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The Role of Cationic Polymers in Water Removal on a Paper Machine

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THE ROLE OF CATIONIC POLYMERS IN WATER REMOVAL ON A PAPER MACHINE

by

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Abstract

Cationic polymers have often been termed as both retention and/or drainage aids. A distinction was made between these two terms. Essentially drainage aids should be viewed as dewatering aids and retention aids should be viewed as those polymers that give superior retention. These effects may be interrelated, therefore the dominant characteristic should be used to classify these polymers. There have been many claimed benefits associated with the use of these cationic polymers in stock furnishes. The author felt that claimed dewatering benefits were mostly a matter of conjecture and contradictions existed. Therefore a pilot paper machine study was designed to primarily analyze any dewatering effects and to isolate these effects.

Four trials were run with two controls (an initial and final control) ran during each trial. Moisture samples were taken so that various sections of the paper machine could be isolated. The sections isolated were the wet end (headbox to couch roll), the press section, the first section of dryers and the final section of dryers. The results indicated that the cationic polymers tested (guar gum, polyacrylamide) did not significantly improve dewatering under the conditions tested. The physical properties of the sheet were unchanged, with the exception of a slight tensile strength increase.

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Introduction

The use of polymeric bonding agents or drainage and retention aids at the wet end of a paper machine have shown signs of a growing acceptance in the paper industry. This paper will be limited to a discussion of the various types of drainage aids. The characteristics of these polymers that have led to increase usage, along with the drawbacks that have limited their use, will also be discussed. The term "drainage aid" has been widely used in the industry, but not well defined. Klass and Urick (17) defined a drainage aid as a polyelectrolyte which improves water removal. This improvement may take place at various points during the papermaking process. Thus dewatering aids may be a more appropriate term for these substances.

Drainage aids have been used for a number of reasons that can be related to improved (or increase rate of) water removal. Klass and Urick (17) claimed a papermaker could use this occurrence to his advantage in a number of ways: (1) the speed of a machine can be increased, therefore production will increase and the cost per ton of paper produced will decrease; (2) steam consumption can be cut down, thereby save on energy costs; (3) decrease headbox consistency, this will enable one to improve formation; (4) strength characteristics of a sheet can be improved with increased refining, while the drainage aid can compensate for expected lower drainage rates.

The difference between drainage and retention aids has not been well understood. This is due mostly to the closeness with which drainage and retention are related. Both of these processes rely on flocculation to some degree to achieve maximum results. The same polymer can be used as both a retention and a drainage aid. The optimum point for retention occurs before the optimum point of drainage is reached. Foster (21) stated that synthetic polyelectrolytes for retention are usually added in the range of 0.01% to 0.05%, based on dry paper solids and dry polymer solids. When used as drainage aids, synthetic polyelectrolytes are used at levels ranging from approximately 0.03% to about 0.20%. Entin (12) found that optimum retention occurred at a dosage of 0.02%, while the optimum dosage for dewatering occurred at 0.05%. This work involved a non-ionic polymer, polyethylene oxide. Otrhalek and Gomes (29) claimed that a high molecular weight polymer (MW≥100,000) was most efficient for retention. They also claimed that medium range molecular weight polymers (MW 50,000-100,000) were desirable as drainage aids since the tendency to overflocculate was minimized.

Mechanisms of Dewatering

From the time stock leaves the slice until the resulting paper is on the reel, controlled dewatering is taking place. An understanding of how drainage aids have been hypothesized to work necessitates a complete understanding of the dewater-

ing process. Dewatering can be broken up into three basic parts; drainage, pressing, and drying, which will be discussed below.

Drainage

Neogi (3) describes drainage and has produced empirical formulas to describe drainage. When the stock comes out of the headbox, only the wire resists the flow of water being removed. As fibers deposit and the fiber mat grows, the resistance to flow increases. To maintain drainage during the forming process one needs application of a pressure gradient. The time and pressure available determines, together with the drainage properties of the pulp, how much of a given sheet can be formed under a given set of conditions. Due to the mat compression and its effect on retention and the drainage cycle, together with the complexity of the fiber systems, the application of basic knowledge to these practical problems have been very limited. The following formula illustrates drainage capacity:

$$t = G/S \times (\Delta Pm)^{-n} W^{a} u$$

where
t = time needed to a fiber mat of weight W
G = drainage constant, characteristic of pulp
S = consistency of suspension
Pm = pressure drop across the mat
n = constant characterizing the compressibility of the mat
a = constant characteristic of type of pulp + beating

The various mechanisms by which drainage is obtained on a fourdrinier wire have been classified by Kennedy and Wrist

(23). They are: (1) hydrostatic pressure resulting from the weight of the stock on the wire; (2) inertial pressure resulting from angular impingement of the slice on the wire; (3) hydrodynamic vacuum forces resulting from the motion of the wire over the table rolls or foils; (4) externally generated vacuum forces; (5) pressure from rolls, such as a dandy roll or couchpress. Cylinder machines use the pressure differential caused by the respective levels of the stock inside and outside the mold, and this can be varied by raising or lowering the level of water in the molds. The following factors are likely to play a part in the resistance to drainage (8): a) temperature of the stock; b) presence of surfactants; c) air in the stock; d) degree of refining of the stock; e) fiber surface chemistry; and f) flocculation by chemicals.

The Darcey equation (18) gives a value for K, the permeability coefficient. $K = \frac{QrL}{Ap}$ Where: Q = volumetric flow rate, r = viscosity of permeating liquid, L = length of pad, p = pressure drop across a pad, A = cross-section area of pad. This shows that by reducing viscosity one will increase the flow rate, other factors remaining constant. Viscosity has often been reduced by raising the temperature. This method was often used in secondary fiber and glassine mills, where stocks have tended to drain very slowly mainly because of the presence of fines, fibrous debris and colloidal material. Surfactants have been found useful, but there was a

tendency for such materials to affect sizing, cause severe foam problems, and possibly produce adverse effects on strength properties by interfering with fiber-fiber bonding. Brecht and Kirchner (24) have reported that small amounts of air, as little as two percent, have caused significant decreases in drainage rates.

Urick and Fisher (8) claimed that the wetness of the stock and fiber surface chemistry were closely linked to flocculation by chemicals. The wetness of stock was suggested to be modified chemically by altering the surface chemistry of the fiber. This modification was believed to be carried out effectively by the use of both natural and synthetic chemicals.

Foster (21) hypothesized that drainage aids could alter the structure of the web in three primary ways. First they could flocculate or agglomerate the small particulate matter to the large whole fibers. Second drainage aids could redistribute the small particulate matter within the web structure. Without the use of flocculant, fines and fillers tended to be retained in the sheet via a filtration mechanism, whereby they tended to plug the pores in the structure and decrease permeability. On the other hand, when a flocculant was used to agglomerate the fines to the larger fibers, the fines were not free to move with the water stream. If they were stopped by a pore restriction, they would reduce the wet and dry permeability of the web. This concept of fines redis-

tribution was reinforced by the observation that the dry porosity of handsheets of many commercial papers was increased by the use of drainage aids. This indicated that the fines are distributed differently with a drainage aid.

The third way in which drainage aids could alter the structure of the web was by reducing or collapsing the hydration shell on the fibers and fines. The cause of this was believed to be flocculation of the surface fibrillation, developed on the fibers and larger fines, during refining of the stock. Collapse or reduction of the swollen hemicellulose on the surface of fibers and fines, were also ways in which the polyelectrolytes could have reduced the hydration shell on the fibers and fines. Any of these could increase the wet permeability of the web (21).

Penniman observed (14,5) that addition of cationic chemicals to pulp slurries have a pronounced effect on zeta potential until a -8mV to 0mV level was reached. Depending on the system, zeta potential stabilized in this range and formed a plateau upon further addition. Then after cationic demand of fibers was satisfied zeta potential rose steeply and became positive. Refining had the effect of exposing more functional groups on the surface of the fibers, increasing demand and length of the plateau. Maximum drainage was found to usually occur at the end of the cationic demand plateau. Penniman also suggested that maximum physical strength properties occurred at the same point, although no evidence was cited to

back up this point.

Penniman (5) and Dobbins (32) hypothesized that cationic chemicals added to a furnish had a progressive nature of flocculation. Drainage aids first reacted with soluble anionics, including hemicellulose, ligins and humic acids. Anionic chemicals circulated in the white water and built up in closed or partially closed white water systems. These materials could be present in large quantities and comprise "anionic trash" that could effectively inhibit conventional approaches to maximizing retention, drainage, and physical properties.

The next most reactive components according to Dobbins (32) were fillers and fines, continued addition of cationic chemicals caused them to be flocculated. Maximum retention with minimum chemical usage occurred at some point in this region. As chemical addition progressed increasingly large fibers were flocculated, and an interlaced structure was formed by cationic chemical bridging between fibers. The creation of the structure was complete at the end of the plateau, at which point all of the anionic groups on the fiber have been neutralized and bridged by flocculation. The resulting interlaced structure accounted for superior drainage and physical properties in contrast to the packing, plugging and lack of intrinsic structure which would have occurred on the wire in the absence of controlled flocculation. Further addition of cationic resin was counterproductive. An excess created a positive zeta potential, which usually deflocculated

and redispersed the system.

A mechanism of action of cationic polyelectrolytes was proposed by Lapin (19). It took into consideration the pulp consistency, the nature of the flocculant, the spontaneous fiber flocculation in the absence of the polyelectrolyte. According to this mechanism, polymer reacted not with individual fibers, but with fiber flocs and its action was both electrostatic and dehydrating. Milichovsky and Lebr (28) developed an equation describing the stock suspension dewatering process as a function of cake resistance coefficient, compressibility coefficient, and uniformity coefficient. It was found that the use of polyelectrolytes tended to reduce the cake resistance, but this benefit was to some degree offset by the higher compressibility of the cake with addition of polymer.

Kufferath (3) stated that the open area of a wire was not responsible for drainage, because a mathematical function between open area and drainage did not exist. Instead the drainage resistance of the wire was determined only by the wetted surface and internal free volumes of the wire body. The interaction between wire and fiber filtration mat decided the real dewatering of a fourdrinier system. Kufferath also stated that this interaction could not be correlated by using one coefficient, but the frame and the three dimensional topography of wire must be taken into consideration. To get auxiliary data for practical purposes, it was necessary to

determine in simulated experiments the influences of the various wire textures, the fines and the hydraulic system in combination with different classes of pulp.

In summation the mechanism by which drainage aids improved drainage was believed to be primarily fines redistribution as a result of flocculation and, to some extent, hydration-shell collapse, resulting in an increased wet-web permeability (21). The optimum conditions for flocculation, retention, and dewatering (three main effects of drainage aids) do not occur at the same time and may differ for various types and amounts of additives.

Pressing

The effect of drainage aids on the efficiency of the pressing section has not been well documented. Therefore a review of the fundamentals of sheet water removal in the press section would be helpful. Special attention is paid to mechanisms that could be affected by drainage aids.

Wahlstrom (25) divided the wet press nip into four phases based on the interaction of hydraulic and mechanical pressures. This is shown in Figure 1 on page 12. Phase 1 started when the felt and paper contacted the press rolls and the pressure began to rise. It continued to the point where the paper web became saturated. Phase 2 began when the paper web became saturated and continued to the point of maximum pressure (at or near midnip of the press). Phase 3 extended from midnip to

the point of maximum paper dryness (point of maximum mechanical pressure). Phase 4 was a rewetting phase where both paper web and the felt were expanding and water moved across the interface from felt back into sheet.

Bleisner (2) stated the factors which influenced wet pressing. They were: press load, drainage forces (hydraulic pressure difference), sheet quality factors, paper compression properties, the flow resistance of paper, and time of pressing. Felt factors affecting water removal included: compression properties, flow resistance, and compaction. Sheet quality factors influenced water removal in the press in unknown ways. Such things as sheet formation, fines retention and distribution, furnish components, etc. could all play a role in the response of the sheet to wet pressing. Unfortunately, even though this is a topic of interest to the practical papermaker, it is an area where little research results have been published. In addition, applying research results and pressing theory to specific individual situations still remains a difficult task. Paper compression properties is another area where we have little knowledge under conditions of importance to commercial wet pressing.

Flow resistance of paper represented the major resistance to sheet water removal in many commercial conditions (2). Here the primary determinants were sheet basis weight and degree of refining indicated by filtration resistance analysis. Other components of the furnish also played a part in this

mechanism. Busker (26) in a carefully conducted study, also concluded that the "one major controlling variable in wet pressing today, assuming the use of transverse flow presses and other modern equipment, is the resistance of water flow out of the paper itself." Since freeness goes up with the use of drainage aids, it was possible that improved pressing efficiency could result from decreased flow resistance of paper. It was also hypothesized (22) that the reduction of the hydration shell by a drainage aid could increase wet web permeability and allow one to increase the pressure applied to the presses, therefore increasing dewatering.

Drying

A review of some fundamental concepts of the drying section will be helpful in understanding how drainage aids could effect drying efficiency. During the drying of a sheet of paper certain intricate processes occur that cause the moisture in the sheet to move from the interior of the sheet to the surface where it is vaporized.

A general review of drying was given by Pearson (27). There were four definite stages to a drying sequence which are shown in Figure 2. In the first stage, from A to B, the paper surface was covered with water and the rate of evaporation was constant. From B to C the evaporation dropped at a rate determined by the various factors controlling the flow of water to the surface. At C there was a transition point

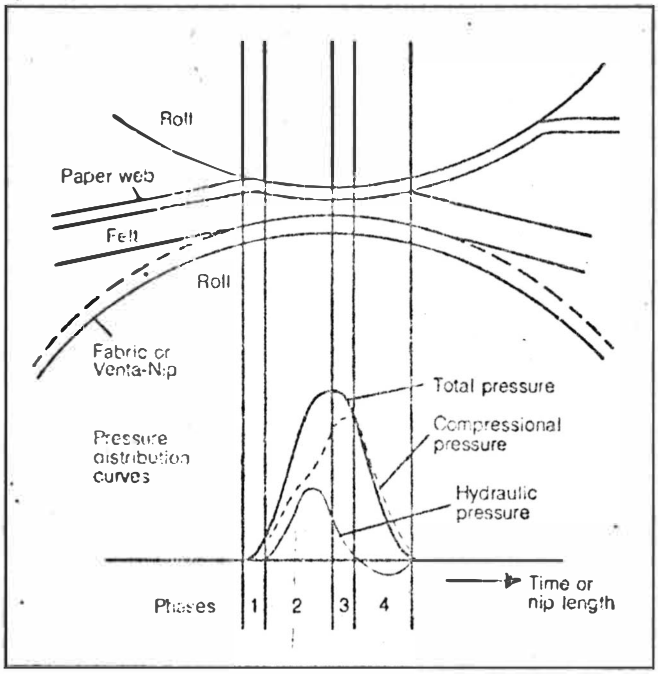
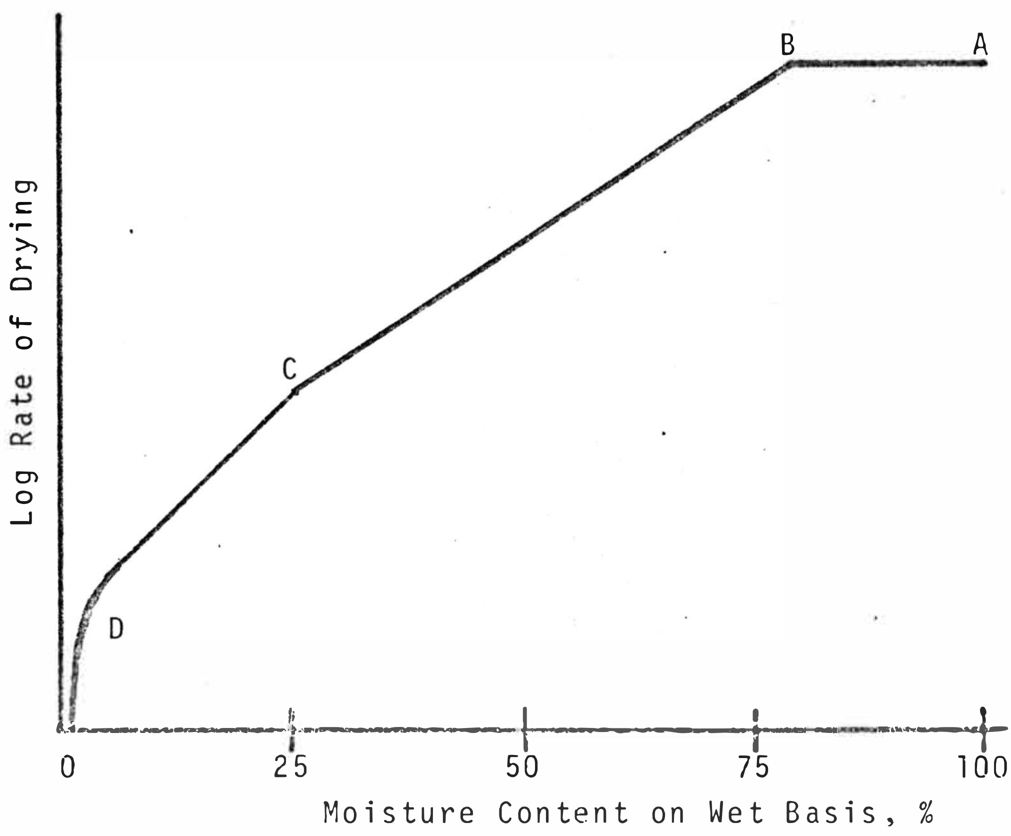


Figure 1. **Pressure profiles** in a press nip—Wahlstrom's theory.

Figure 2: Typical Drying Curve for Paper

A-B: Constant Rate of Drying
B: Surface Film Broken
C: Absorbed Water Evaporating
D: Bound Water Evaporating



indicating that absorbed and capillary water began to evaporate. Since this water was acted upon by capillary forces, the rate of evaporation would drop further. At D, only bound water remained and this water was even more difficult to remove.

The bound water was attached to the cellulose and the hemicellulose molecules or absorbed on them as a monomolecular layer. The bound water may amount to nearly one percent. Subsequent layers of water molecules made up the absorbed water which was characterized by a higher density, a lower vapor pressure, and a higher specific heat than free water. Water in small capillaries would also have a lower net vapor pressure. To have absorbed water removed from a sheet of paper, the heat of desorption has to be added to the heat of vaporization of free water.

An improvement in reel dryness observed with the use of drainage aids was attributed to the more efficient use of the dryer section by Penniman (1). Penniman hypothesized that this occurrence may have been caused by one or more of the following: 1) improved formation and therefore improved smoothness provided better heat transfer and water removal; 2) the intimacy of contact of cationic guar with the cellulose cell wall facilitated heat transfer and water removal; 3) physical displacement of the water bound to fiber surfaces enabled it to be volatilized with less heat. Penniman also stated that water removal differences of 10-20% are not un-

usual. It had also been hypothesized (16, 20) that the resultant increase in sheet porosity would probably allow steam to escape from the sheet more rapidly in the dryer.

Harvey et al (10) stated that one must be totally cognizant of the overall effect, as the reduced water in the sheet does not necessarily improve drying efficiency. The dryer sheet going to the press section may be tighter making it more difficult to remove moisture, consequently requiring more energy for drying. An explanation of the term tighter was not given.

The mechanisms of dewatering has been affected by drainage aids, but the relative importance of improved steam release, better water removal at the presses and increased water removal on the wire were not known as very little work has been published in this area. The relative importance of each of these factors will probably vary widely with different furnishes, machines, and polymer types.

Drainage Aid Performance

Exactly how drainage aids work and where on a paper machine dewatering takes place has been mostly a matter of conjecture. The purpose of this section is to summarize findings and hypotheses that have been based on reported data and figures. Also a review of pilot machine and laboratory studies will be discussed.

A lower moisture content going into the dryer section was one reason given for the use of drainage aids. There were two

such cases that were actually recorded with the use of mois-meters. Both cases involved cylinder board operations. An example illustrated by Atkinson and Malcolm (13) indicated an improvement of 17 lb/1,000 sq. ft. down from the normal wet weight of 172 lb/1,000 sq. ft. The moisure was measured with a beta gauge type meter. Falcione (9) found an improvement of 38.5 lbs/min in a 100 tpd operation. The moisure was read by a portable moisture meter. The drainage aid used in this trial was a high molecular weight polyampholyte. The moisture at the reel remained constant during these improvements. In both of these cases, the increased water removal was calculated directly into steam conservation and fuel saving without actually monitoring the dryer section for this improvement.

A laboratory study related to this was carried out by Ellis and Foster (20). A series of handsheets were made on a Noble and Wood sheet machine with gradually increasing pressure on the press roll. The sheets were then passed through an accelerated dryer which gave a constant, but not complete, amount of drying energy to each sheet. This was repeated with sheets containing a drainage aid. The results are shown in Figure 3 on page 16. This particular drainage aid increased the solids content out of the press section by about three percent and increased the solids out of the drying section by about seven percent. This showed that a decrease in sheet moisture out of the press section gave a magnified

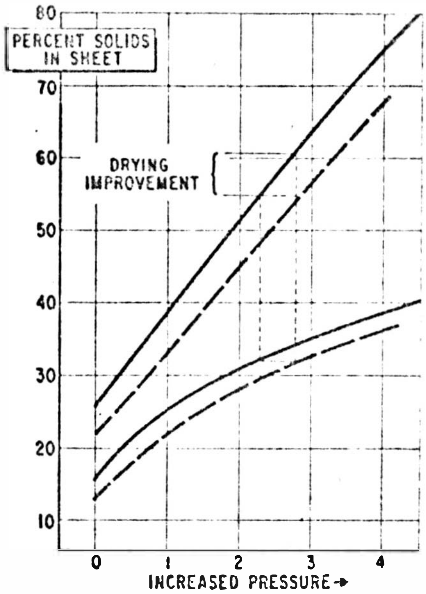


FIGURE 3. Improvement in water removal in press (lower curves) and dryer with drainage aids (solid curves) for laboratory sheets.

Figure 4 - (8)

Equilibrium Moisture Contents of Handsheets

Additive[a]	*Sheet weight, g (avg. of 6)*	*Moisture, %*
None	49.4	89.9
Cationic PAM	49.5	89.9
PEI	49.6	89.9

[a] All additives added at the rate of 0.1%.

Figure 5 - (8)

Equilibrium Moisture Contents Using Laboratory Press

Additive[a]	*Sheet weight, g*		*Moisture, %*	
	Before pressing	*After pressing*	*Before pressing*	*After pressing*
None	27.7	10.4	82.0	51.9
	28.0	10.8	82.2	53.8
	28.0	11.0	82.5	54.5
PEI	30.4	10.7	83.6	54.3
	25.9	10.4	80.7	51.9
	29.6	10.6	83.1	52.8
Cationic PAM	31.6	11.2	84.7	55.3
	30.5	10.5	83.6	52.4

[a] All additives added at the rate of 0.1%.

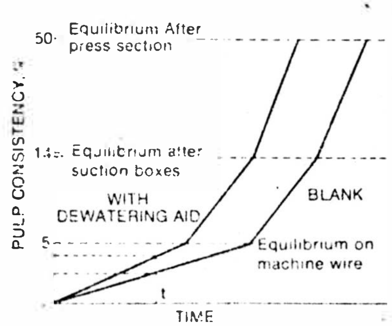
Figure 6 - (8)

Equilibrium Moisture Contents After Centrifuging

Additive[a]	*Dry weight attained, g*	*Average moisture, %*
None	37.1	62.4
	38.2	62.4
Cationic PAM	37.1	62.8
	37.3	62.8
	38.7	62.4
PEI	37.4	62.4

[a] All additives added at the rate of 0.1%.

Figure 7 - (8)



Effect of dewatering aids on time to reach drainage equilibrium.

effect in the dryer. It also showed that two sheets at the same moisture content, one with and one without the drainage aid, gave similar moisture contents after the dryer section. No experimental data or calculations were shown to strengthen these conclusions.

Initial laboratory work was carried out by Urick and Fisher (8) to determine the equilibrium moisture contents of a standard pulp under static conditions, corresponding to areas along a paper machine. The work was carried out using a corrugated/news "waste furnish." After a sheet had formed, it was allowed to drain until no water visibly drained from the sheet, this represented drainage on a machine. The sheet was then removed and immediately weighed. The results show that the equilibrium moisture content achieved on the sheet is the same with or without a dewatering aid and is shown in Figure 4 on page 16. A Beny nip press was used to duplicate a pressing section. The nip pressure was set at 430 psi and the speed at 3 ft/min. Again the results indicated no difference within experimental error. The results are shown in Figure 5 on page 16.

Imbibed water was defined by Urick and Fisher (8) as the water remaining after centrifuging and cannot be removed mechanically. This imbibed water required heat to remove it and therefore was removed in the drying section of the paper machine. Pulps with and without a drainage aid were centrifuged for five minutes. The results are shown in Figure 6 on

page 16.

Urick and Fisher (8) concluded that under these conditions, time was allowed for equilibrium moisture contents to be attained. However, on a typical paper machine, where a dynamic system existed, these equilibrium conditions were rarely achieved. It was, therefore, most likely that the major effect of a dewatering aid was merely to increase the rate at which equilibriums were approached. Further work, that supported these ideas, was done on a small pilot machine which ran at a speed of 20 ft/min. The freeness of the headbox was increased considerably with PEI and cationic PAM compared with the blank, but the moisture contents at the suction box, couch, and press were all within experimental error. It was believed that the time period during which the pulp was in contact with the wire was long enough for equilibrium moisture contents to be attained, and there was no advantage of using a dewatering aid under these conditions. This was supported by Foster (22) in which Csf of a stock increased from 250 to 650 without improved moisture content out of the press section. An independent study project performed by Watson (34) on the pilot machine at Western Michigan University (WMU) also found no improvement in dewatering upon the use of a drainage aid. A high MW cationic PAM was used with a softwood furnish at a Csf of 230 at a speed of 88 fpm. Only one series of runs was performed and the results were inconclusive, partially due to the limited sample size.

Pendrich (16) explained water-fiber relationships in a unique way. This explanation was adopted by Urick and Fisher (8) with only slight modification. Presumably, these ideas were adopted to help explain the results of their experimentation. A condensation of this discussion is given below.

Water is present essentially as free water and as imbibed water. Free water is water which can be removed mechanically from the furnish, including drainage on the wire and through the press section of the paper/board machine. Imbibed water is water bound to cellulose fibers and other components of the solids fraction, either by hydrogen bonding, capillary action, or interstitial action, and it cannot be removed mechanically.

A polyelectrolyte dewatering aid may affect these water-fiber relationships by one of two mechanisms: 1) by decreasing the hydration of the solids fraction, or 2) by increasing the rate of removal of free water from the slurry.

Decreasing the hydration of cellulose fibers presupposes that a proportion of the water of imbibation is altered, either by altering the surface tension or possibly the structure of the pulp fibrils. Normally cellulose fiber fibrils are splayed out because of electrostatic repulsion. A polymeric dewatering aid may neutralize the charge, allowing fibrils to align themselves and thus force out interstitial water previously held by the fibril structure. A decrease in fiber hydration may occur by this mechanism. In practice, this would mean that a greater

quantity of water could be removed at the press section of the paper/board machine in the presence of a dewatering aid (8, 16, 22).

Increasing the rate of removal of free water presupposes that the water of imbibation is not altered. If less drying time is required at the same machine speed, an explanation for the occurrence related to free water may lie in the attainment of varying equilibrium water contents. This is shown in Figure 7 on page 16. By this mechanism the major dewatering effect would occur on the machine wire. Theoretically, the fiber mat would enter the press section at a lower moisture content in the presence of a dewatering at the same machine speed. In practice when a lower moisture content is not realized, it is believed that this effect is partially or completely nullified by the vacuum boxes.

A pilot plant study was done by Coco (31) on the WMU pilot machine. A cationic guar gum was used with an unbleached kraft stock. The porosity was found to significantly increase with the 400 Csf stock, while the 500 Csf and the 600 Csf stock showed negligible increases. A fifty to sixty percent reduction in the white water consistency was found by the addition of the cationic guar. These results are shown in Figures 8 and 9 on page 21. It was stated that "there was good correlation (with addition of drainage aid) between the movement of the wet line, vacuum pressure, and sheet moisture." Evidence was not given for trials at the WMU paper machine. There was some evi-

Figure 8 - (31)

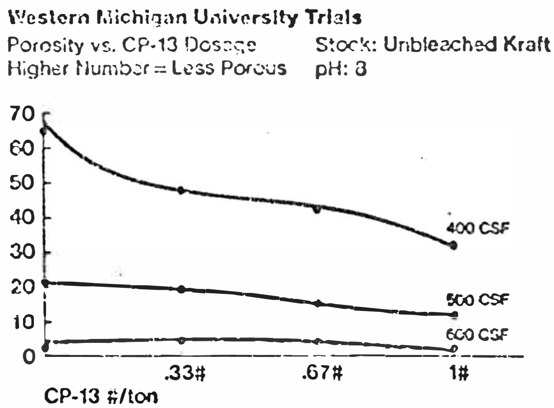


Figure 9 - (31)

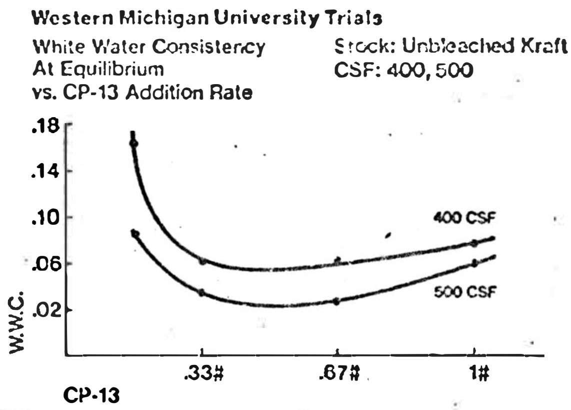


Figure 10 - (32)

EFFECT OF RETENTION AID CONCENTRATION UPON PAPER PROPERTIES

Pilot Machine Trial at Western Michigan University

	RETENTION AID ADDED		
	0.50 LB/TON	0.25 LB/TON	0 LB/TON
ASH, %	13.10	12.86	11.55
RETENTION, %	72.8	71.4	64.2
BRIGHTNESS	69.2	69.0	68.2
OPACITY	84.7	87.2	85.9
BURST FACTOR	11.8	13.8	17.4
MD BREAKING LENGTH, km.	3.9	4.1	4.6
CD BREAKING LENGTH, km.	1.8	1.9	2.3
MD TEAR FACTOR	52	57.5	54
CD TEAR FACTOR	64.5	68.5	65
SHEFFIELD POROSITY	172	94.5	52
FORMATION, QNS LIN C	74.6	69.7	68.0

dence given at a different trial, but a clear relationship did not exist.

Dobbins (32) also worked with the pilot machine at WMU. The object was to duplicate the wet end chemistry of a mill that produced a high groundwood catalogue paper on the pilot machine. The data indicated that tensile and burst were low, the sheet was more open than the mill specifications, and the formation, as measured by the QNS instrument, was very much worse. The retention of clay was very much higher than any commercial machine. It was decided to reduce the polymer addition in half and finally to run with no polymer. The results are shown in Figure 10 on page 21. The difference in clay retention between 0.25 lb/ton drainage aid and 0.50 lb/ton was very slight, which indicated that the optimum polymer dosage in terms of filler retention lied somewhere between 0.25 and 0.50 lbs/ton. But the adverse effects upon tensile, burst, porosity, and formation in going up to just 0.25 lb/ton were considerable, and were further magnified when 0.50/lb ton was reached.

Dobbins (32) suggested that there were two lessons to be learned from this. First, on a relatively small, slow, low turbulence machine such as the one at WMU, there was simply no need for the same level of flocculant that was required on a commercial paper machine. Dobbins (32) and Foster (22) have hypothesized that the effects of polymeric retention aids were most dramatic at high flow velocities found on high speed

paper machines. Secondly, it was clear that a relatively small overdosage of polymer was sufficient to interfere with the physical properties of the sheet. This indicated that overflocculation was a real danger with many adverse effects.

In summary, very little work has been done on the possibility of the increased dewatering ability of drainage aids in the press and dryer sections. Evidence suggests that increased drainage is a flocculation phenomena that involves a more open structure in which free water is removed. One must also realize that wet-web permeability is also an important consideration for the continued improvement of dewatering at the suction boxes and the press section. This may involve the decreased hydration shell (8, 16, 21, 22).

Types of Drainage Aids

Many different types of polyelectrolytes have been used by the paper industry for drainage improvement. Molecular weights ranged from intermediate to high. These polyelectrolytes have taken on different charge characteristics: cationic, anionic, non-ionic, and amphoteric (plus or minus). Dry products were sold, as well as liquid products ranging from 5% solids to about 35% solids. The way in which the polymer absorbs on the fiber surface could affect drainage, sizing, and dry strength. The structure of the polymer determines factors governing absorption.

The electrolytes can be categorized into a number of subgroups: a) natural inorganic chemicals, b) modified

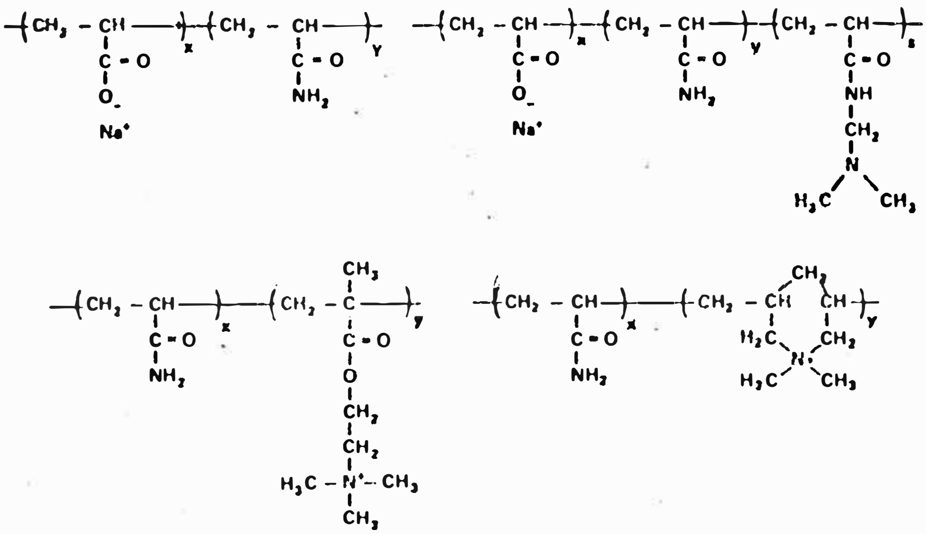
starches and gums, and c) synthetic polymers. Some of the proposed structures for these materials are shown in Figure 11 on page 25. The synthetic polymers can be further divided into groups defined by certain functional groups: 1) Polyamide/Polyamine condensations, 2) Polyethylene amines (PEI), and (3) Polyacrylamides (PAM) and modifications. Polyamide/Polyamine condensation were of limited interest because of their very low efficiency. Condensations of this type were highly cationic, but inherently had low molecular weights which contributed tc their low efficiency. Apart from some specialized applications their use in the paper/board industry was declining rapidly (21).

Polyethylene amines have been used for many years quite successfully. Lapin (4) hypothesized that cationic PEI molecule reacted with pulp by localization on the fiber surface via ion-exchange at negatively charged sites, without however ruling out hydrogen-bonding. The electrokinetic potential was reduced, the hydrate envelopes of the diffuse layer were heavily compressed, and water of hydration was displaced from the fiber surface. The resulting marked reduction of the stability of the colloidal suspension was evidenced by accelerated filtration. It was also hypothesized that the flocculation effect depended on the mean molecularweight.

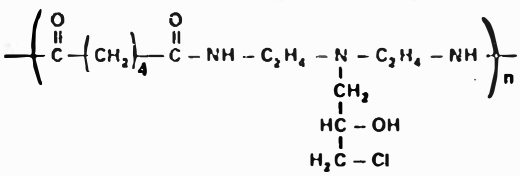
Entin (12) reported that polyethylene oxide was found to considerably increase retention of fines. The effectiveness of this polymer increased with increasing molecular weight.

Figure 11 - (21) Proposed Structures of Polymers Used for Drainage and Retention Improvement

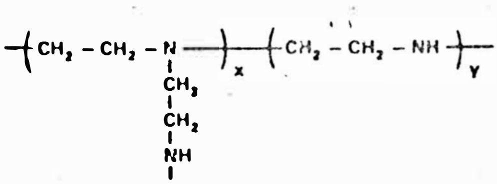
Polyacrylamides

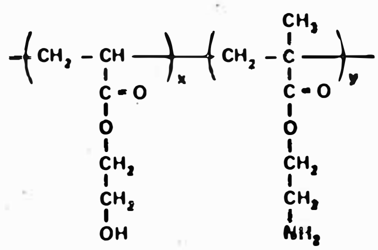


Polyamides



Polyamines





Cationic Guar Gum

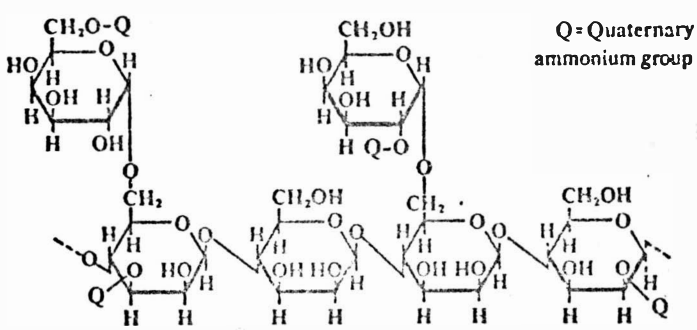
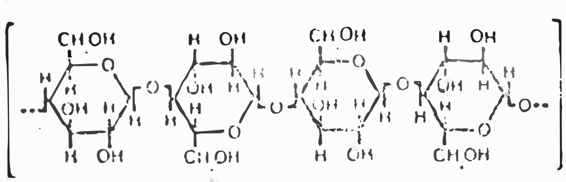
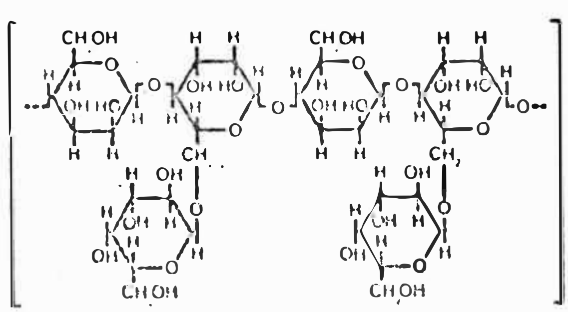


Figure 12 - (1) Relationship of Guar and Cellulose

Cellulose



Guar



The presence of aluminum sulfate had no substantial effect on the system.

Polyacrylamides have been used successfully as retention aids for a number of years. Until recently only anionic and non-ionic types were available, but since the introduction of cationic types their use as drainage aids have increased rapidly. It was these cationic PAM's that have been found to be very effective dewatering/drainage aids. PAM were generally more efficient than PEI and overflocculation has been a problem. For this reason the polymers were diluted to low concentrations.

A derivatized cationic guar gum has recently come on the market and has some unusual properties. The chemical structure has the molecular backbone of guar (a galactomannan). Penniman (1) hypothesized the similarity of guar to cellulose (Figure 12) in spacial configuration facilitated bond formation. This was believed to account for the high affinity of this polymer for cellulose and had been termed "substantivity."

Cellulose has a beta linkage between its glucose units while guar has a beta linkage between its mannose units. These form rigid, rod-like polymers. Because of this all the hydroxyl groups in cellulose and guar are exposed and available for the formation of hydrogen bonds. The positioning of the hydroxyl groups in cellulose and in galactomannan were believed to be responsible for the high absorption rate of guar to hydrated cellulose.

The guar gum had been modified in two ways: 1) addition

of cationic groups (quaternary ammonium groups), therefore the molecules acquire modest charge-neutralizing capabilities, 2) increase of molecularweight, therefore an increase in the potential for bridging and attainment of a measure of flocculating efficiency. This cationic guar gum dispersed easily in water unlike raw and refined guar gums.

Penniman (1) stated that since cationic guar gum "relies on substantivity it does not react with 'anionic trash', thus unlike PAM it can be quite effective in the presence of black liquor." This was believed to be the result of the lesser magnitude of positive charge on the polymer required for similar absorption characteristics (drainage effects). Dobbins (32) contradicted this hypothesis by suggesting that anionic materials are the most reactive components and must be neutralized before the absorption on cellulose can effectively take place. Coco (31) gave some evidence to support Penniman's hypothesis. However, there were a number of trials ran, a blank, a blank with black liquor, a blank with black liquor and varied amounts of cationic guar gum. The black liquor was only tested at one concentration (one percent). The drainage aid was shown to be effective at this concentration of black liquor. Couch vacuum, sheet moisture, and white water consistency were found to be decreased and were shown in data tables.

It has been noted (8, 32) that polyelectrolyte charge density, molecular weight and substantivity were important

parameters of a polymer, combining to determine the ultimate effectiveness of a particular polymer. It has been demonstrated by Urick and Fisher (8) that higher drainage rates were obtained with both increasing molecular weight and increasing cationic charge. Also the fines content of a furnish limited the drainage rate attainable with polyelectrolytes but did not substantially affect optimum dosages.

Practical Considerations

The benefits generally associated with the successful use of drainage aids include: increased production, conserved energy, improved retention, cleared white water, reduced pollution, extended felt life, improved sheet quality, and increased wet strength. These improvements must be transformed into economic gains and compared to the relatively high cost of drainage aids to justify their use. The examples of drainage aid use stress only the positive aspects and downplay the drawbacks. A detailed explanation of methods used to arrive at conclusions were usually not given. These improvements will be discussed below.

Benefits

Increased production and/or conserved energy resulted from a lower moisture content entering the dryer section. If improved moisture content was the result of a more rapid water removal, the speed of a papermachine can be increased. This can result in increased production and a decrease in the cost

per ton of paper produced. Specific examples of increased speed were given by Miller (7), Lowe (15), and Pendrich (16). The magnitude of these improvements ranged from 5 to 10 percent. Lower moisture contents entering the dryer can result in less energy required to dry a sheet. Falcione (9) reported that upon addition of a drainage aid, moisture that entered the dryer section decreased 95 gsm. For this 100 tpd board mill the fuel savings were calculated to be $148 per day with chemical costs of $100 per day. It must be noted that steam savings were not calculated on actual comsumption, but on steam savings expected from lower moisture readings.

Improved retention occurred with the use of a drainage aid. Eastwood and Clarke (6) reported that an amphoteric drainage aid (an aqueous solution of diallyl diammonium copolymer) was used on a pilot machine and increased first pass retention from 67 percent to 85 percent. In this case the amount of fiber saved by increased retention more than made up for the cost of polymer. Increased retention of fillers and other additives was hypothesized to make drainage aids feasible (7, 13).

If more fines and filler were retained by the paper sheet, cleaner white water may result (29). White water reuse was claimed to be facilitated due to a decreased level of suspended solids (9, 13, 16). This was also conjectured by the same authors to reduce load and maintenance requirements of savealls. This in turn would improve the efficiency

of the saveall and lower solids and BOD content in the effluent. Much of the materials that were part of the waste water would be incorporated into the sheet and less equipment, energy, and capital expenditure would be required to treat the effluent.

Otrhalek and Gomes (29) hypothesized felt life can be extended due to increased retention of fines, since heavy loads of fines was believed to be the primary cause for felt filling. These authors also suggested the absence of drainage aids could lead to a dirty system. Pitch and slime were hypothesized to be more difficult to control in systems with high white water solids. They further conjectured that pitch and slime have deposited on felts or other processing equipment and have led to increased downtime.

A drainage aid can lead to a better quality sheet by improving formation (29). Falcione (9) described the impact a drainage aid had on a board mill. Improved drainage was noted in the vats, this allowed for flexible machine operation to meet formation and strength specifications that were not possible before drainage aid use. When improved formation was needed stock consistency was reduced. Increased refining to bolster sheet physical tests without affecting machine production rate was also possible. These statements were not substantiated by any data. The use of drainage aids was also hypothesized to improve wet strength (29).

Foster (21) and Otrhalek (29) stated that the fines were

redistributed in the sheet in such a way to give less two-sidedness. Evidence of this was given by Pendrich (16). Hydrocol (a modified PAM) was used on a multiply board and there was a reduction in the tendency to delaminate. A hypothesis explained this occurrence by suggesting that fines were more firmly attached to the long fibers and were less likely to be washed out of the underside of the ply. As a result, the fines were believed to be much more evenly distributed through the cross section. This was believed to improve the bonding of each ply by allowing more long fibers to mat with each other at the pressing stage.

The factors one should consider in the selection of a drainage aid were discussed by Otrhalek and Gomes (29) of which the following discussion is taken from.

The factors include: 1) charge characteristics of a drainage aid, 2) molecular weight of a drainage aid, 3) pH of a system, 4) pulp type, 5) other additives, 6) water hardness, 7) temperature, 8) reaction time, 9) machine conditions.

The polymeric drainage aids may be non-ionic, cationic, anionic, or amphoteric. The charge characteristics of the furnish are usually negative and a cationic drainage aid was chosen. If the furnish contains inorganic fibers such as asbestos, then an anionic retention aid was selected. If the furnish was close to the isoelectrical point, then non-ionic drainage aids were frequently used. High molecular weight

polymers ($MW \geq 100,000$) were most efficient for retention. However, high molecular weight polymers were quite sensitive to degradation by mechanical shear. Medium range molecular weight polymers (MW 50,000-100,000) were desirable as drainage aids since the tendency to overflocculate was minimized.

The pH of the system was an important factor since most drainage aids have an optimal effective pH range. Changes in the acidity of the system could also alter the zeta potential. Generally cationic demand of a furnish increased with increasing pH. Increasing alum concentration decreased the pH and reduced the cationic demand of the furnish. Alum was effective in a narrow pH range of 4.5 to 6.0. Mills using recycled water generally operated at low alum levels and required highly cationic drainage aids.

The type of pulp can markedly affect the selection of a drainage aid. Softwood pulps generally contain the lowest number of fines and were therefore the easiest to retain. A low cationic charge level polymer of moderate molecular weight would be suitable for a softwood pulp. A hardwood pulp would require a high molecular weight cationic drainage aid.

Drawbacks

Although much has been written on the benefits of drainage aids, little attention has been focused on their weaknesses. This may be due to the high percentage of literature written by authors associated with the chemical supply industry. Drawbacks mentioned were related to the prospective use of drainage

aids, as opposed to control and optimization of a process once drainage aids were in the papermaking system.

For chemical additives to be used for dewatering improvement certain conditions must be present. A paper machine must be restricted in speed by a limitation in dryer capacity. Essentially if one wanted to improve the output without capital expenditures it was necessary to modify the pulp suspension of the wet ply or plies in such a manner that either more water was removed in the same period of time, or the same amount of water was removed in less time. To accomplish this increased sheet porosity normally resulted, this was believed to be due to the flocculation of fillers and fines and their absorption on to long fibers which caused a more open sheet. Therefore, a grade of paper must be able to tolerate this change in sheet structure from runnability and performance aspects. If the addition of a drainage aid resulted in increased production rates, more refining capacity will be required for the same grade of paper.

The optimum point of drainage aid addition was difficult to define in a commercial operation (32). A problem associated with this has been the inability to monitor polymer addition. Anderson and Penniman (14) claim that drainage aids could be monitored through the use of zeta potential meters. Otrahalek and Gomes (29) also suggest that drainage aids could be controlled by monitoring: 1) white water solids, 2) water content of sheet, 3) stock freeness, 4) zeta potential. All

of these characteristics can be greatly influenced by other variables. Of these parameters, zeta potential has the most direct affect on polymer addition level and potential for effectiveness.

Zeta potential readings between -8mv and 0 mv were hypothesized (5, 14) to give maximum drainage. The reliability of online zeta potential meters have been questionable and have required frequent maintenance. This was evident by the very few mills that use this approach of process control. An interview by Lowe (15) stated that a mill measured cationic demand on every shift and was unclear as to reliability of the electrophoresis meter used. These measurements were used to control amount of alum added. The alum was used to precipitate lignins and in this way cationic demand was controlled. The amount of polymer added must be accurately controlled to achieve maximum cost benefit. This was because increased benefits in a system can occur at higher levels of polymer addition, but with decreased economic efficiency. Foster (21) stated that overflocculation was probably the biggest problem associated with the use of drainage aids. This may be related to the inability of mills to monitor drainage aids online.

Dobbins (32) stated that overflocculation occurred when too much flocculant was added to the system and some of the long fibers were flocculated. This destroyed on a micro scale the random orientation of the fibers, which seriously affected the optical and physical properties of a finished sheet. An

inferior product can result with an additional economic loss due to inefficient use of an expensive drainage aid.

Dobbins (32) further hypothesized that retention and drainage were sequential processes, rather than simultaneous. This was because fillers have both a higher surface area and a high charge density in solution, relative to the fines, so that the polymer was preferentially absorbed first on the filler surface. Similarly, the fines undoubtedly have a higher surface area per unit weight and a higher surface charge density than the long fibered fraction of the pulp. Therefore, retention was primarily governed by the flocculation of fillers, while drainage improved primarily through the flocculation of fines; therefore, retention was affected by polymers before drainage.

Dobbins (32) gave several examples of overflocculation to illustrate specific points. The first example of a drainage aid trial involved a glassine furnish. Data from this trial indicated that the flocculation of fines and long fibers often overlap; the second process began long before the first had been completed. Therefore, one cannot always achieve a satisfactory drainage improvement before the sheet structure begins to deteriorate. This was based on the assumption that fines flocculation was required for drainage improvement and flocculation of long fibers was detrimental to sheet structure.

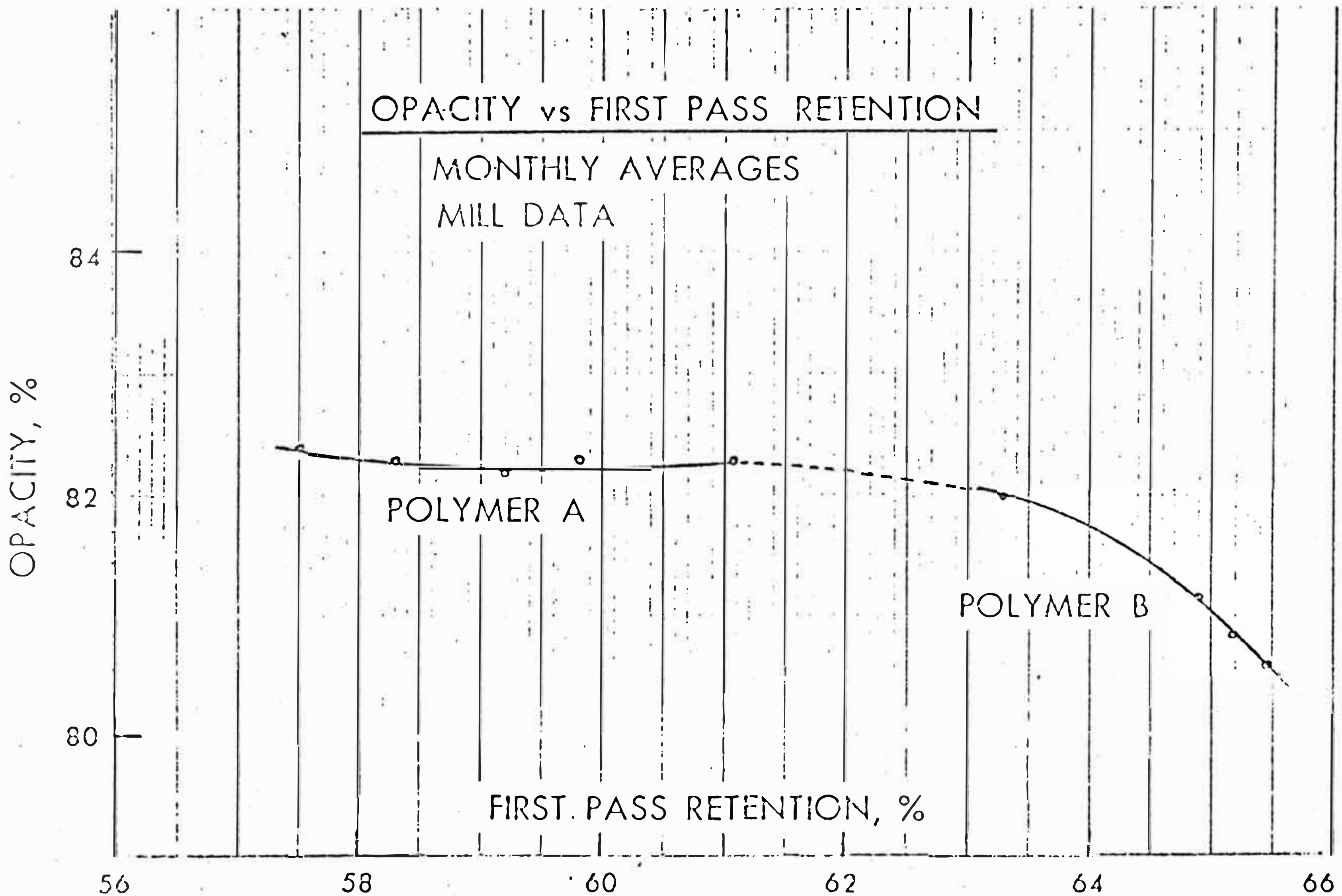
Another example with overflocculation involved a groundwood mill. The mill switched from one polymer to a second

product. In a comparison of data the most significant facts involved the opacity and retention data shown in Figure 13 on page 37. Dobbins (32) suggested this Figure revealed there was a maximum achievable opacity for a particular furnish on a particular paper machine. If more polymer, or a more efficient polymer was used to increase retention of fines, one did not necessarily increase opacity and at high levels of retention decreased opacity could result. These examples illustrated the detrimental effects that could accompany an overdose of polymer.

Robinson (11) stated the physical changes which may be brought about by chemical additives at the wet end. In the order of decreasing importance, they were: 1) retention in the paper of titanium dioxide, other mineral fillers, fiber fines, and debris; 2) fiber bonding or debonding; 3) fiber or filler embedding by a bonding additive; 4) structural changes which effect the density of the paper or affect the response to calendering; 5) uniformity.

Opacifying efficiency was shown to decrease with increased retention (11), similar to the decrease represented by over-flocculation of fines. Polyamide amines caused somewhat greater light-scattering efficiency in the retained fillers than did polyacrylamides. Pummer (33) ascribes the difference to a "flocculating" type of retention agent, which was inferior in this respect, compared to a "coagulating" type of retention agent. Although termed here as retention aids, both of these

Figure 13 - (32)


OPACITY vs FIRST PASS RETENTION
MONTHLY AVERAGES
MILL DATA
OPACITY, %
84
82
80
POLYMER A
POLYMER B
FIRST PASS RETENTION, %
56
58
60
62
64
66

types of polymers have been used as drainage aids.

The benefits and drawbacks of drainage aids have covered a wide range of process variables. The magnitude of these changes have also shown significant variance. Klass and Urick (17) suggested, after proper prescreening of chemicals, an 8 - 24 hour time period was required for initial proof that acceptable paper can be made. Demonstration of increased profitability took several days to several weeks.

Summary and Conclusions

The claimed effects of drainage aids are numerous. Positive aspects have included increased profitability, increased production, improved pollution abatement, improved runnability of machines, and improved sheet properties. Negative aspects have included 1) a lack of compatibility with a paper machine and/or furnish, 2) inability to monitor drainage aid performance (efficiency), 3) control of drainage aid addition to prevent overflocculation. The mechanisms involved with drainage aid use have not been well understood. Therefore, why some mills show favorable results from drainage aid use, while others do not, is merely left to conjecture.

Increased drying efficiency caused by drainage aids has not been shown. There have been cases of improved dewatering efficiency taking place up to the dryer section. Whether this improvement occurred at the wire, or at the press, or some combination of these factors is not known. It has been suggested that an increase in freeness was responsible for

creating a more porous structure and increasing the rate of dewatering on the wire. This increase in freeness does not, however, guarantee increased moisture improvement out of the press section. The reduction of the hydration shell of the fibers has been hypothesized to give increased wet-web permeability and improved pressing efficiency.

Other evidence suggests that the mechanisms responsible for dewatering were dependent on time. Therefore slow speed machines reach equilibrium and drainage aids were ineffective, while high speed machines do not reach these equilibrium points and drainage aids could be effective. Most pilot plant and laboratory studies have shown no improvement in dewatering. Whether the moisture improvement was due to the time equilibrium hypothesis or the ineffectiveness of the drainage aid was not known. These hypotheses indicate that there is a need for more work to be done on where and to what extent dewatering is taking place.

Supplement to the Literature Review

Recently an article (35) written by Straton came to the author's attention that brought up some interesting points concerning the performance of cationic polymers in the press section and the wet end. The main topic of the article was wet pressing. Straton determined that swollen volume was the controlling factor in wet pressing; it was also found that surface area was not a controlling factor. It was also stated that swollen volume "depends strongly on the amount of internal voids created by refining and on the amount of fines."

This article also explored the use of polymeric drainage aids to improve water removal. An example was given of a corrugating medium pulp at an unpressed solids content of 30%. Pressing increased the solids to 34.5% without additives. Use of polymer A produced a sheet with 36% solids after pressing, while polymer B caused a reduction in the amount of water removed. Both polymers A and B improved retention and drainage on the wire. Apparently the polymers also produced changes in the sheet structure which affected the pressing operation. An important feature was that polymer B was the additive of choice at the wet end. It provided superior filler and fines retention and enhanced drainage on the wire - factors which depended on surface area while pressing does not. The better fines retention may have resulted in a higher swollen volume which would have reduced the increase in per-

cent solids upon pressing. Fines also have been reported (36) to contain 4 to 5 times the amount of water on a weight basis as long fibers. Therefore, the location and retention of fines should be known in evaluating causes and effects of polymeric drainage aids.

This report represented ongoing research. The author stated that through continued research the net effect of a polymer could be predicted by an increased knowledge of mechanisms and the scope of interactions found in these systems.

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Presentation of Problem

There have been many hypotheses and conjectures brought forth to explain the effect drainage aids have on dewatering on a papermachine. There has been very little concrete evidence of increased dewatering. In these few cases the increased dewatering had not been sufficiently isolated to support hypotheses on possible mechanisms associated with dewatering. Pilot plant studies involved with drainage aids have generally shown little or no effect of increased dewatering. In many instances effects on other process variables and sheet properties have been emphasized.

A pilot plant study by Coco presented data that indicated movement of the wet line, vacuum pressure, and sheet moisture with addition of a cationic guar gum. These results were inconclusive and were not emphasized in his report. The author believes that the results indicate a need for a more detailed study that will concentrate on the locations and magnitudes of dewatering. To accomplish this goal an approach will be taken that is similar to the work done by Watson. The objectives will be to determine and isolate any increased dewatering effects that may be attributed to drainage aids.

Experimental Design

The primary objective of this study was to study and isolate the dewatering effects of cationic polymers. To accomplish this task a very simple furnish was chosen. This furnish

consisted of 75% hardwood, 25% softwood, hydrochloric acid (pH control) and the cationic polymers. Often drainage and retention aids have been unjustly classified together. The author believed that by using a filler free furnish the effects of retention could be minimized. This allowed one to concentrate on the possible dewatering effects of the cationic polymers.

A laboratory study was designed to study the effect of polymer concentration on freeness. Two pulps that differed only in the degree of refining were tested. This study was used to determine the polymer concentrations and the freeness of the pulp to be used on the paper machine trials.

On the papermachine, moisture samples were taken at various points to isolate various sections of the machine. Moisture samples were taken: at the couch roll, after the final press, at the size press and at the reel. Three samples were taken at each point across the sheet to get a cross-machine profile. In this way the dewatering could be categorized into four areas: the wet end (headbox to couch roll), the press section, first dryer section and the second dryer section.

The importance of fines retention has been mentioned. The retention of fines was monitored by taking three water samples. The water samples were taken at the headbox, the no. 1 white water tray and the no. 2 white water tray. First pass retention was taken as the difference in percent

solids of the headbox and the no. 1 white water tray.

The physical properties of the sheets were analyzed. The basis weight and caliper of the sheets were accurately measured, this allowed one to calculate the bulk of the sheet. The porosity, opacity, tensile and tear tests were performed to determine if any structural differences resulted from polymer addition.

The pilot paper machine trials were conducted at Western Michigan University. Four trials were conducted with each trial lasting about three hours. Each trial consisted of five runs: an initial control; followed by a low, medium and high addition level of cationic polymer; followed by a final control. The machine was allowed to run for twelve minutes between runs; this enabled the furnish to attain the new addition level of polymer or allow enough time for the polymer to be purged from the system. A number of parameters were monitored at each run. Parameters measured included: machine speed, basis weight, inframike moisture reading, dryer can temperatures and headbox freeness.

A relatively low molecular weight cationic guar gum was used for the first three trials. A relatively high molecular weight polyacrylamide was used for the last trial. The first two trials were ran at .33, .67 and 1.0 pounds of polymer per ton of fiber. The last trials were ran at .5, 1.0 and 1.5 pound of polymer per ton of fiber. The change was made to insure that the polymers were being tested at the full range

of the recommended concentrations. Details of the experimental procedure are given in the Appendix.

Presentation and Discussion of Results

Laboratory Studies

Drainage aids have been reported in literature to increase the freeness of a pulp slurry. The results of a laboratory study, designed to study this effect, are shown in Table 1 on page 49. The freeness increased more by a percentage basis for the higher freeness pulp. This could have indicated an optimum freeness level for freeness improvement. Both pulps showed that the polymer had diminishing effects with higher addition levels. The point of insignificant improvement upon further addition of polymer was reached at a lower concentration of polymer for the lower freeness pulp. The fines appeared to have a detrimental effect on the polymer to improve freeness. This trend may be due to a decreased efficiency of flocculation, in terms of surface area change. A lower surface area for a given weight of fiber would give a higher freeness.

Another laboratory approach was undertaken to determine if this cationic polymer could increase drainage in a handsheet device. It was found that a blank could not be controlled accurately and the polymer seemed to have no influence. High dilution and low shear conditions could have overshadowed any effect the polymer had on drainage rate. This concluded

the laboratory studies.

Pilot Paper Machine Trials

The importance of fines retention has already been mentioned. The percent retention and whitewater consistencies are shown in Table 2 on page 49. The effect of the polymers on fines retention was unclear as half of the samples with polymers showed higher retention values while the other half showed lower values. One would expect the first pass retention to peak as it passed the zero electrokinetic potential, therefore one might expect lower retention values at the higher levels of polymer. Since zeta potential measurements were not made, it was not known whether first pass retention was being effected by variations in electrokinetic potential. There was some evidence that the polymers caused lower consistencies in the no. 2 tray, that may have resulted in a slightly higher overall fines retention.

The percent moisture of the webs at the couch is shown in Table 3 on page 49. At a 95% confidence level a significant difference resulted from a .5 percent moisture difference. For the first three trials (with cationic guar gum) the final control was significantly higher than most of the other samples. The low and medium levels of polymer addition for trial 4 were significantly lower than the first control. These effects did not carry over into the press section. The other values did not show any significant differences.

The moisture of the webs after the final press is shown

Table 1 Effects of CP-13 on Canadian Standard Freeness

lbs of polymer / ton of fiber	Pulp I	Pulp II
Blank	371	135
.33	401	147
.67	434	151
1	445	153
1.5	452	-

Table 2 Water Samples - Percent Solids

	Polymer lb/ton	0	.33	.67	1.00	0
#1	Headbox	.482	.478	.468	.514	.513
	#1 Tray	-	.053	.052	.052	.053
	#2 Tray	.048	.041	.042	.043	.046
	% Retention	-	88.9	88.9	89.9	89.7
#2	Headbox	.484	.483	.482	.469	.439
	Slice	.040	.034	.047	.049	.038
	#2 Tray	.030	.030	.037	.026	.038
	% Retention	91.7	93.0	90.2	89.6	91.3
	Polymer lb/ton	0	.5	1.0	1.5	0
#3	Headbox	.517	.500	.514	.532	.518
	#1 Tray	-	.042	.039	.046	.049
	#2 Tray	.040	.032	.039	.042	.045
	% Retention	-	91.6	92.5	91.4	90.5
#4	Headbox	.539	.519	.549	.533	.482
	#1 Tray	.044	.051	.046	.041	.042
	#2 Tray	.037	.042	.039	.031	.036
	% Retention	91.8	90.2	91.6	92.3	91.3

Table 3 Effect of Polymer on the Percent Moisture at the Couch

Dosage	O	L	M	H	O
#1	75.4	75.5	75.3	75.4	75.8
#2	76.0	76.1	76.3	76.0	76.6
#3	75.6	75.9	75.6	75.8	76.4
#4	76.2	75.7	75.6	76.3	75.9

in Table 4 on page 51. An F-test was performed on these values and the samples were not significant at a 95% confidence interval; therefore the sample means could have come from the same lot.

It was felt that after the press section the moisture values should be corrected for basis weight. Dewatering in pounds of water per hour was calculated from the basis weight, percent moisture, machine speed and sheet width. (The results are shown in Table 5 on page 51.) Values are given for the last two trials as the dryer section was not well monitored during the first two trials. The wire values were variable due to the variation in headbox consistency. The press section showed no tendencies. The dryer section also did not reveal any significant changes. These trials were run on the same day and the steam was further cut back during the afternoon. This cutback occurred in the first section of dryers and was evident by the reduced evaporation in the first section. It should also be noted that the drying efficiency of the second half of the dryer section increased. This increase was significant and almost made up for the initial decrease. This increased drying efficiency was probably due to an increased percentage of the water that was not bound. Therefore it was also believed that since the polymers did not produce such a change that the polymers did not significantly reduce the percentage of bound water.

An important part of the analysis was the possible detri-

Table 4 Effect of Polymer on the Percent Moisture After the Final Press

Dosage	0	L	M	H	0
#1	61.7	61.2	60.8	60.8	60.9
#2	59.3	59.6	59.6	59.5	58.9
#3	59.9	60.9	60.2	59.9	60.9
#4	59.4	59.9	59.3	59.8	58.9

Table 5 Effect of Polymer on Dewatering (lb/hour)

	Dosage	0	L	M	H	0
	Wire	22,200	22,800	23,400	22,200	22,200
	Press	190	186	194	198	197
#3	Dryer 1st	139	149	145	139	150
	2nd	32	27	34	35	29
	Dryer Total	171	176	179	174	179
	Wire	21,400	23,100	20,800	22,400	24,300
	Press	205	220	192	211	205
#4	Dryer 1st	120	126	122	126	123
	2nd	44	49	42	47	42
	Dryer Total	164	175	164	173	165

Table 6 The Effect of Polymers on Tensile Strength

Machine Direction - Breaking Length in Meters

Dosage	0	L	M	H	0	F-Test
#1	5.47	5.50	5.81	6.00	5.73	NS
#2	5.27	5.09	5.15	5.90	4.90	S
#3	5.04	5.59	6.02	6.05	5.79	S
#4	5.78	6.06	6.43	6.46	6.20	S

Cross Machine Direction

Dosage	0	L	M	H	0	F-Test
#1	2.87	2.70	2.83	2.91	2.52	S
#2	2.72	2.63	2.75	2.77	2.80	NS
#3	3.26	3.40	3.42	3.51	3.19	S
#4	3.40	3.68	3.58	3.98	3.47	S

mental effects of the polymers on the final sheet properties. A number of tests were performed: basis weight, caliper, porosity, opacity, tensile and tear. An accurate measurement of basis weight and caliper was used to determine the bulk of the sheet. Porosity and opacity were determined to measure any changes in permeability or refractive index. The strength was measured by performing tensile and tear tests.

The results of the tensile tests are shown in Table 6 on page 51. An F-test was performed on the results for each trial. If the F-test showed a significant difference an analysis of variance was performed. Not one control run had a significantly higher tensile strength than one of the runs with the polymer. Twenty-five percent of the trials failed the F-test and the variations were insignificant. The other trials indicated different amounts of significance. The results indicated that the polymers slightly improved the tensile strength of the sheets. The results of the tear test are shown in Table 7 on page 53. The results proved to be inconclusive and the polymer did not seem to affect tear.

The results of the porosity testing are shown in Table 8 on page 53. The first two trials indicated that the porosity was increased with the addition of the polymer. The third trial indicated no change and the fourth trial was inconclusive. It was believed that by flocculating the fines to the longer fibers, that porosity would increase. There was some evidence to indicate this effect. It must also be noted that

Table 7 The Effect of Polymer on Tear

Machine Direction

Dosage	0	L	M	H	0
#1	.98	1.03	1.06	1.13	1.15
#2	.94	1.00	1.01	1.04	1.08
#3	.95	.96	.91	.92	1.05
#4	.88	.86	.89	.92	.93

Cross Machine Direction

Dosage	0	L	M	H	0
#1	1.09	1.01	1.05	1.10	1.23
#2	.98	1.05	1.07	1.14	1.13
#3	1.08	1.00	1.07	1.09	1.08
#4	1.00	1.01	1.04	.98	.99

Table 8 The Effect of Polymer of Porosity - cc/min.

Dosage	0	L	M	H	0
#1	103	125	133	112	106
#2	89	99	102	110	98
#3	124	123	119	124	124
#4	78	66	69	90	103

Table 9 Effect of Polymer on Bulk cm^3/g

Dosage	0	L	M	H	0
#1	1.37	1.40	1.41	1.35	1.30
#2	1.32	1.35	1.34	1.35	1.34
#3	1.41	1.40	1.35	1.37	1.40
#4	1.24	1.25	1.30	1.27	1.33

Table 10 Effect of Polymer on Opacity (Opacity/BW)

Dosage	0	L	M	H	0
#2	1.08	1.10	1.07	1.02	1.05
#3	1.11	1.10	1.07	1.07	1.09
#4	1.08	1.05	1.06	1.03	1.05

this is dry permeability and wet permeability may be more affected and of greater consequence to dewatering.

Bulk determinations are shown in Table 9 on page 53. Bulk has been reported in literature to increase as one approached the zero electrokinetic potential. Therefore the maximum bulk should have been reached before the maximum levels of polymer added. The bulk for the most part varied within a small range and the results were insignificant.

Opacity was analyzed because it was felt that if the smaller particulate matter was redistributed that the amount and types of interfaces would change and lead to different opacity values. The results are shown in Table 10 on page 53. These results indicate a small amount of variation and the results were inconclusive. It should be noted that in each case the lowest value occurred for the high level of polymer addition.

Summary of the Results

After analyses of all the data only one test seemed to show some significance at a high confidence level. The test was tensile strength and the effect was small. Therefore based on these analyses, the results indicated that the cationic polymers tested did not significantly improve dewatering under the conditions tested. The author felt three factors must be kept in mind: 1) the trials were conducted on a pilot paper machine - low speeds; 2) the paper machine

was dryer limited; 3) the furnish consisted of a simple system.

The topic of dynamics has often come up when reviewing pilot paper studies. The importance of dynamics on polymer related dewatering mechanisms was not known. Although, the consensus was that the dewatering effects of polymers will be minimal at low speeds. No real good explanation has been given as to why this should occur.

The second important factor was that the pilot machine was dryer limited. The importance of dryer limitation had been indicated in literature. The reasoning was as follows: if one had a dryer limited system one could benefit easily from a decreased moisture content leaving the press section. The question may be posed, must one have a press or wire limited machine to be able to notice the effects of the polymer?

Lastly, the furnish used was very simple, consisting of only hardwood fibers, softwood fibers, hydrochloric acid (for pH control) and the cationic polymers. Retention and drainage aids are commonly bunched together. The purpose of this study was to analyze drainage aids or more appropriately dewatering aids. Therefore a furnish (filler free) was used in which retention effects would be minimal. In this way one could study dewatering with as little interference as possible.

Conclusions

The results indicated that the cationic polymers tested did not significantly improve dewatering under the conditions

tested. The water samples indicated that these cationic polymers did not significantly affect the retention of fines under these conditions. The physical properties of the sheet remained unchanged; the exception was tensile strength. A statistical analysis revealed that the polymers may have increased tensile strength slightly.

Suggestions For Further Work

There are a number of aspects related to this topic that lend themselves to further study. It may be desirable to analyze dewatering of a press or wire limited machine. Laboratory devices that simulate dynamic situations should be utilized for further studies; such as the device described by Straton (34). Efforts to continue this type of research should lead to a fuller understanding of the mechanisms involved in dewatering. The effect of fines could also be studied with these laboratory devices. It is believed that the effects of fines could be a major factor in dewatering and more knowledge is needed in this area.

Some rather simple studies could be made to study dewatering effects that have been attributed to polymers in the dryer section. One study could measure the drying rate of sheet in an oven. This would be done to test the hypothesis that polymers reduce the bound water in a sheet; therefore drying rate should increase. Also handsheet studies could be performed on a Noble and Wood dryer. This would test the hypothesis as to whether increased permeability helps improve

drying significantly. It is not known whether dry or wet permeability is responsible, or if each has an effect. It may be wise to first check if one obtains a sheet with a higher porosity upon addition or some other means of measuring permeability before starting a comprehensive analysis. These are some of the more important areas that require further attention.

APPENDIX

Experimental Procedure

Materials

The furnish used was 75% Weyerheauser and 25% Espanola softwood. Hydrochloric acid was used to decrease the pH to a 4.5 to 5.5 level. The pulp was refined to a 300 Canadian standard freeness (Csf). No other materials, besides the cationic polymers, were added to the furnish.

There were two cationic polymers used in this experiment, CP-13 and CP-7. CP-13 was manufactured by the Celanese Polymer Specialties Company and was shipped in a powder form. CP-13 was a derivatized guar gum made cationic by the addition of quarternary ammonium groups. CP-13 was a relatively low molecular weight (MW) polymer and was similar to cellulose in configuration. CP-7 was manufactured by the Dow Chemical Company. This polymer was a high MW cationic polyacrylamide that was shipped in liquid form at a 5% solids concentration. CP-7 had a nominal MW of 1,000,000 and a pH of 10-11. The cationic polymers were dispersed in a cowles dissolver for approximately fifteen minutes. This solution was diluted to a concentration of .01% before it was added to the pulp furnish.

Paper Machine Trial Procedures

Each trial was run at 160 pounds per hour and was completed within three hours. The basis weight was 45 pounds per 3,000 square feet for three of the trials, for one trial

it was 40 pounds per 3,000 square feet. The basis weight was controlled within a pound during each trial. The speed of the paper machine ranged from 70 feet per minute (fpm) to 90 fpm, within four fpm for any given trial. The sheet width was approximately 20 inches. An attempt was made to run the blank runs at a relatively high moisture, 6-7%. This was done to simulate a dryer limited machine. The machine speed, basis weight, inframike moisture meter, dryer can temperatures and headbox freeness were recorded.

Each trial consisted of five runs: an initial control run, three runs with different levels of cationic polymer and a final control run. The machine was allowed to run for twelve minutes between runs; this enabled the machine to attain the new addition levels of polymer or allow enough time for the polymer to be purged from the system.

Water samples were collected in quart jars at three points: at the headbox, the no. 1 tray and no. 2 tray. The samples were evaporated in small steel weighing cans. The percent solids was calculated. All weighings were performed on the same Mettler balance.

Moisture samples were taken at various points on the papermachine: at the couch, following the last press, at the size press and at the reel. The samples were obtained by using a bear claw sampler. The samples were taken at three points across the sheet to give a profile of moisture. The samples were placed into preweighted polyethylene zip-

lock bags. The bags were then weighed with the samples inside. The samples were then taken out of the bags and allowed to dry in an oven set at 105 ^{o} C. The samples were then returned to the plastic bags to be weighed a final time. From this data the dry weight, wet weight and original percent moisture was calculated.

Differences in Trials

All of the trials were not run in the same manner. The cationic guar gum was used for the first three trials and the cationic polyacrylamide was used for the last trial. The first two trials were ran at .33, .67 and 1.0 pounds of polymer per ton of fiber. The last two trials were ran at .5, 1.0 and 1.5 pound of polymer per ton of fiber. The moisture samples taken during the first trial were obtained by tearing off samples from the edge. Subsequent samples were taken using a bear claw sampler. The second trial demonstrated that the bear claw sampler could not be used at the reel due to the small size of the sample and the low moisture contents at the reel. Therefore for the last two trials it was decided to tear out sheets in the middle of sheet at the reel; also to supplement these values, samples were taken at the size press. It was felt that these changes enabled a more complete and accurate monitoring of the dryer section.

Laboratory Study Procedures

The first laboratory experiment evaluated the magnitude of freeness changes induced by the cationic polymers. The cationic guar gum was used for this experiment. The furnish was composed of hardwood and softwood fibers as described earlier. No hydrochloric acid was added. Two pulps were used, one at a 140 Csf and the other at a 370 Csf. The polymer was added to a pulp slurry by a pipette at a concentration of 0.006%. The pulp slurry was then immediately mixed and allowed to stand for approximately five minutes, at which time the freeness test was performed according to TAPPI standards. The polymer was added at an increasing rate, by increments of one-third pound per ton of fiber, until an insignificant increase of freeness occurred.

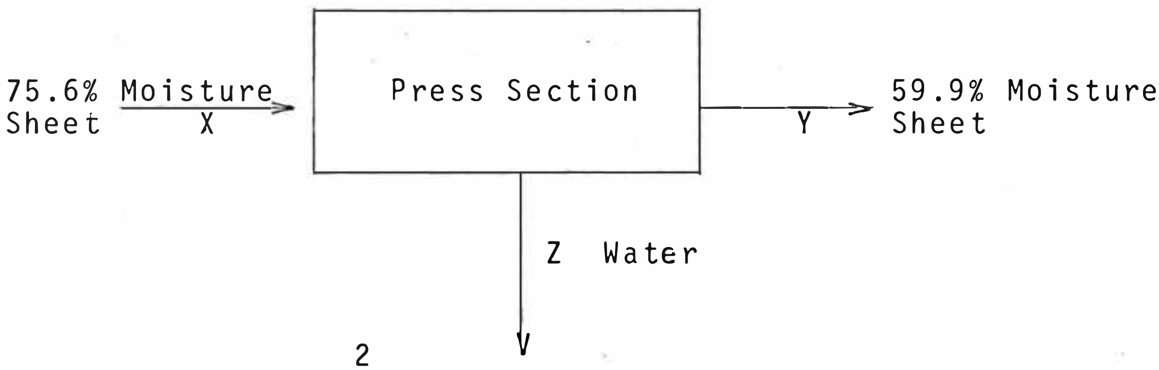
Another laboratory experiment was performed using the Noble and Wood handsheet forming device. A proportionator was used to obtain a standard handsheet (2.54 grams). A standardized amount of pulp slurry was added to a fixed volume of water. The polymer was added in the same manner as above. This stock solution was mixed by using three strokes with an agitator. Two minutes was given for the polymer to adsorb onto the fiber surface. The sheet was then formed after two strokes of agitation. The time required for the water to drain was recorded by a stopwatch to the nearest tenth of a second. The time to drain was measured by starting the stopwatch when the drain lever was pulled and stopped when the sheet could be seen without water from above. This con-

cluded the laboratory portion of this study.

Sample Calculations

Dewatering - lb/hr

Basis: 100 lbs of Fiber



Basis Weight = 71.7 g/m^2
Width of Sheet = 2 feet
Machine Speed = 77.9 fpm
Basis Weight at 7% Moisture

X = lbs of sheet entering
Y = lbs of sheet exiting
Z = lbs of water pressed
X = Y + Z

$$\text{Oven Dry Basis Weight} = (71.7\ g/m^2)(.93)$$
$$= 66.7\ g/m^2$$

(.244) (X) = 100 lbs OD fiber
X = 409.8 lbs entering with sheet

(.401) (Y) = 100 lbs OD fiber
Y = 249.4 lbs exiting with sheet

X - Y = lbs of water pressed out of sheet
= 409.8 - 249.4
= 160.4 lbs of water pressed out per 100 lbs OD fiber

$$\frac{\text{lbs of Water}}{\text{Area}} = \frac{\text{lbs Water}}{\text{lbs Fiber}} \times \text{Basis Weight}$$

$$= \frac{160.4 \text{ lbs of Water}}{100 \text{ lbs of Fiber}} \times \frac{66.7\ g}{m^2} \times \frac{(.304 m)^2}{ft^2} \times \frac{1\ lb}{454\ g}$$

$$\frac{\text{lbs of Water}}{ft^2} = \frac{.02178\ lbs}{ft^2}$$

$$\frac{\text{lbs of Water}}{\text{Hour}} = \frac{.02178\ lbs}{ft^2} \times \frac{77.9\ ft}{min.} \times \frac{60\ min.}{hr.} \times 2\ \text{feet}$$

$$= 204\ lbs/hr$$

Data

Test Statistics Used:

F-test S - Significant difference between sample means
NS - No significant difference between sample means

If F-test was significant then the Least Significant Difference (LSD) was calculated using following formula

$$LSD = \left[t_{.025,\ N-K}\right] \left[MSE \left(\frac{1}{Ni} + \frac{1}{Nj}\right)\right]^{\frac{1}{2}}$$

Table 11 List of Statistical Values for Selected Properties

Property	Trial	F-Test	LSD
Couch % Moisture	3	S	.49
Couch % Moisture	4	S	.48
Press % Moisture	3	NS	-
Press % Moisture	4	NS	-
Size Press % Moisture	3	S	2.01
Size Press % Moisture	4	NS	-
Reel % Moisture	3	S	.48
Reel % Moisture	4	S	.58
Porosity	1	S	7.4
Porosity	2	S	6.7
Tensile - MD	1	NS	-
Tensile - MD	2	S	.48
Tensile - MD	3	S	.30
Tensile - MD	4	S	.39
Tensile - CD	1	S	.18
Tensile - CD	2	NS	-
Tensile - CD	3	S	.19
Tensile - CD	4	NS	-

Table 12 Data from Trial #1 - January 26, 1981

		Dosage - Cationic Guar Gum, lb/ton				
		0	.33	.67	1.00	0
Couch % Moisture	1.	75.34	75.17	75.16	75.09	75.45
	2.	75.29	75.32	74.79	75.26	75.99
	3.	75.38	75.25	74.91	75.34	75.87
	4.	76.81	75.80	75.57	75.61	75.88
	5.	75.40	75.77	75.69	-	75.92
	6.	75.39	75.97	75.60	-	75.87
Press % Moisture	1.	61.32	61.77	60.93	60.84	60.70
	2.	61.72	61.42	60.78	61.18	61.01
	3.	61.64	61.46	60.88	61.09	61.11
	4.	61.76	60.82	60.85	60.76	60.97
	5.	61.71	60.94	60.56	60.69	60.49
	6.	61.83	60.86	60.88	60.73	61.21
Reel % Moisture	1.	2.72	2.64	2.89	4.32	3.83
	2.	4.53	3.27	2.98	4.73	3.55
	3.	4.08	3.30	2.78	4.47	3.59
	4.	4.33	3.87	3.17	5.34	4.54
	5.	4.22	3.97	3.78	5.43	4.98
	6.	3.87	5.37	4.26	5.36	4.76
Machine Speed fpm		78.3	77.8	76.4	77.1	76.2
Inframike Moisture Meter (at reel)		-	64	61	64	60
Basis Weight g/m^2		74.4	72.5	74.5	79.2	77.0

Percent Moisture (1-3) taken off operator side

Percent Moisture (4-6) taken off other side

Table 13 Data from Trial #2 - January 30, 1981

		Dosage - Cationic Guar Gum, lb/ton				
		0	.33	.67	1.00	0
Reel % Moisture	1.	7.47	4.05	6.62	3.88	4.34
	2.	6.24	5.30	3.50	3.83	2.83
	3.	4.40	6.78	3.90	3.00	4.17
Press % Moisture	1.	60.57	61.64	61.18	60.94	60.42
	2.	59.44	59.28	59.15	59.49	57.91
	3.	57.74	57.76	58.41	57.98	58.39
Couch % Moisture	1.	76.04	75.80	75.91	75.59	76.56
	2.	76.09	76.47	76.25	76.42	76.72
	3.	75.99	76.17	76.60	75.86	76.43
Machine Speed fpm		88.6	90.2	87.2	87.4	87.8
Inframike Moisture Meter		62	61	57	51	43
Headbox Freeness		-	184	203	222	253
Basis Weight g/m^2		67.4	63.8	67.6	65.4	66.7

Moisture Samples: 1 - operator side of sheet

2 - middle of sheet

3 - other side

Table 14 Data from Trial #3 - February 17, 1981

		Dosage - Cationic Guar Gum, lb/ton				
		0	.5	1.0	1.5	0
Reel % Moisture	1.	4.25	3.9	5.1	4.7	3.8
	2.	4.10	4.3	4.9	4.5	3.9
	3.	-	4.0	5.0	5.5	4.0
Size Press % Moisture	1.	22.9	20.8	24.8	25.3	20.7
	2.	22.1	21.7	23.9	25.3	21.7
	3.	25.1	22.4	25.8	26.1	23.4
Press % Moisture	1.	59.5	59.9	59.7	59.5	60.4
	2.	60.0	60.4	60.3	60.1	60.5
	3.	60.3	62.4	60.6	60.2	61.8
Reel % Moisture	1.	75.6	75.9	75.5	75.6	76.5
	2.	-	76.2	76.0	75.9	76.3
	3.	-	75.6	75.4	76.0	76.5
Machine Speed fpm		77.9	77.5	78.1	77.6	77.0
Inframike Moisture Meter		69	62	52	56	50
Basis Weight g/m^2		71.7	71.6	75.0	74.2	72.7
Headbox Freeness		235	255	245	240	-

Moisture Samples:
1 - operator side of sheet
2 - middle of sheet
3 - other side

Table 15 Data from Trial #4 - February 17, 1981

		Dosage - Cationic Polyacrylamide, lb/ton				
		0	.5	1.0	1.5	0
Reel % Moisture	1.	6.8	7.0	4.9	6.2	4.8
	2.	6.9	6.6	5.6	5.8	5.2
	3.	7.3	6.1	5.5	5.9	5.2
Size Press % Moisture	1.	33.4	33.7	30.9	32.5	30.9
	2.	31.4	31.2	29.3	31.1	28.2
	3.	28.2	30.7	27.9	29.6	26.8
Press % Moisture	1.	59.9	60.6	60.4	60.9	59.0
	2.	59.4	59.7	58.9	59.8	58.5
	3.	58.8	59.3	58.6	58.7	59.2
Couch % Moisture	1.	76.0	75.6	75.5	76.1	75.6
	2.	76.2	76.1	75.4	76.3	75.9
	3.	76.4	75.5	76.0	76.5	76.1
Machine Speed fpm		80.0	79.8	76.7	77.0	77.3
Headbox Freeness		252	233	255	284	265
Basis Weight g/m^2		71.9	74.7	74.2	77.3	75.2

Moisture Samples: 1 - operator side of machine of sheet

2 - middle of the sheet

3 - other side of the sheet