T-271 pm-91
Water Retention Value	Centrifuge Cup	T-256 um
Canadian Standard Freeness	Freeness Tester	T-227 om-89
Zero-Span Tensile Strength	Pulmac	T-231 cm-85
Tensile Strength	Instron	T-494 om-88
Tear Strength	Elmendorf	T-414 om-88
Burst Strength	Mullen	T-403 om-91



## CHAPTER V

### RESULTS AND DISCUSSION

The main focus of this investigation is to characterize the chemically treated pulp and untreated pulp at each stage of recycling and study the effect of chemical treatment methods in restoring the recycle potential of papermaking fiber. Thus the objectives of this investigation can be fulfilled by observing the selected factors like fines percentage, fiber length, fiber strength, water retention value and their combined effect on strength properties (tensile, burst, zero span, and tear strength) during the recycling. The effect of recycling on fines percentage, fiber length, fiber strength and water retention values are explained further in detail.

Under the assumption that fiber swelling and strength are related, several researchers have used fiber swelling as an explanation of the strength improvement. The same strategy is adopted during this study while analyzing the results. Earlier, borax was tried as an additive to paper making stock suspensions to aid the wetting and swelling properties and to improve strength (26). Also during the internal studies conducted at Western Michigan University, 1% borax was found to be suitable in improving the strength.

There is no evidence of any other published results on the variation of paper strength during recycling when borax is used as swelling agent or strength aid. Hence

this study is the first of its nature and these results cannot be compared with the findings of any earlier research. The average values of the repeated experiments conducted for individual variables are tabulated with their standard deviations. Comparative graphs for control experiments and experiments conducted with addition of borax are plotted, showing the effect of recycling and the addition of borax on each specific factor and strength property discussed. Virgin stage is designated as 0 cycle and the successive recycles are designated as 1, 2, 3 and 4.

### Experimental Data Analysis

One-way analysis of variance was conducted to analyze the data and identify significant changes in strength properties between stages of recycling. Thus, the significant change in the strength properties between cycles 0 to 4 of control experiments and experiments with borax addition are each explained by ANOVA.

Two-tailed t-test was used to determine the significance of difference in strength between control experiments and experiments with borax addition at each recycle. The mean values obtained at each recycle stage of control experiments and experiments conducted with the borax addition were compared at 5% significance level to determine the statistical difference. A pooled standard deviation was used in the calculations (28).

## Effect of Recycling on Specific Fiber Property

### Effect of Recycling on Fines Percentage

Percentage of fines was calculated as the moisture free weight of the pulp lost through 100-mesh screen based on the feed to the Clark classifier. The average values of two duplicate readings are shown in Table 4 for all the recycling stages for control experiments as well as experiments conducted with borax addition.

Table 4

#### Percentage of Fines

Recycle #	Control Experiments	Borax to Virgin Stage
0*	36.2	35.8
1	28.5	27.3
2	26.8	27.6
3	26.2	24.8
4	25.0	26.0

\* Virgin Stock

Figure 6 is a comparative graph for the effect of recycling and effect of borax on fines percentage. As shown in this comparative graph, there is a decrease in fine percentage in the first and second stage. The initial fine percentage is around 36%

both in the case of control experiments and the experiments conducted with the addition of borax to the virgin stock. Since there was no recirculation of back water, fines loss took place in the first cycle of handsheet making. Secondary refining was carried out between each cycle to bring down the freeness to a range of about 320-350 CSF. Despite the lack of backwater recirculation, there is a uniform fine percentage in all the stages after first stage, and this may be due to the interstage refining.

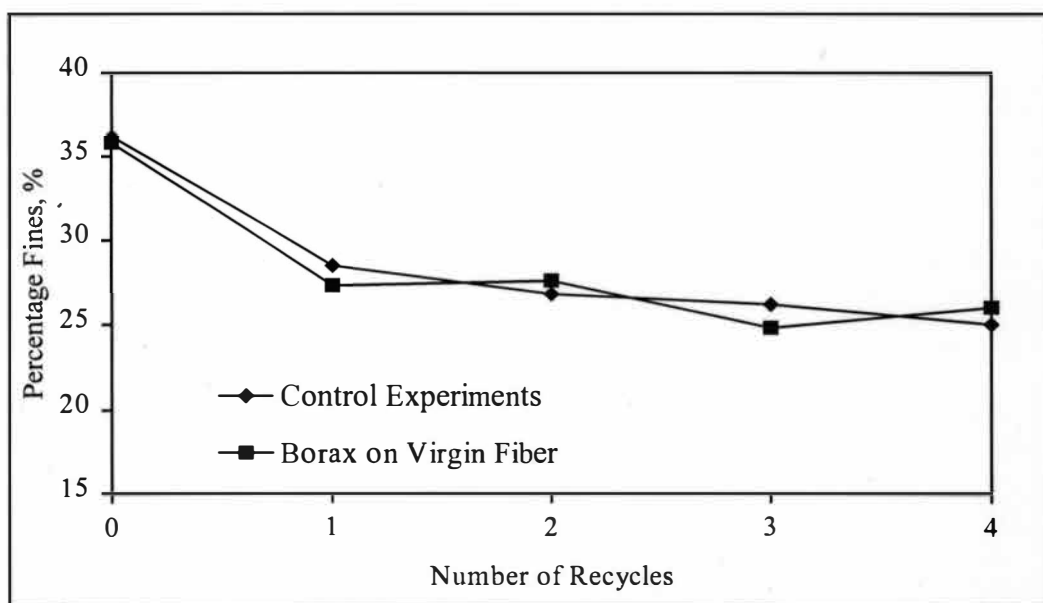


Figure 6. Effect of Recycling on Percentage of Fines.

#### Effect of Recycling on Fiber Length

Weighted average fiber length data are presented in Table 5 and Figure 7. Fiber length was determined on a Kajaani fiber analyzer. The principle of measurement consists of passing the fibers through the optics section provided in a

Table 5  
Weighted Average Fiber Length (mm)

Recycle #	Control Experiments	Borax to Virgin Stage
0	2.78	2.72
1	2.76	2.74
2	2.70	2.69
3	2.62	2.59
4	2.65	2.60

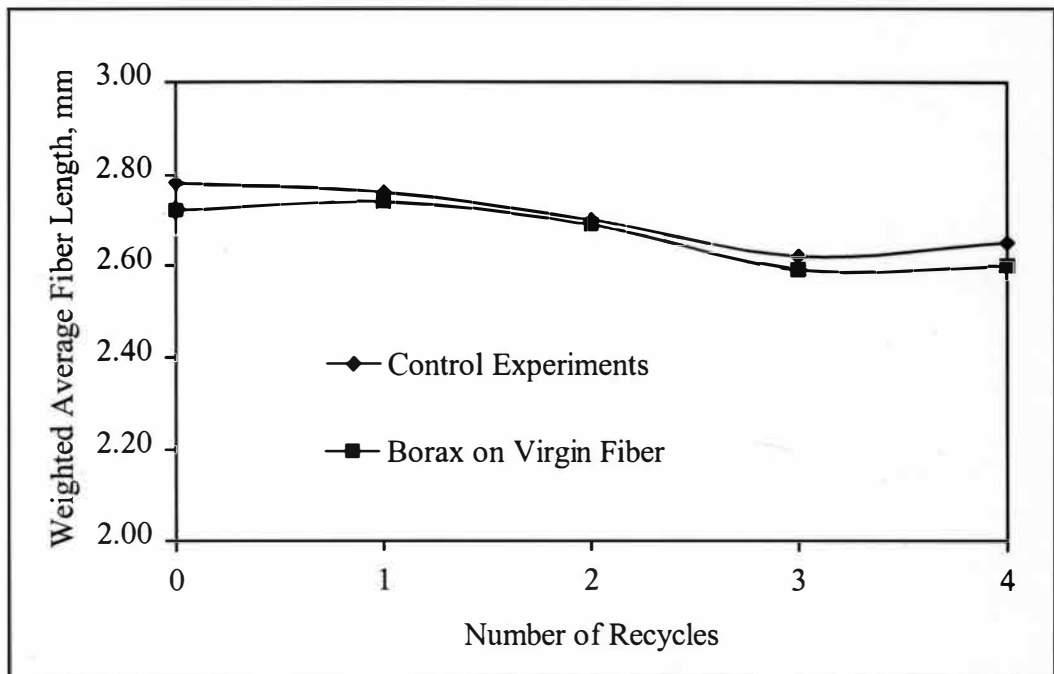


Figure 7. Effect of Recycling on Fiber Length.

capillary funnel. A laser beam forms a light image of the fibers on the detector. This image is proportional to fiber length. The detector signal is amplified and converted into digital form for calculations in the microprocessor.

As shown in Figure 7, fiber length changes are small and they are probably explained by the small changes in fines content. There is a continued loss of fines during recycles owing to the absence of closed white water system and there is almost an equal amount of new fines generated during the interstage refining.

A separate experiment was conducted to determine the amount of fines lost and the amount of fines generated due to interstage refining and the data are presented in Table 6. The amount of fines lost during sheet making and the amount of secondary fines created during refining of recycled sheets were evaluated by fiber classification. Initially, virgin pulp was refined to a freeness of 340 mL CSF and then sheets were made after determining the fines content in pulp. Then the sheets were disintegrated for 10 minutes in a disintegrator after a soaking period of 24 hours.

Table 6

Percentage of Fines During Interstage Refining

Percentage Fines at	Percentage Fines
Fines in refined virgin pulp (340 mL CSF)	21.63
Fines retained in handsheets	13.30
Fines in pulp post refined (350 mL CSF)	19.33

Freeness of disintegrated stock was found to be 450 mL CSF. Then the disintegrated pulp was refined to adjust the freeness to match with the original freeness. Fines content were determined both for reslushed and post refined pulps. As it can be seen from the table, there is a loss of 8.4% fines during sheet making and 6.1% of fines are created when the disintegrated stock was refined to a freeness of 350 mL CSF.

#### Effect of Recycling and Borax Addition on Zero Span Fiber Strength

Zero span strength is measured using Pulmac instrument. Average zero-span strength, values with standard deviations are reported in Table 7.

Figure 8 is a comparative graph of zero span breaking length values between control experiments and experiments with borax added to the virgin stock. Figure 9 shows the comparison of zero span strength between control experiments and experiments with borax added to the recycled fiber. In both cases a little or no change in fiber strength with increase in number of recycles can be observed. It can be seen from the figure that, in no case does the fiber strength change significantly either due to the number of recycles or due to the addition of borax as a swelling agent during sheet making.

The present results can not be compared in a meaningful way with the earlier research. A few researchers (6) have reported some drop in zero span strength and a few others have reported little or no change in the intrinsic strength (3).

Table 7

## Zero Span Fiber Strength

Recycle #	Control Experiments	Borax Addition to	
		Recycled Fiber	Virgin Fiber
<u>Zero Span (Breaking Length), Km</u>			
0	8.61	-	8.70
1	8.32	8.41	8.60
2	8.70	8.50	8.59
3	8.50	8.51	8.60
4	8.42	8.35	8.54
<u>Standard Deviations</u>			
0	0.38	-	1.20
1	0.42	0.32	1.30
2	0.33	0.38	1.60
3	0.33	2.20	0.80
4	0.52	0.80	1.45



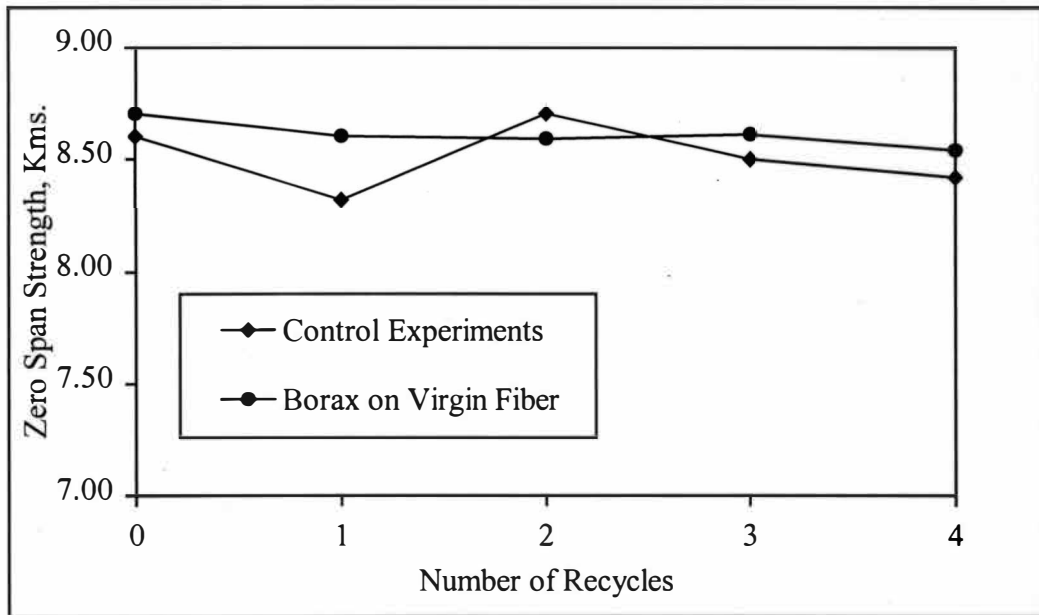


Figure 8. Effect of Recycling on Fiber Strength ( Zero Span); a Comparative Plot Between Control and Experiments With Addition of Borax to Virgin Fiber.

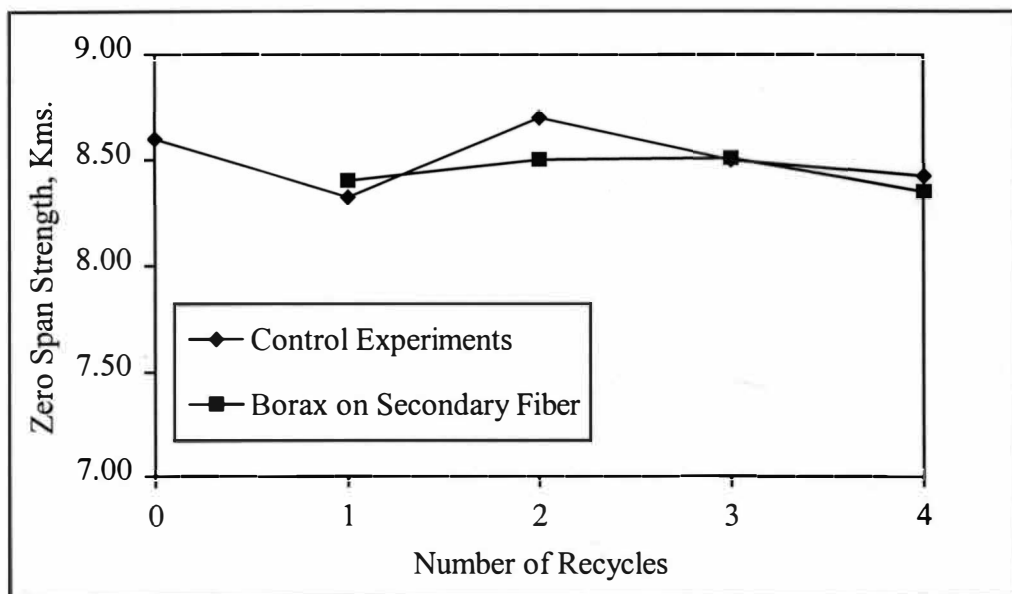


Figure 9. Effect of Recycling on Fiber Strength (Zero Span); a Comparative Plot Between Control and Experiments With Addition of Borax to Secondary Fiber.

The loss of fiber strength is expected because the fibers underwent a repeated number of recycling process; they must become fragile and brittle and hence strength should go down. Also recycling might promote brittle fiber to be shortened by mechanical forces produced during refining.

These results indicate little or no loss in fiber strength due to recycling. This might be due the reason that hornified fibers are stiffer because of the internal collapse of the fibers and more resistant to fibrillation. Chemical pulps, particularly bleached chemical pulps, are more susceptible to this kind of phenomena.

#### Effect of Recycling on Water Retention Value

Average water retention values of repeated experiments with the standard deviations for control experiments as well as borax added experiments are tabulated in Table 8. Water retention values can be used as a measure of internal fiber swelling capacity and are bound to vary with the change in fiber flexibility and plasticity.

Figure 10 shows the water retention values of control experiments. There is a major change in water retention value between virgin stage and first recycles and not much change in latter stages. A comparative graph between control experiments and experiments with borax to the virgin stock and to the recycled stock is shown in Figure 11. There is an improvement in water retention value in the virgin stage with the use of borax. However, even with the use of borax in the virgin stage, the water retention values dropped with increase in number of recycles exhibiting similar trends as control experiments.

Table 8

Water Retention Values (gm of water/gm of O.D. fiber)

Recycle #	Control Experiments	Borax Addition to	
		Recycled Fiber	Virgin Fiber
<u>Average Water Retention Values</u>			
0	2.26	-	2.28
1	1.92	1.96	1.98
2	1.83	1.83	1.85
3	1.82	1.83	1.82
4	1.80	1.82	1.78
<u>Standard Deviations</u>			
0	0.12	-	0.14
1	0.09	0.16	0.10
2	0.11	0.08	0.05
3	0.03	0.09	0.05
4	0.12	0.08	0.23

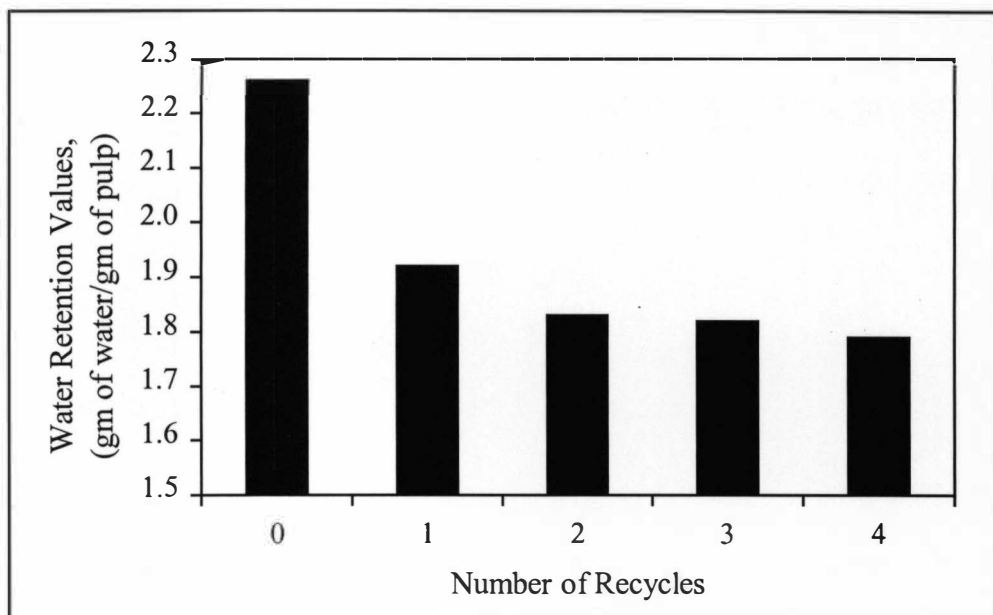


Figure 10. Effect of Recycling on Water Retention Values in Control Experiments.

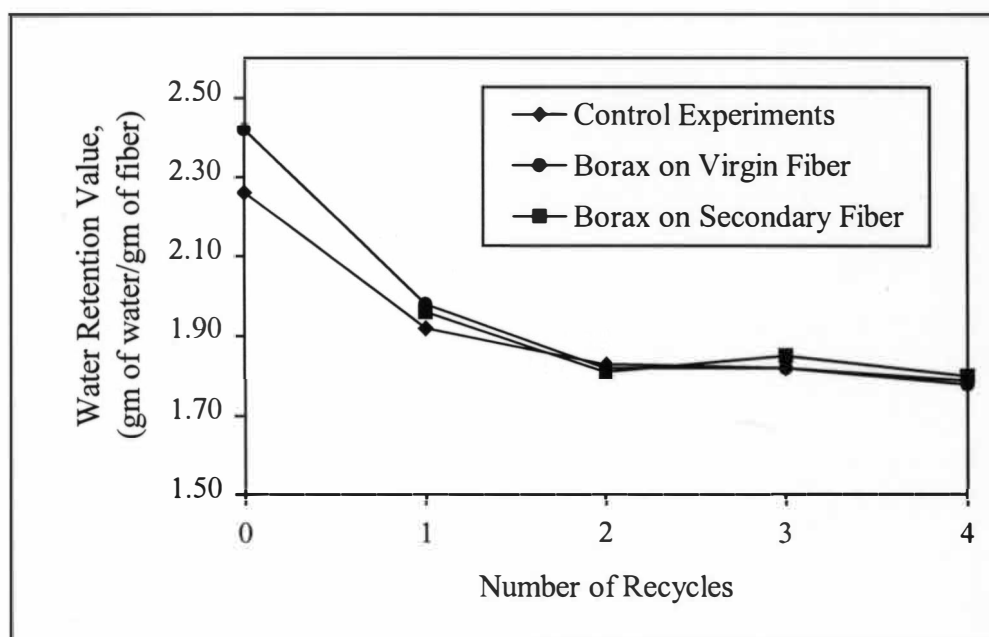


Figure 11. Comparative Plot of Water Retention Values Between Control Experiments and Experiments With Borax Addition.

It can be seen from the data that addition of borax to the recycled fiber at any given stage has not improved the water retention values significantly. However, there is a slight indication of increasing trend in every stage when compared to the respective stage in the control experiments.

As the fibers underwent a repeated drying between recycles they might have become brittle and stiffer. A reduction in water retention value corresponds to the loss of internal swelling resulting in the loss of recycle potential. This is due to a fact that as the fiber cell wall loses water in the initial drying process, the lamellae of the fiber are brought together. These lamellae are bonded in planes that are so tight that some of these regions will not permit water molecules to penetrate and swell the fibers.

The macroscopic effect of this would be that fibers never recover their original swollen diameter and, as result, flexibility decreases. The resultant stiffer fiber is not as conformable to other fibers and there is less opportunity to bond. Swelling characteristics of a fiber seem to be very important for improving the strength. As already mentioned, regardless of the recycling procedure followed, the water retention values decreased with increase in number of recycles.

#### Effect of Recycling on Specific Strength Property

##### Effect of Recycling on Tensile Strength

Average tensile index values with their standard deviations are presented in Table 9. As can be seen from the table, tensile index values decreased rapidly with

the number of recycles. Results of ANOVA shown in Table 10 indicate that the drop in tensile strength with number of recycles is significant both in control experiments and with the use of one percent borax.

Table 9  
Tensile Strength Data

Recycle #	Control Experiments	Borax Addition to	
		Recycled Fiber	Virgin Fiber
<u>Average Tensile Index, NM/gm</u>			
0	79.80	-	85.19
1	66.81	66.68	73.42
2	62.62	63.29	62.72
3	56.04	57.45	56.85
4	50.56	51.83	51.20
<u>Standard Deviations</u>			
0	0.77	-	1.39
1	1.43	0.20	1.16
2	0.81	0.24	0.24
3	0.2	0.12	1.13
4	1.41	0.11	0.42

Table 10  
Analysis of Variance for Tensile Strength Results

Source	DF	SS	MS	F	P
<u>Control Experiments</u>					
Number of Recycles	4	25.99	6.497	32.71	0.0001
Error	25	4.97	0.1986		
Total	29	30.95			
<u>Borax Addition to the Virgin Stock</u>					
Number of Recycles	4	35.71	8.928	179.76	0.0001
Error	25	1.24	0.0497		
Total	29	36.95			
<u>Borax Addition to the Recycled Furnish</u>					
Number of Recycles	3	7.02	2.340	76.95	0.0001
Error	20	0.61	0.0304		
Total	23	7.63			

The effect of recycling on tensile strength can be seen from Figure12. A major loss in tensile strength took place between initial and first recycle and a gradual change in later stages. The first recycle lowered the tensile strength by 16.3 percent,

and after four recycles the tensile strength decreased approximately 36.6 percent. The possible reasons for drop in tensile strength could be the loss in bonding between fibers, loss in intrinsic strength of fiber or changes in fiber length. The reduction is primarily associated with inter-fiber bonding as there is not much change in intrinsic strength or

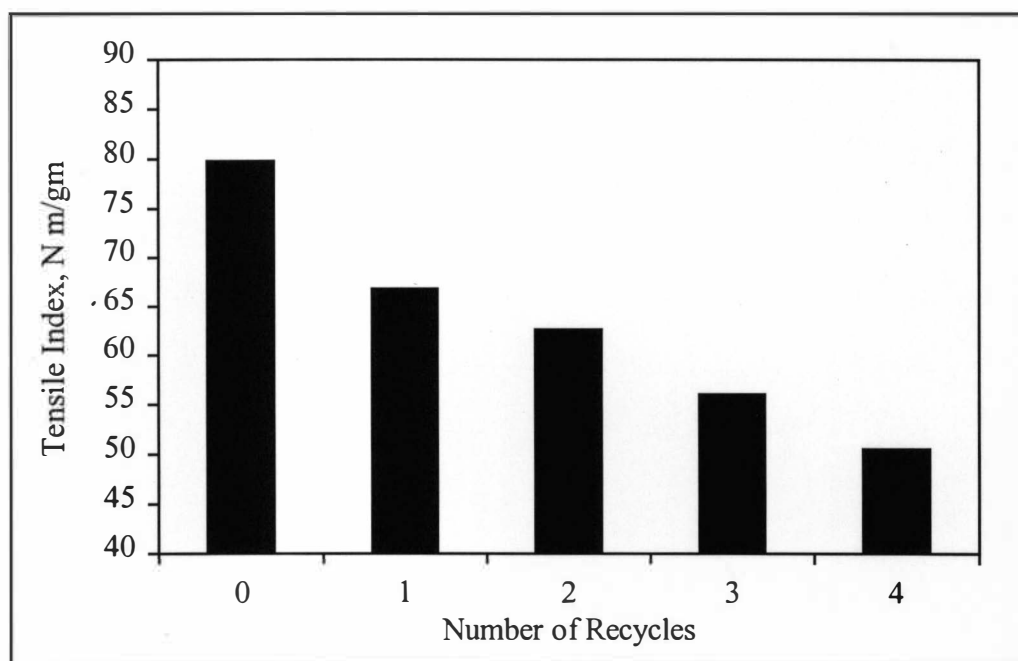


Figure 12. Effect of Recycling on Tensile Strength in Control Experiments.

fiber length with recycling. The loss in bonding and fiber conformability is attributed to hornification of fibers taking place between recycles due to the drying process. This is due to a fact that the fiber cell wall loses water in the initial drying process, and the lamellae of the fiber are brought together. These lamellae are bonded in planes that are so tight that some of these regions will not permit water molecules to



penetrate and swell the fibers when they are re-wetted (9). The whole phenomenon is known as hornification of fibers.

Figure 13 is a comparative plot of tensile index values for both control experiments and the experiments conducted with the addition of borax on virgin fiber. A comparison can be made between the tensile index values during recycling with the use of borax and without using any swelling or strength aid. As it can be seen from the figure, there is a loss in tensile with increase in number of recycles. However, the tensile index achieved in the virgin stage with the addition of 1% borax is more than that achieved in the virgin stage of control experiments. Results of t-test shown in Table 11 indicate that this difference in virgin stage is statistically significant. As there is a strength improvement in the virgin stage, it can be inferred that borax acted as a strength additive.

Between virgin stage and first recycle, tensile index is lowered by 16.3 percent in control experiments and 13.8 percent in borax added experiments. Tensile index in first recycle with borax in virgin stage is 9 percent higher than that obtained in the first recycle of control experiments; this difference is also statistically significant as tested by the "t" statistic. However, in additional recycling stages, there is not much difference between the control and borax added pulps. Hence the addition of borax to the virgin stage, is effective in holding the bonding ability only in the first recycle.

Figure 14 is a comparative graph of tensile index between control experiments and the experiments conducted with borax addition in a particular recycling stage. As

we can see from the plot, the tensile index results are same both in case of control experiments and with borax addition to the secondary fiber. Many of the fibrils and

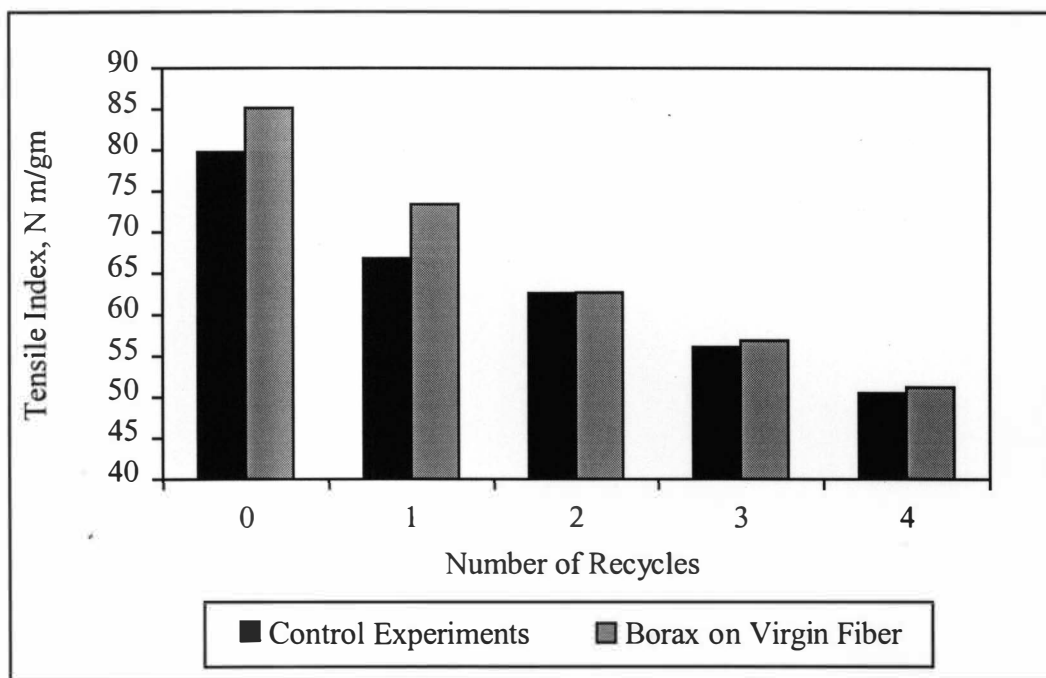


Figure 13. Comparative Plot of Tensile Index Values Between Control Experiments and With Borax Addition to Virgin Stage.

microfibrils might have been already dried down in to the fiber surface and they do not recover even after adding swelling or strength aid. The loss in inter-fiber bonding was more pronounced than the loss in fiber strength as indicated by the fact that recycling has almost no effect on zero-span tensile index but has a pronounced effect on the tensile index.

Table 11

## Two Sided t-test Results for Tensile Strength

Recycle #	Mean Burst Index Values			Comparison of Mean Burst Strength Values			
	Control Experiments	Borax Addition to		Control Vs Borax to Virgin Fiber		Control Vs Borax to Secondary Fiber	
		Secondary Fiber	Virgin Fiber	Pooled Variance	“t”-statistic	Pooled Variance	“t”-statistic
0	79.80	-	85.19	1.12	8.31	-	-
1	66.81	66.68	73.42	1.52	7.13	-0.62	-0.36
2	62.62	63.29	62.72	0.60	0.29	-0.65	1.76
3	56.04	57.45	56.85	0.81	1.73	-0.65	3.75
4	50.56	51.83	51.20	1.38	0.81	-1.35	1.63

\*t distribution value ( $t_{0.025, 10}$ ) = 2.23

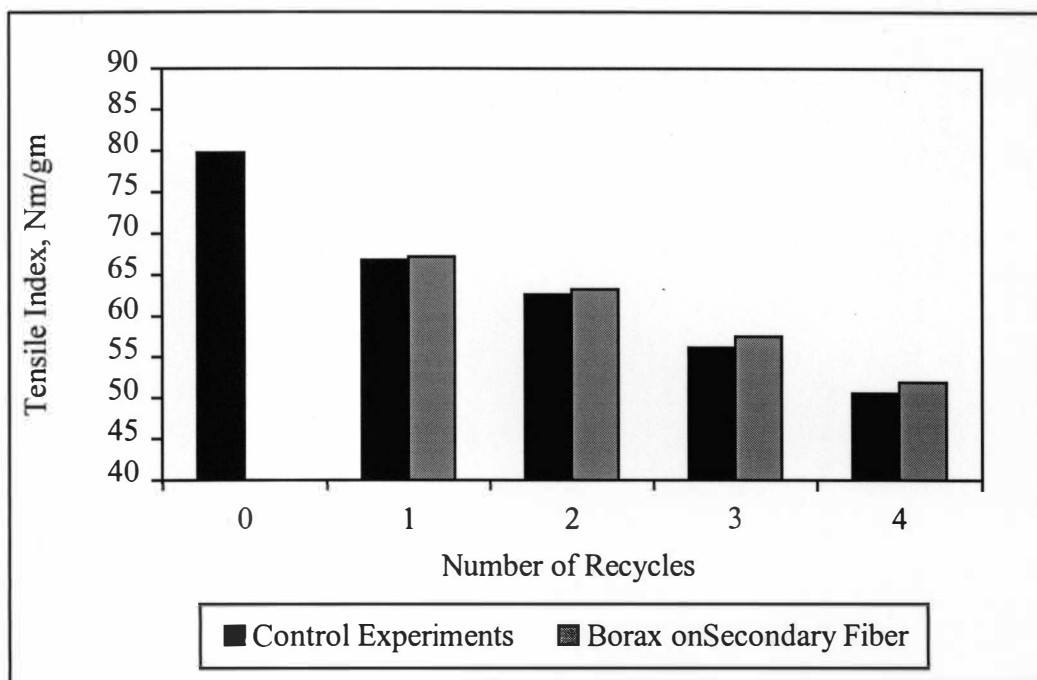


Figure 14. Comparative Plot of Tensile Index Values Between Control Experiments and With Borax Addition to Secondary Fiber.

#### Effect of Recycling on Tear Strength

Average tear index values with the standard deviation are reported in Table 12. There is an increase in tear index values with number of recycles up to third recycle and later in fourth recycle there is a slight drop. Results of ANOVA shown in Table 13 indicate that the change in tear index with number of recycles is significant both in control experiments and with the use of 1 percent borax.

Figure 15 is a comparative plot of tear index of both control experiments and experiments conducted with the borax addition. Tearing strength gives an indication of the force required to delaminate the sheet and pull out or break the fiber (4). Tear

strength exhibits the opposite trend in that tearing strength increased with increase in number of cycles. However, there is an indication of slight drop in tear index after third recycle. Results of t-test shown in Table 14 indicate that there is no significant difference between mean values of control experiment and experiments conducted with borax addition.

Table 12

## Tear Strength Data

Recycle #	Control Experiments	Borax Addition to	
		Recycled Fiber	Virgin Fiber
<u>Average Tear Index , mN m<sup>2</sup>/gm</u>			
0	12.81	-	11.97
1	15.07	15.17	14.91
2	17.63	17.50	17.13
3	20.10	20.00	20.40
4	18.70	19.10	19.40
<u>Standard Deviations</u>			
0	0.41	-	0.55
1	1.03	1.03	1.10
2	0.41	0.51	0.75
3	1.10	0.82	0.55
4	1.00	1.03	0.84

The results of experiments with borax addition to both virgin stock as well as to the recycled furnish are also shown in Figure 15. Similar trends are observed in all cases.

Table 13

## Analysis of Variance for Tear Strength Results

Source	DF	SS	MS	F	P
<u>Control Experiments</u>					
Number of Recycles	4	1071.67	267.92	248.1	0.0001
Error	25	27	1.08		
Total	29	1098.67			
<u>Borax Addition to the Virgin Stock</u>					
Number of Recycles	4	1722.53	430.63	702.12	0.0001
Error	25	15.33	0.613		
Total	29	1737.87			
<u>Borax Addition to the Recycled Furnish</u>					
Number of Recycles	3	734.46	244.82	152.22	0.0001
Error	20	32.17	1.61		
Total	23	766.63			

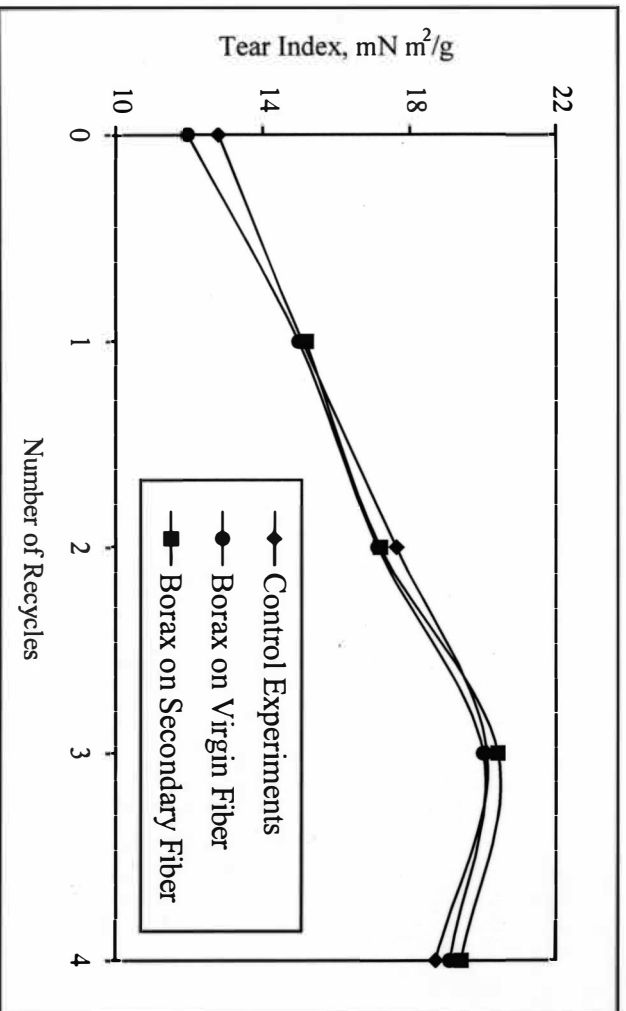


Figure 15. Comparative Plot of Tear Index Values Between Control Experiments and With Borax Addition.

#### Effect of Recycling on Burst Strength

Average burst index values with their standard deviations are shown in Table 15. As it can be seen from the table, the bursting strength decreased rapidly with the number of recycles. Results of ANOVA shown in Table 16 indicate that the drop in tensile strength with number of recycles is significant both in control experiments and with the use of borax. Results of t-test are shown in Table 17 to compare the significant difference between any two means.

The effect of recycling on burst strength can be seen from Figure 16. The first recycle lowered the bursting strength by 4.7 percent, and after four recycles burst

Table 14

## Two Sided t-test Results for Tear Strength

Recycle #	Mean Tear Index Values			Comparison of Mean Tear Index Values			
	Control Experiments	Borax Addition to		Control Vs Borax to Virgin Fiber		Control Vs Borax to Secondary Fiber	
		Secondary Fiber	Virgin Fiber	Pooled Variance	“t”-statistic	Pooled Variance	“t”-statistic
0	12.81	-	11.97	1.13	-1.28	-	-
1	15.07	15.17	14.91	1.07	-0.26	-1.31	0.17
2	17.63	17.50	17.13	0.60	-1.43	-0.46	-0.49
3	20.10	20.00	20.40	0.87	0.60	-0.97	-0.18
4	18.70	19.10	19.40	0.92	1.31	-1.02	0.68

\*t distribution value ( $t_{0.025, 10}$ ) = 2.23



strength approximately decreased by 25 percent. As explained earlier in the tensile strength results, the possible reason for drop in burst strength could be the loss in bonding between fibers due to fiber hornification.

Table 15  
Burst Strength Data

Recycle #	Control Experiments	Borax Addition to	
		Recycled Fiber	Virgin Fiber
<u>Average Burst Index, KPa-m<sup>2</sup>/g</u>			
0	6.24	-	6.59
1	5.95	5.99	6.29
2	5.43	5.85	5.67
3	5.09	5.13	4.98
4	4.66	4.73	4.62
<u>Standard Deviations</u>			
0	0.50	-	0.42
1	1.02	1.30	0.56
2	0.98	0.98	0.69
3	0.88	0.75	0.74
4	1.80	1.20	1.10

Table 16

## Analysis of Variance for Burst Strength Results

Source	DF	SS	MS	F	P
<u>Control Experiments</u>					
Number of Recycles	4	748.26	187.07	149.26	0.0001
Error	25	31.33	1.25		
Total	29	779.59			
<u>Borax Addition to the Virgin Stock</u>					
Number of Recycles	4	779.28	194.82	303.30	0.0001
Error	25	16.06	0.64		
Total	29	795.34			
<u>Borax Addition to the Recycled Furnish</u>					
Number of Recycles	3	449.83	149.94	115.34	0.0001
Error	20	26	1.3		
Total	23	475.83			

A comparative plot of burst index results of control experiments and with addition of borax to the virgin fiber is shown in Figure 17. As indicated in the figure, although there is a decrease of burst index in both cases with increased recycling, the

Table 17

## Two Sided t-test Results for Burst Strength

Recycle #	Mean Burst Index Values		Comparison of Mean Burst Strength Values				
	Control Experiments	Borax Addition to		Control Vs Borax to Virgin Fiber		Control Vs Borax to Secondary Fiber	
		Secondary Fiber	Virgin Fiber	Pooled Variance	“t”-statistic	Pooled Variance	“t”-statistic
0	6.24	-	6.59	0.46	1.31	-	-
1	5.95	5.99	6.29	0.35	1.68	0.82	0.06
2	5.43	5.85	5.67	0.85	0.49	0.85	0.74
3	5.09	5.13	4.98	0.81	-0.23	0.81	0.08
4	4.66	4.73	4.62	1.49	-0.55	1.49	1.43

\*t distribution value ( $t_{0.025, 10}$ ) = 2.23

burst index achieved in the virgin stage with the addition of borax is more compared to the virgin stage of control experiments.

The first recycle lowered the burst strength by 4.6 percent both in control experiments and in experiments with borax. Burst index in first and second recycle with borax in virgin stage is 5.7 percent and 4.4 percent higher respectively than the first and second recycle of control experiments. Thereafter the burst index values

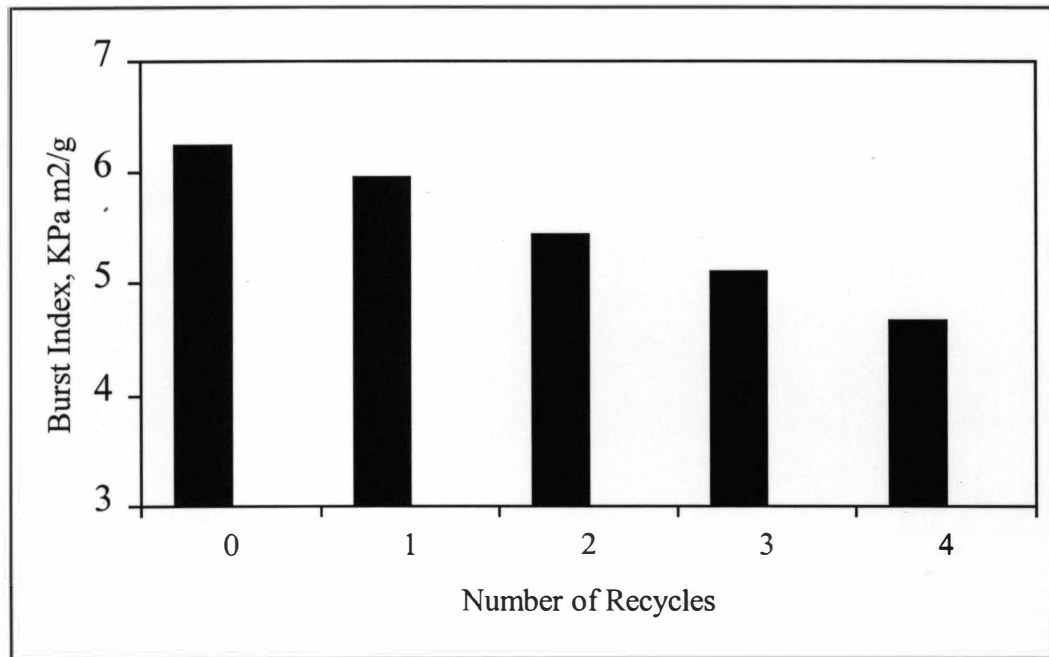


Figure 16. Effect of Recycling on Burst Strength in Control Experiments.

are approximately same both in control experiments and experiments with borax in any given recycle number. Hence addition of borax to the virgin stock and recycling further held the bonding ability of borax up to second recycle. However, these differences are not statistically significant. Figure 18 is a comparative graph of burst

index between control experiments and the experiments conducted with borax addition in a recycling stage. As we can see from the plot the burst index values obtained with the addition of borax to the secondary fiber are almost equal to

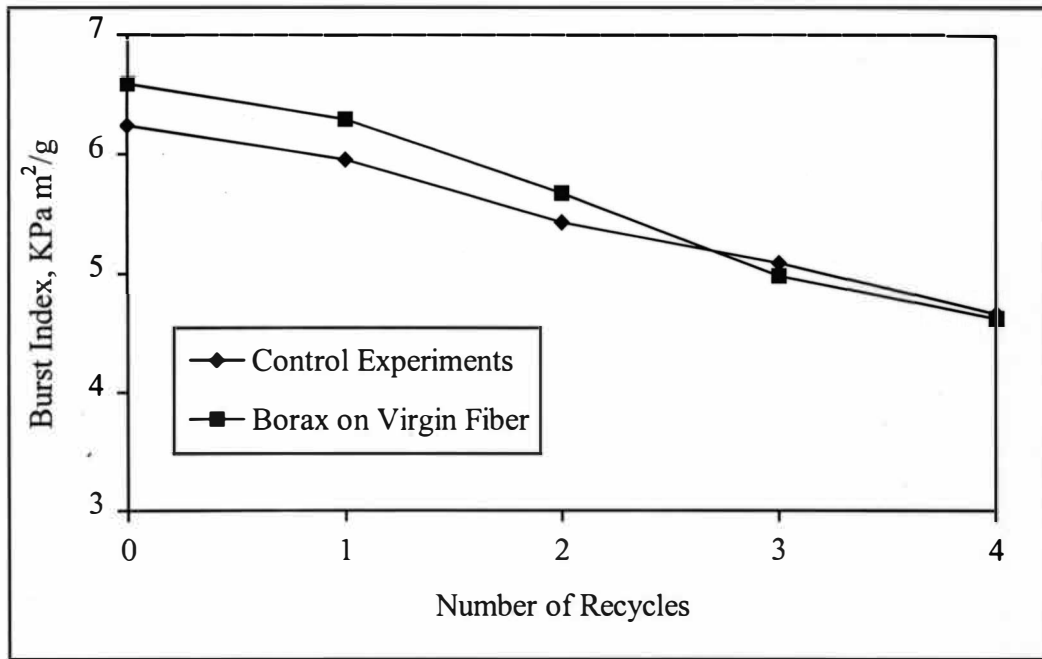


Figure 17. Comparative Plot of Burst Index Values Between Control Experiments and With Borax Addition to Virgin Stage.

that of control experiments except in second recycle. In case of second recycle the burst strength is 7.7% higher than the respective cycle in control experiments. It is difficult to argue the benefits of borax on secondary fiber in improving burst strength because of the inconsistent results as shown in the plot. Results of t-test from Table 17 indicate that these differences are not significant.

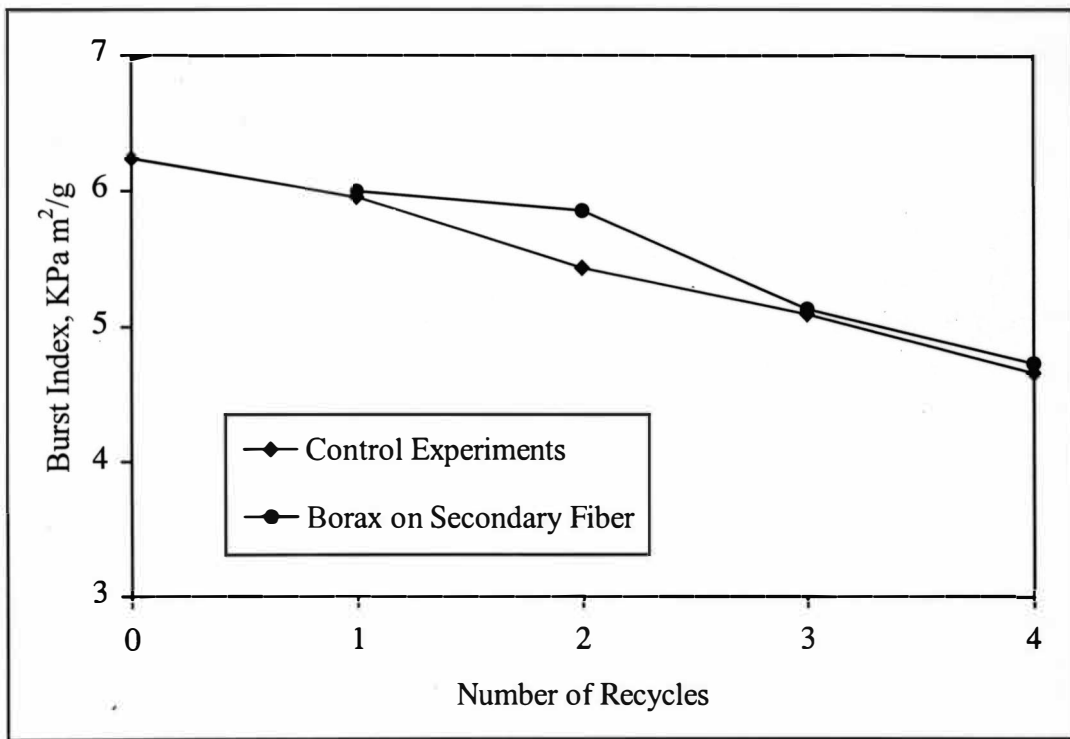


Figure 18. Comparative Plot of Burst Index Values Between Control Experiments and With Borax Addition to Secondary Fiber.

Burst strength is one of the bonding related properties. As the bonding between fibers proved to be dependent on the flexibility of fibers, the drop in burst index with increase in number of recycles can be directly related to the loss in fiber flexibility. As already indicated a slight increase in water absorption is observed with the addition of one-percent borax to the virgin stock in the initial cycle. This may be due the fact that refining of pulp containing borax in the original papermaking helped to open the fibrils more and increased the opportunity for better bonding and development of a network.

## CHAPTER VI

### CONCLUSIONS

Recycling Experiments with borax addition as a swelling agent and strength additive under specific experimental conditions were accomplished in this study. The following conclusions may be drawn from the results of this study.

Water retention values decreased with number of recycles. Addition of 1% borax to the virgin stock has improved the water retention value by 6.6% when compared to the virgin stage of control experiments. Multiple recycling of pulp containing borax in its virgin state also showed a higher water retention value when compared to control experiments up to first recycle and there was no further improvement. Addition of 1% borax to the recycled furnish collected after each recycle of control experiments showed better water retention values than the respective cycles of control experiments. However, addition of borax to the secondary fiber improved the water retention values to a lesser magnitude than its addition to the virgin stock.

In general, recycling has no effect on fiber strength. Multiple recycling did not affect the zero span strength. Addition of 1% borax to the virgin stock or to the recycle stock did not affect the zero span strength very much.

Fiber length changes are small and no major reduction in fiber length is evident. Based on the observations of earlier researchers (3) it was expected that

fiber length would drop since fibers become fragile as a result of recycling, and are dramatically shortened. During this study the fiber length did not change. It should be remembered, however, that the handsheets were not calendered unlike in the case of earlier researchers. Calendering would make the fiber more fragile and lead to increase cutting when refined in further cycles.

Recycling affects negatively the fiber bonding potential. There was a steady decrease in tensile and burst strength with increase in number of recycles. Loss in strength properties should primarily be associated in this case with the bonding potential of fibers, as there was no evidence of major reduction in fiber length or intrinsic fiber strength. However, tear strength exhibited an increasing trend up to third recycle and then a slight drop.

When 1% borax is added to the virgin stock and recycled further, tensile index achieved in the virgin stock is 6.3% higher than the strength achieved in the virgin state of the control experiments. When this pulp was recycled further, the increased bonding ability is held up to first recycle. When borax is added to the recycled furnish during sheetmaking, there was little or no improvement in strength.

Burst index decreased with number of recycles. The burst index achieved in the virgin stage with the addition of borax is 5.3% higher than the burst index achieved in the virgin state of the control experiments. Burst index in first and second recycle with borax in virgin stage is 5.7% and 4.4% higher respectively than the first and second recycle of control experiments. Addition of borax to the secondary fiber did not have any effect on the burst index.



It can be concluded from this work, that if the chemical pulp is subjected to multiple recycling, all the bonding related strength properties go down. Also the swelling ability of pulp suffer with recycling. The primary cause for this could be changes in fiber morphology due to hornification.

There is no evidence to state whether this loss in bonding potential of fibers is irreversible. Although there was no improvement in tensile index with addition of borax on secondary fiber, there was a slight improvement in burst index. Also there was a slight improvement of water retention values with 1% borax addition to the recycled pulp taken from control experiments.

The following three overall conclusions stand out from this research work:

1. Borax at 1% acts as a strength additive in virgin chemical pulps.
2. The effect of borax as a strength additive wears off pretty quickly, after first recycle.
3. Addition of borax to recycled (already hornified) fibers does not have any significant effect on strength properties.

The above results are limited to the experimental conditions followed in this project, viz., (a) no recycling of white water during the sheet making process and (b) interstage refining of fibers to the same freeness level.

## CHAPTER VII

### RECOMMENDATIONS

Similar experiments can be conducted to evaluate the effect of different levels of borax on strength properties in recycling. For these experiments, secondary fiber generated from each recycle can be treated with different amounts of borax. Then a statistical analysis can be conducted to evaluate the effect of recycle number and percentage of borax used on strength properties.

In these experiments, the fibers were refined to a constant freeness in every recycling stage. In stead, it will be better to develop a beater curve to find out the maximum potential.

## LITERATURE CITED

1. Bobalek, J. F., Chathurvedi, M. "The effects of recycling on the physical properties of handsheets with respect to specific wood species," *Tappi J.* 72 (6): 123-125 (1989).
2. Jonathan, P., "The effects of recycling on the strength properties of paper," *Paper Technology* 42 (8): 33 (1994).
3. Howard, R. C. and Bichard, W., "The basic effects of recycling on pulp properties," *Journal of Pulp and Paper Science* 18 (4): 120 (1992).
4. Bouchard, J. and Douek, M., "The effects of recycling the chemical properties of pulps," *Journal of Pulp and Paper Science* 18 (5): 131 (1992).
5. Loreen, D. F., "Effects of recycling on strength properties," *Paper Technology* 33(10): 14 (1992).
6. McKee, R., "Effect of repulping on sheet properties and fiber characteristics," *Paper Trade J.* 155 (21): 34 (1971).
7. Peel, L. R., "Technical break through in wet end additives," *Paper Technology* 28(12): 44 (1989).
8. Nanko, H., and Ohsawa, J. "Mechanisms of fiber bond formation," *Proceedings of 1989 Fundamental Research Symposium*, MECHANICAL ENGINEERING PUBLICATIONS LIMITED, Cambridge, p.783.
9. Lavins, G. V. and Scallan, A.M. "The influence of drying and beating on the swelling of fines," *Journal of Pulp and Paper Science* 22 (5): 178 (1996).
10. Oye, R., Okayama, T. and Yamazaki, Y., "Changes of pulp fiber cell wall by recycling," *Research Forum on Recycling*, Toronto, p. 191-195 (1996).
11. Lundberg, R., and de Ruvo, A., "The influence of drying conditions on the recovery of swelling and strength of recycled fibers," *Svensk Papperstidning* (81) 11: 355 (1978).
12. Scallan, A.M. and Tigerstrom, A.C. "Swelling and elasticity of the cell walls of pulp fibers," *Journal of Pulp and Paper Science* 18 (5): 188 (1992).

13. Minor, J. L. and Atalla, R.H. "Improving the interfiber bonding of recycled fiber," *Journal of Pulp and Paper Science* 19 (4): 82 (1993).
14. Carlsson, G., "Hornification of cellulosic fiber during wet pressing," *Svensk Papperstidning* 87 (15): 119 (1984).
15. Chatterji, A., Roy, D.N., and Whiting, P., "Effect of recycling on strength, optical and surface properties of handsheets," *Proceedings of 1992 CPPA Annual Meeting*, CPPA PRESS, Montreal, p. A227.
16. Htun, M., and de Ruvo, A., "The implications of the fines fraction on the properties of bleached kraft sheet," *Svensk Papperstidning* 87 (15): 119 (1984).
17. Stone, J.E., and Scallan, A.M., "Influence of beating on the cell wall swelling and internal fibrillation," *Svensk Papperstidning* 71 (19): 694-786 (1984).
18. Yamagishi, Y., "Change of pulp fiber cell wall by recycling," *Tappi J.*, 72 (6): 123 (1989).
19. Nissán, A.H., "Fiber-water interactions in papermaking," Vol. II, London, U. K. p. 875-876 (1978).
20. Luminainen, J., "Refining a key to upgrading the papermaking potential of recycled fiber," *Paper Technology* 18 (9): 42 (1994).
21. Howarth, P., "Fiber-water interactions in papermaking," *Trans. BPBIF Symposium.*, Vol. II, London, U. K. p.823-831 (1975).
22. Klungness, J. H., "Secondary fiber research at the forest products laboratory," *Tappi J.*, 58 (10): 129 (1975).
23. Ferguson, L. D., "Multiple recycling the impact of chemical addition on optical and physical properties," *Proceedings of 1991 CPPA Recycling Forum*, CPPA PRESS, Montreal, p.57.
24. Okayama, T., Ochi, T., and Oye, R., "Alkali soaking ups quality of OCC used in boxboard furnish," *Japan Tappi* 41 (6): 515-512 (1987).
25. Scallan, A. M., "The effect of acidic groups on the swelling of pulps: a review," *Tappi J.*, 66 (11): 73 (1983).
26. Vorka., "Additives for stock preparation in papermaking," *Ger.Pat.*, Patent No. 2303751, (1984).

27. McBroom, R., "Borate Chemistry in aqueous solution," *Research Symposium on Borate Chemistry*, MUSKEGON, Aug (1997).
28. Douglas, C.M., "Design and Analysis of Experiments," *Third Edition*, John Wiley & Sons, New York, 1991, P.28-38.

## BIBLIOGRAPHY

- Bobalek, J. F., Chaturvedi, M. "The effects of recycling on the physical properties of handsheets with respect to specific wood species," *Tappi J.* 72 (6): 123-125 (1989).
- Bouchard, J. and Douek, M., "The effects of recycling the chemical properties of pulps," *Journal of Pulp and Paper Science* 18 (5): 131 (1992).
- Cildir, H., Howarth, P. "The effect of reuse on paper strength," *Paper Technology*, 13 (5) : 333-335 (Oct 1972).
- Carlsson, G., "Hornification of cellulosic fiber during wet pressing," *Svensk Papperstidning* 87 (15): 119 (1984).
- Chatterji, A., Roy, D.N., and Whiting, P., "Effect of recycling on strength, optical and surface properties of handsheets," *Proceedings of 1992 CPPA Annual Meeting*, CPPA PRESS, Montreal, p. A227.
- Douglas, C.M., "Design and Analysis of Experiments," *Third Edition*, John Wiley & Sons, New York, 1991, P.28-38.
- Ferguson, L. D., "Multiple recycling the impact of chemical addition on optical and physical properties," *Proceedings of 1991 CPPA Recycling Forum*, CPPA Press, Montreal, p.57.
- Howard, R. C. and Bichard, W., "The basic effects of recycling on pulp properties," *Journal of Pulp and Paper Science* 18 (4): 120 (1992).
- Howarth, P., "Fiber-water interactions in papermaking," *Trans. BPBIF Symposium.*, Vol. II, London, U. K. p.823-831 (1975).
- Htun, M., and de Ruvo, A., "The implications of the fines fraction on the properties of bleached kraft sheet," *Svensk Papperstidning* 87 (15): 119 (1984).
- Jonathan, P., "The effects of recycling on the strength properties of paper," *Paper Technology* 42 (8): 33 (1994).
- Klungness, J. H., "Secondary fiber research at the forest products laboratory," *Tappi J.*, 58 (10): 129 (1975).

- Lavins, G. V. and Scallan, A.M. "The influence of drying and beating on the swelling of fines," *Journal of Pulp and Paper Science* 22 (5): 178 (1996).
- Loreen, D. F., "Effects of recycling on strength properties," *Paper Technology* 33(10): 14 (1992).
- Luminainen, J., "Refining a key to upgrading the papermaking potential of recycled fiber," *Paper Technology* 18 (9): 42 (1994).
- Lundberg, R., and de Ruvo, A., "The influence of drying conditions on the recovery of swelling and strength of recycled fibers," *Svensk Papperstidning* (81) 11: 355 (1978).
- McBroom, R., "Borate Chemistry in aqueous solution," *Research Symposium on Borate Chemistry*, Muskegon, Aug (1997).
- McKee, R., "Effect of repulping on sheet properties and fiber characteristics," *Paper Trade J.* 155 (21): 34 (1971).
- Minor, J. L. and Atalla, R.H. "Improving the interfiber bonding of recycled fiber," *Journal of Pulp and Paper Science* 19 (4): 82 (1993).
- Nanko, H., and Ohsawa, J. "Mechanisms of fiber bond formation," *Proceedings of 1989 Fundamental Research Symposium*, Mechanical Engineering Publications Limited, Cambridge, p.783.
- Nissan, A.H., "Fiber-water interactions in papermaking," Vol. II, London, U. K. p. 875-876 (1978).
- Okayama, T., Ochi, T., and Oye, R., "Alkali soaking ups quality of OCC used in boxboard furnish," *Japan Tappi* 41 (6): 515-512 (1987).
- Oye, R., Okayama, T. and Yamazaki, Y., "Changes of pulp fiber cell wall by recycling," *Research Forum on Recycling*, Toronto, p. 191-195 (1996).
- Peel, L. R., "Technical break through in wet end additives," *Paper Technology* 28(12): 44 (1989).
- Scallan, A. M., "The effect of acidic groups on the swelling of pulps: a review," *Tappi J.*, 66 (11): 73 (1983).
- Scallan, A.M., and Tigerstrom, A.C. "Swelling and elasticity of the cell walls of pulp fibers," *Journal of Pulp and Paper Science* 18 (5): 188 (1992).

Stone, J.E., and Scallan, A.M., "Influence of beating on the cell wall swelling and internal fibrillation," *Svensk Papperstidning* 71 (19): 694-786 (1984).

Vorka., "Additives for stock preparation in papermaking," *Ger.Pat.*, Patent No. 2303751 (1984).

Yamagishi, Y., "Change of pulp fiber cell wall by recycling," *Tappi J.*, 72 (6): 123 (1989).