IMPROVED FILLER RETENTION BY COFLOCCULATION OF FINES AND FILLER PARTICLES

By

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DECLARATION

I, the undersigned hereby declare that the work contained in this thesis is my own original work and has not in its entirety or part been submitted at any university for a degree.

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ABSTRACT

The retention of filler particles and drainage are important aspects of papermaking. A number of important paper properties depend in the quality and quantity of filler retained in the paper. Fines, fillers and pulp fibres all have a negative charge and are kept apart by electrostatic forces. This causes a decrease in the effectiveness of cationic retention aids thereby causing a high cationic demand. This in turn implies that the retention of fines and filler particles in a formed sheet is not efficient, especially in the presence of anionic trash. In order to improve printability, print quality and dimensional stability, a large percentage of mineral pigments / fillers either in the form of internal loading or external coating should be added.

It was found that coflocculation of fines and filler particles resulted in an even distribution of filler particles in the form of micro-flocs and the filler retention was maintained. Opacity was improved without much reduction in paper strength. An increased filler content without coflocculation of fines reduced sheet strength properties. The filler particles interfered with the development of fibre-to-fibre bonds and occupied spaces that otherwise might have contained fibres.

This study showed that the most beneficial effect of coflocculation of filler with fines was obtained, with regards to paper strength, opacity, filler retention and printability, when the charge of the fibre furnish was maintained at -0.1 ICu with the 0.1% addition of cationic PAM retention aid.

OPSOMMING

Twee belangrike aspekte van papiervervaardiging is die retensie van vulstowwe en ontwatering. 'n Aantal belangrike papiereienskappe is afhanklik van die hoeveelheid en kwaliteit van vulstowwe wat in papier voorkom. Veselpuin, vulstowwe en pulp-vesels is almal negatief gelaai, gevolglik verseker elektrostatiese kragte dat hierdie deeltjies los van mekaar bly. Laasgenoemde verminder die doeltreffendheid van kationiese retensiemiddels en dit gee aanleiding tot 'n hoë kationiese aanvraag. Die retensie van veselpuin en vulstof deeltjies in papier is gewoonlik nie voldoende in die teenwoordigheid van anioniese afvalkomponente nie. Om aan papier verbeterde druk-eienskappe, drukkwaliteit en dimensionele stabiliteit te gee, moet 'n groot persentasie minerale pigmente en/of vulstowwe as 'n interne lading of eksterne bestryking voorsien word.

Daar is bevind dat koflokkulasie van fynstowwe en vulstofdeeltjies, 'n egalige verspreiding van vulstof-partikels as mikro-flokke tot gevolg het en dat vulstof-retensie op aanvaarbare vlakke behou is. Ook is ondeurskynendheid verbeter sonder 'n beduidende verswakking in die papiersterkte. 'n Toename in vulstofinhoud, sonder koflokkulasie van fynstowwe, het die papier sterkte-eienskappe verlaag. Vulstofdeeltjies bëinvloed die ontwikkeling van vesel-tot-vesel binding. Hierdie deeltjies beset ruimtes wat andersins deur vesels benut sou word.

Hierdie studie het getoon dat die voordeligste effek van koflokkulasie van vulstowwe met fynstowwe verkry is, ten opsigte van papiersterkte, ondeurskynendheid, vulstof retensie en drukeienskappe, wanneer die lading van die pulpsuspensie by -0.1 ICu gehou was met 'n byvoeging van 0.1% kationiese PAM retensie-hulpmiddel.

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CHAPTER 1

INTRODUCTION

1.1 General

Retention of filler particles and dewatering (drainage) of the paper formed are important aspects of papermaking[1]. A number of important properties depend on the quality and quantity of filler retained in the paper[2]. The optimum retention is of economic importance for recovery of materials costs, improvement of paper properties and water reuse. Fillers and fines suspended in water carry a negative charge and they repel each other. The result being that these fines and fillers tend to be well dispersed and become small enough to pass through the wire. There are two things that need to be done in order to retain these fines and fillers in the sheet: (i) reduction of repellent forces between particles (coagulation) and (ii) formation of a bridge between the neutralized particles in order to produce discrete agglomerates (flocculation) that are large enough to be entrapped in the formed sheet.

It is well known that the presence of filler particles prevents development of interfibre bonds and as a result tensile strength suffers a lot, hence there is a limit to the amount of filler to be added. It is conceivable that per unit mass, dispersed filler particles cover more of the fibre surface areas and therefore are more effective in reducing bonding area. High molecular mass water-soluble polymers (retention aids) are routinely added to improve fines and filler retention. The unretained fines were found to be major sources of organic stream pollution in paper mill effluents[3].

Microflocculation contributes towards the filtration process that occurs on the paper machine and it is achieved by the addition of retention aids. The retention aids function by causing the colloidal filler particles to deposit onto fibres ensuring that the filler is retained in the paper[4]. Fines and fillers react differently to retention aids and other chemicals and they produce flocs of different nature. There appears to be a synergetic effect that results in stronger and more voluminous aggregates when fines

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and filler particles are coflocculated. This is obtained by separate flocculation of the two constituents[5].

Anionic interfering substances impair the effectiveness of the cationic additives and paper properties. The higher anionic nature of the fines allows them to compete with the fibres and filler surfaces for cationic species and their presence is therefore an important variable in the retention of cationic paper chemicals[6]. The determination of charge demand in papermaking is of great importance. The monitoring of the Zeta potential is more beneficial than cationic demand to optimize the process chemistry caused by the stock becoming cationic[6]. It should be noted that there is no correlation between Zeta potential and cationic demand.

Durgueil[7] recommended a system of coagulation of fines and detrimental anionic substances to the fibre and then flocculation of the fibre. The charge of the stock should still be negative after coagulation addition to allow the flocculant to act and bridge the matrix. Zero Zeta potential is not optimum[6], because at zero charge the colloidal water layer adsorbed on the surface of the capillaries is thicker than when the charge is slightly negative or positive. As the layer becomes thinner, there is more open space in the capillaries for drainage and a greater capability of Van der Waal's forces to increase retention.

1.2 Coflocculation

Coflocculation is defined as the mixing of filler particles with fines, i.e., filler pre-treatment, before preflocculation[8]. Filler suspension is coflocculated with a fine fraction (10-20% fines) of mechanical pulp after first being well dispersed. Fillers are coflocculated with mechanical pulp fines because the mechanical pulp fines have a large specific surface area and a high negative charge load. The basic idea of coflocculation is to separately precipitate the filler onto a small portion of fibre furnish about 5% of the paper weight and then form fines-filler flocs in which the filler is retained while still imparting opacity to the paper[5]. It is important for the preflocculated system to produce stable flocs, which are also shear resistant. It should contribute to sheet strength, produce good filler retention and it should be economically effective. The floc size must be of the right magnitude and be easy to

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control[9]. The coflocculation fines-filler flocs are small and do not interfere with paper formation. They are strong enough to withstand the dilution and agitation in the sheet machine.

The coflocculation process originated from work done at the Central Laboratory of the Swedish Paper Mills[5] in the early 60-ties, and later continued in the laboratory of Commento Consulting AB[5]. It was noted that when a blend of fines and filler was precipitated with a cationic polymer, polyacrylamide (PAM), a very large floc resulted and the liquid between the flocs became clear. The flocculation of fines alone resulted in smaller flocs in turbid water. This was a striking observation, which appeared to merit an explanation[5]. Following this, some sediment concentrations were determined[5]:

Table 1: Sediment concentrations[5]

	Sediment concentration, (g/l)
Fines only	8.1
Fines + PAA	7.1
Clay + PAA	160
(Clay + PAA) + fines	8.3
(Fines + PAA) + Clay	10.1
(Fines + clay) + PAA	5.3

Sediment concentration refers to the size or amount of flocs, i.e., large or small. The sediment concentration should be small. On flocculation of fines with cationic PAM, the sediment concentration decreased, the flocs became larger and stiffer. On addition of clay, the flocs became compressed owing to the weight of the clay particles. This compression was stronger. When fines and clay were first mixed and then precipitated with cationic PAM, a very fluffy precipitate with a concentration of only 5.3 g/l was obtained. On precipitation of clay separately, as is normally done, this effect was not found. Preflocculated clay had a high sediment concentration. It was then concluded

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that the phenomenon was a genuine process, and the word "coflocculation" was given to it[8].

The main aim of coflocculation is to wrap the filler particles in envelopes of fibrils and lamellas. This helps to keep the fillers apart and preserve their light scattering ability in the paper and at the same time anchoring them more securely so that they do not migrate through the fibre network and get washed out from the wire. It is believed that coflocculation promotes the hydrogen bonding capacity. The whole concept of coflocculation presupposes that preliminary flocculation of fines and fillers is the normal way in which filler retention is achieved[5]. It had been shown that this process of coflocculation has good benefits, such as better pressability and lower steam consumption during drying.

1.3 Objective

The objectives of this study were

1. To investigate if coflocculation between fines and filler particles would improve the filler distributioin without impairing other sheet properties, whilst at the same time the filler distribution would remain satisfactory.

2. To establish the effect of coflocculation on opacity, air permeablility and printing performance of paper.

3. To determine the effect of electric charge on coflocculation.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of fines

Fines can be defined in different ways. They can be defined as those particles that pass through a screen with 76 micrometers holes or nominally 100 mesh[10, 11], or as the small material (less than 7 micron in length) liberated during the bleaching or pulping process[12], or as pulp fibre fragments that are formed by the mechanical and hydrodynamic forces on a pulp suspension[3]. All particles visible with a light microscope, whether fibre or filler, are included in the fines category while soluble and colloidal particles are excluded, even though they will pass through the screen.

Fines are categorized into pulp fibre fines, filler fines and size fines[11]. Fibre fines may be introduced into the system with virgin pulps, recycled broke or secondary fibres. Filler fines are introduced as new raw materials, with recycled broke, or secondary fines. Only pulp fibre fines will be discussed. The word 'fines' will be used throughout to address pulp fibre fines. Primary fines are those associated with virgins pulps and secondary are those generated by refining during stock preparation. Primary fines include elements such as parenchyma cells, ray cells and vessel elements that are formed most abundantly in hardwoods. In mechanical pulps, the primary fines also include pieces of fibre and shives. Primary fines show a tendency to swell less than secondary fines[11].

Brecht and Klemm as quoted by Luukko and others[13], identified two types of fines, namely, flour stuff and slime stuff. The flour stuff is the one consisting of granular fibre pieces, fibre fragments, and ray cells whereas the slime stuff contains mostly fine fibrils. It was proved that the flour stuff and slime stuff had different effects on sheet properties[13]. Many studies have shown that the slime stuff is a good bond-forming material while the flour stuff has poor bonding ability.

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Fines are not just small fibre fragments but often very long and thin threads[5]. Fibrils and lamellas which are scaled of the fibre wall are mainly particles with a uniform thickness. Their length is more difficult to measure and it is understandable that these fine particles are not so easily retained in paper. The long fibrils are split off from the secondary wall and they have a high hydrogen bonding capacity. The unretained fine particles result in potential problems. These include poor sheet quality, two sidedness, pick outs or holes, inefficient wet pressing ability, deposits and printing difficulties[8]. It is envisaged that the coflocculation of fines and filler particles will control or regulate the loss of fines with water through the wire.

The fines of mechanical and chemical pulps have a character very distinct from their respective fibre fractions. Mechanical pulp fines consist of pieces of fibre such as cell wall and middle lamella fragments, ray cells, filaments and lamella particles[14]. In current high quality printing papers, the fines fraction may account up to 40% of the whole mechanical pulp. The chemical composition of fines, especially their surface chemical composition varies widely.

2.2   Generation of fines

Most of the fines result from the heat and mechanical action of grinders. Fines are also generated during beating and refining and a substantial amount of fines are introduced with the use of secondary fibre[12]. The mechanical defibration process produces a large amount of fine material that consists of a wide range of different types of particles. Mechanical pulp use causes the fines content of the furnish to increase throughout the system. This implies that, the fines that are normally preferred are those from mechanical pulps. They have a large specific surface area (up to $10 m^2/g$) and a high negative surface charge due to the carboxyl groups of the hemicellulose, orientation and dissociation of polar groups on the surface, adsorption of additives and crystal disorder[15].

Under normal papermaking conditions the carboxyl and sulphonic acid groups are major contributors to the fibre charge. When they are mixed with filler particles, which normally have the same negative surface charge, a very uniform mixing is obtained. Mechanical pulp fines with filler particles precipitated onto them will be

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even more efficient in opacifying the paper and the filler will retain its efficiency in spite of flocculation[9]. This is due to their stiffness as opposed to chemical pulp fines that reduce opacity.

2.3   Effect of fines on sheet properties

The fines play a significant role in properties of paper containing mechanical pulps. This can be attributed to the small particle size and the large specific surface area of fines compared to the fibre fraction[16]. The amount of fines has a more important influence on the paper properties than their quality[14]. The quality of fines varies depending on the process conditions and the raw materials used. The basic effect of fines is that they fill interstices between fibres[13]. It had been shown that the fines, which originate in the manufacture of groundwood, readily bond to each other and to larger fibres[17]. Such fines cement the sheet structure together, thereby increasing density and tensile strength. It was found that the presence of fines increased the scattering coefficient (opacity) of groundwood containing papers[18, 19]. This is in contrast to heavily beaten, high fines content, chemical pulps.

Chemical pulp primary fines contribute less towards the development of mechanical properties. Poorly bonded vessel segments are responsible for picking, a problem occurring in hardwood containing papers. Mechanical pulp fines are important to the development of interfibre bonding, as are fines originating from recycled chemical pulps.

In mechanical pulps, fines are the most important fraction because of their significant effect on most paper properties. Chemical pulp fines have a strong tendency of intensifying the interaction between fibres, though the amount of fines is small. The increased density of the fibre network causes this. As an example, a handsheet made of thermomechanical pulp (TMP) fines has a low density of about 450 kg/m^3 whereas a handsheet made of Kraft fines has a remarkably high density[19] of about 1100 to 1200 kg/m^3. The smaller particles have a better bonding ability. The lignin content of the mechanical pulp fines is higher than that of the unbleached chemical fibres[14]. It was proposed that the high lignin content of mechanical pulps restricts the ability of

the particles to form bonds. A high extractives content may, among other effects, reduce the bonding ability.

The fines can be either advantageous or detrimental to both machine performance and the development of product quality, depending upon the source and composition of the fines and the way they are handled in the paper mill. High total fines in the system can produce deposits of the fines themselves and of materials carried by them. Primary fines can contain high amounts of extractives that produce pitchy deposits. Fines can also act to stabilize foam that in turn, can directly degrade paper properties and interfere with paper machine runnability. Therefore, it is important for the papermaker to maintain a vigorous fines management program to minimize the adverse effects of fines and to optimize their positive contribution in papermaking.

2.4   Fillers

The improvement of important paper properties depends on the quality and quantity of the filler retained in the sheet. Finely dispersed white mineral fillers are added to papermaking furnishes for several purposes, such as to improve the optical (opacity and whiteness) and physical properties of the sheet. The main one being that of filling voids between the fibres in the printing papers in order to produce a denser, softer, brighter, smoother and more opaque sheet. Fillers make the paper surfaces to be less hydrophilic and thus more receptive to oily printing inks. They also help in the prevention of a strike-through of the ink. In some cases they help to offset the coarseness of the pulp fibres. They improve colour and increase dimensional stability. Fillers are also used as an aid in producing special paper properties[20, 21]. Fillers only have a negative effect on paper strength properties but they enhance optical properties, increase light scattering ability and improve paper printability.

There are three types of filler retention that were identified, namely,

1. sieving or filtration which is the process of removing particles larger than the pore openings during sheet formation,

2. entrapment which is the physical collection of particles in the fibre lumens or in the fibril structure of the fibre surface, and

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3. coflocculation which is the interaction of the interfacial forces of the particles which control ordinary colloidal flocculation[3, 22].

There are three factors that are known to influence coflocculation retention mechanism namely,

1. the collision process that is controlled by the extent of agitation, concentration and particle size,

2. the aggregate formation and

3. the overall strength of the aggregate[3].

Among these three mechanisms coflocculation had been found to be the dominant mechanism for retaining pigment fillers and pulp fines.

In many cases fillers are added in dry form directly to the pulper or other stock preparation equipment. In some cases, the paper can be made cheaper because the fillers are often less costly than the fibre. There is a limit to the amount of filler that can be used, since increased filler content tends to decrease the strength of the paper. This is due to the fact that the filler interferes with the potential development of fibre-to-fibre bonds and occupies space that might otherwise contain fibres[2, 21]. The result being the decrease in the effective cohesion. Thus the paper becomes weakened and the dusting tendency during printing increases. The paper becomes high in density. The filler causes more rapid wear of the wire on the paper machine and of the printing plates in the printing press. The use of filler and pigments in different paper grades can be seen in Table 2.

Table 2: Use of fillers and pigments in different paper grades[28].

Paper grade	Content	Type of filler/pigment
Newsprint	0-10%	Clay, talc, special pigment
Magazine paper (uncoated, SC)	20-30%	Clay, talc
Fine paper	0-25%	Clay, talc, chalk, TiO_2
Wrapping paper	0-10%	Clay, talc, chalk, TiO_2

Fillers with no affinity to the fibres are held in paper in two ways, namely, as surface forces in aqueous phase (sorption mechanism) and as mechanical adhesion of filler particles in the fibre mat (mechanism filtration).

The most common available fillers are clay, calcium carbonate, titanium dioxide and talc. They are available either in dry powder form or as dispersed slurries, and are nearly always added as slurry. The slurry may contain a dispersant. The dispersant is usually a highly anionic product, either natural or synthetic. The dispersed fillers have a tendency of lowering the retention during papermaking. The explanation for this is that the anionic dispersant changes the ionic balance and inhibits the action of cationic retention aid. Dispersing at high solids creates a slurry with a higher proportion of fine particle size filler and it is these fine particles that lower the retention.

It should be noted that the use of fillers in general, calcium carbonate in particular, has two problems:

1. fillers have a small particle size which makes their retention hard to accomplish without using special additives. Moreover both fibres and fillers are negatively charged, consequently they repel each other thus making their retention more difficult, and

2. to maintain the mechanical properties of filled papers, dry strength additives are generally added[23].

2.4.1   Brief description of common available fillers

2.4.1.1 Clay

Clay was the most popular common papermaking filler or loading agent until alkaline sizing was introduced and the use of calcium carbonate became possible. It was also the most widely used pigment in the coating of paper and board. It improves the appearance of paper, which is characterized by gloss, smoothness, brightness and opacity, and of the greatest importance, it improves printability. It is cheap, plentiful, and stable, and provides generally good performance. The cheapness of clay lowers the cost per ton of finished paper. The inclusion of it improves the color of the paper and the general appearance.

The small clay particles are normally retained in the porous network of the cellulose fibres in which they fill up the spaces and increase the opacity and surface smoothness of the paper. The improved characteristics result in a better printing performance of paper and board.

Clay is a natural occurring mineral that is derived from the decomposition of feldspar by hydrothermal action[9, 24]. Its deposits exist in two forms, either in (i) the original place of formation (primary or residual), or (ii) as deposits of comparatively pure clay (secondary sedimentary). In the case of residual, the clay is intermixed with large amounts of kaolinitic material from which it has to be separated whilst in the case of sedimentary, the pure clay is carried from the original source by water and laid down as a clay bed deposits[9]. Clay is amenable for beneficiation that makes it ideal for an assortment of industrial applications[25]. The properties of clay from both types of deposits are modified by small quantities of non-kaolin minerals such as silica, which makes the clay abrasive, iron-stained titanium, or other minerals which worsen its colour and montmorillonite, which makes it to be viscous[9].

Clay is described as a relatively fine, white inert mineral with a number of interesting properties that give it a wide range of applications[26]. In chemical terms it is a hydrated aluminium silicate with individual particles in the form of thin hexagonal plates. It is considered as chemically inert and insoluble in water for all practical paper filling purposes. It is known that in suspension clay releases silicon into the surrounding water to the extent of a few parts per million[9]. Purity, rheology and particle geometry of the processed mineral, are one of the greatest characteristics that have a greater influence on the quality of paper. Opacity, gloss, printability and to a lesser extent, brightness of paper imparted by coating and filling with clay, are largely functions of particle size and particle size distribution[27].

2.4.1.2 Calcium carbonate (CaCO₃)

The most important $CaCO_3$ products added to the wet end of paper machines have calcite crystal form. In nature, $CaCO_3$ is abundantly provided in the form of limestone deposits, marble deposits, and chalk deposits. Of these three, chalk deposits are by far the softest and most easily converted into suitable filler. Precipitated $CaCO_3$ (PCC)

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can be produced by "calcining" limestone at very high temperature to drive of CO_2, "slaking" the resulting lime by addition of water, and then treating the resulting "milk of lime" suspension with CO_2 gas under highly controlled conditions of temperature, pH and ionic composition.

$CaCO_3$ is used as filler for making bright, opaque paper at minimum cost. It also keeps the pH in the alkaline range (unless controlled with acid tolerant technology). The rosette form of PCC tends to produce a bulkier sheet of paper, when calendered it yields improved smoothness at given levels of caliper. The dissolution of $CaCO_3$ under acidic pH conditions was the cause for the revolutionary worldwide switch from acid to alkaline or slightly neutral papermaking.

2.4.1.3 Titanium dioxide (TiO_2)

Titanium dioxide is produced at various locations worldwide. It has a remarkable effect on paper brightness and opacity due to its high brightness and refractive index. TiO_2 strongly absorbs UV light, thus adversely reducing the performance of optical brightening agents (OBA). The only limit for its use is its high costs.

2.4.1.4 Talc (Magnesium silicate)

Talc is a natural occurring clay mineral, being a hydrated magnesium silicate. It is a very soft, low abrasive, chemically inert, platy water insoluble, organophilic, and hydrophobic pigment. As filler it provides excellent rotogravure printability. Talc can cause surface dusting problems.

2.5   Filler and optical properties

The opacity depends on the number of individual particles in the sheet structure namely, grammage, the number of surfaces in the structure and the differences in refractive index between the particles and the surrounding medium. The light scattering ability depends on the difference in refractive index between air (1.00) and cellulose (1.53) in an unfilled paper[28]. Clay, talc and $CaCO_3$ increase the opacity by creating air/cellulose and air/filler surfaces in the structure.

2.6 Effect of filler addition on the mechanical properties of paper

Optical properties improved at the expense of mechanical properties[28, 29, 30]. The paper strength depends on the extent to which the fibres are bonded to each other, i.e., interfibre bonding and the distribution of the fibres within the sheet, i.e., formation. Bonding is a result of the formation of hydrogen bonds between the fibre surfaces during drying. The bonds are easily disrupted and their overall strength is dependent on the extent to which the fibres overlap (contact area) and the intrinsic strength per unit area[29]. The decrease in mechanical properties depends partly on the fact that a filled sheet contains fewer fibres per unit grammage and partly on a blocking of fibre-fibre bonds. The bond between cellulose and filler is probably good while the bonds between the filler particles are poor[28]. This occurs because fillers have no strength properties of their own as a result they interfere with interfibre bonding[29]. Figure 1 shows the effect of filler content on strength and stiffness of paper. It can be said that a 10% increase in the filler decreases strength by about 20% while the effect on the toughness properties such as fold number is even greater.
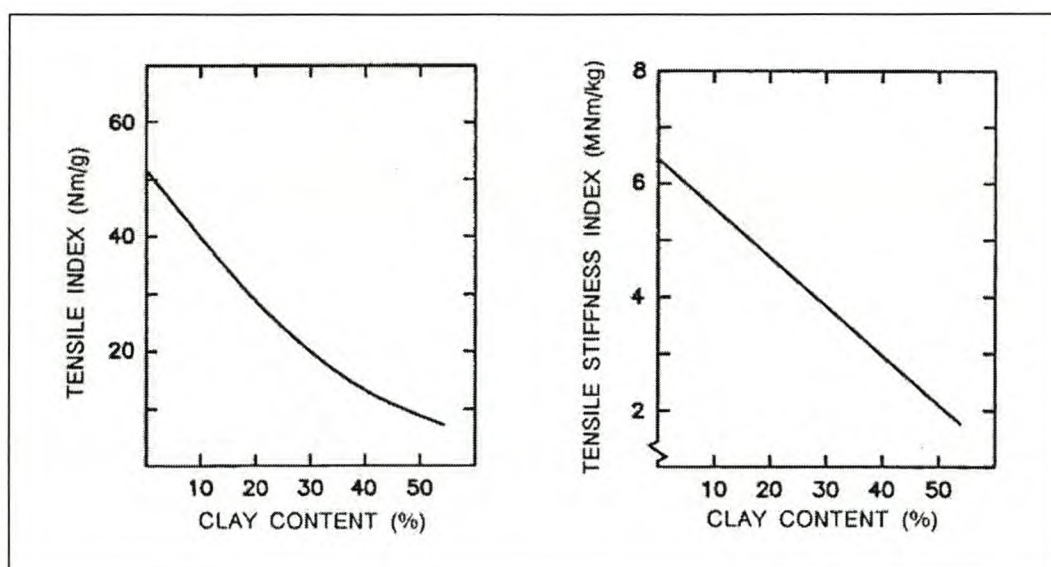
Figure 1: The effect of filler content on strength and stiffness of the paper.[28]

The effect on the mechanical properties depends on how the filler is distributed in the network structure. The filler can be distributed in three different ways (Figure 2)[28].
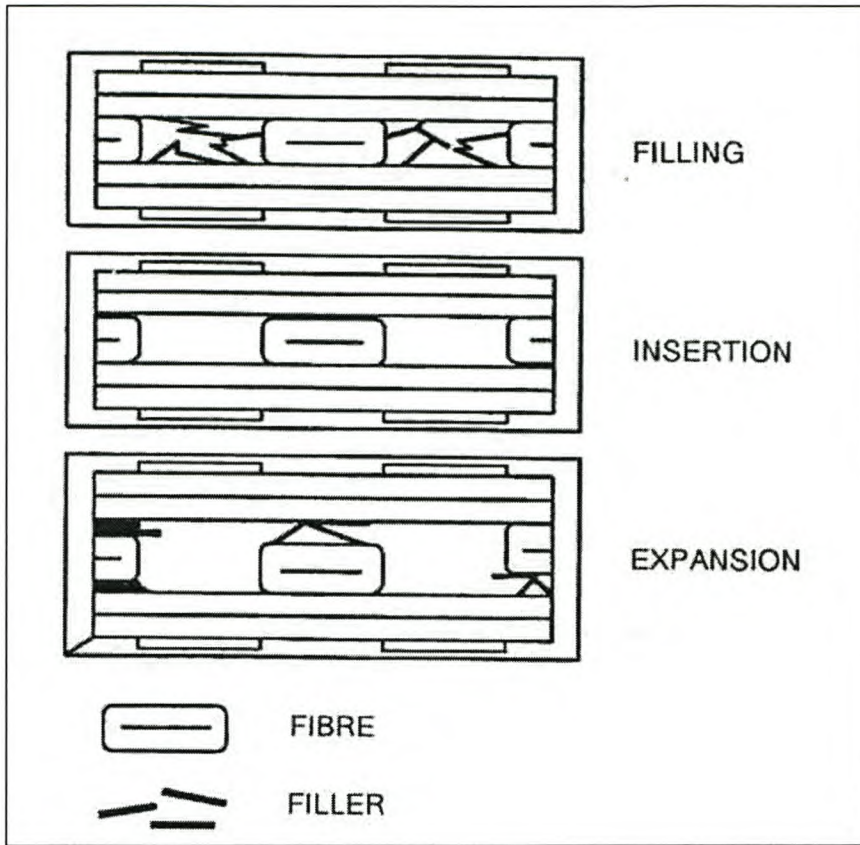
Figure 2: Three different ways of filler distribution.[28]

In filling, only the light scattering ability of the sheet is affected but not the mechanical properties. This is due to the fact that the stresses in the structure are transmitted via the fibre bonds. When the filler is inserted between the cellulose fibres, the mechanical properties can be improved provided that the adhesion between filler and cellulose is sufficiently high. Otherwise, both stiffness and strength decrease since no strength transfer takes place between the adjacent fibres. In this case, there is no marked improvement in the light scattering ability. In the expansion case, the filler affects both light scattering and mechanical properties of the filled sheet. Most added filler is found in the sheet as expanded material. Expansion leads to an increase in the number of potential stress concentration sites, such as cracks, notches, pores, etc, which is a disadvantage for the mechanical properties. The density of the paper increases with an increasing filler content. This is due to the fact that the density of mineral fillers is higher than that of cellulose fibres. Simultaneously, a thickness increase takes place since the filler expands the structure.

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2.7   The mechanism of retention

Retention of fines and filler particles involves two basic mechanisms, namely, coagulation of the particles and the bridging of the particles. Poor retention of particles can create disposal and deposit problems. High level of retention aids can help to prevent these problems. There are two kinds of retention that the papermakers are concerned with, namely: overall retention and first-pass or single pass retention[31, 32]. Overall retention refers to the retained fraction based on the initial quantity supplied in the manufacture and it is useful to understand the economics of the system. First-pass retention represents the retained fraction of a given material passing through the headbox slice. It indicates how efficiently the wire section succeeded in binding fibres, fillers and fines to form a continuous paper web. It should be regarded as being composed of two components: the long fibre retention and the fines retention. The long fibre retention values are normally very high and approach 100%. This is attributed to the fact that they are first efficiently filtered by the wire and then by the forming paper web[11, 33]. The fines fraction retention is found to be in the range of 30-70%. The lowest value of fines retention that can be tolerated depends on the water and solid losses from the machine.

All retention aids function by modifying the state of flocculation of the papermaking stock. Flocculation has an effect on sheet formation that must remain acceptable and on drainage, which must also be good. Retention aids aim to achieve complete separation between the particulate stock components on the wire. Retention aids function according to three main mechanisms[15, 37], (Figure 3) namely:

1. Charge neutralization: It is also known as effective charge mechanism. It is a destabilization mechanism, which is referred to the compression of the double layers to such an extent that the repulsive barrier is reduced, and the particles are coagulated due to the attraction forces between the particles[38]. The negative charge of cellulose fibres and the fillers is removed and the particles are no longer repelling each other. The added polymer neutralizes the particle charge. The flocculation effect is moderate and the flocs are less stable. The effect of alum is mainly based on charge neutralization.

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2. Patch model bridging (charge mosaic model): This refers to a local charge reversal of the particle surface with adsorbed oppositely charged polymers. The electrostatic interaction between the sites of opposite charge leads to aggregation[38]. The polymer chains of cationic retention aids can adhere on the negatively charged particles in positions similar to a mosaic pattern and thereby reversing the charge of individual areas. Fibre and filler zones, which remain negative, attract each other. This results in a stable flocculation. This mechanism applies mainly to synthetic retention aids of average molecular mass, for example polyethyleneimine (PEI) and polyamideamine (PAAM). There is no need for Zeta potential to be zero in order for patch flocculation to occur, instead there is often a maximum agglomeration in the region around the isoelectric point[38].

 3. Polymer bridging: Polymer bridges are formed if the polymer chains are long enough to overcome the electrostatic repulsion barrier. This is the case with compounds of high molecular mass, for example polyacrylamide (PAM). Polymer bridges are less stable to shear forces and exhibit a lower reflocculation tendency. The degree of extension, or length of the polymer in solution, greatly determines how well fines and fillers are retained via the bridging mechanism. It should be noted that the effect of agitation is irreversible.
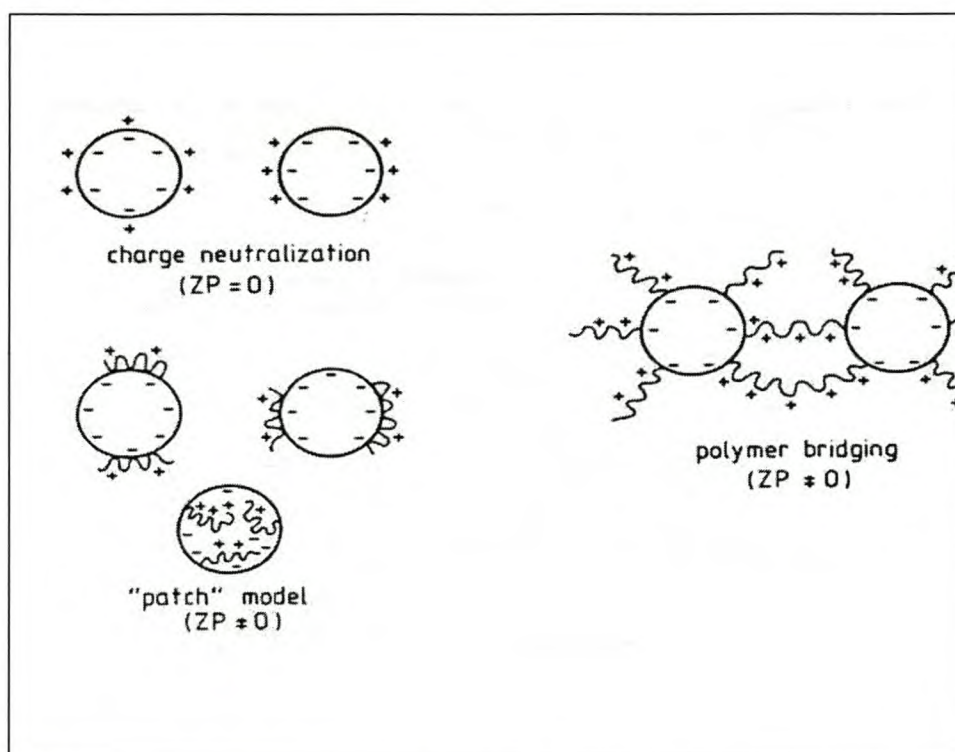
Figure 3: The three main flocculation mechanisms[15, 37].

Patch model-bridging produces soft flocs that are usually small and compact, which upon high turbulence break up easily. They show poor flocculation since they readily disperse during turbulence. Ideal flocs are those that have a compact structure, appropriate size, resistance to shear, and high retention properties[39]. When the turbulence subsides, the same level of aggregation can recur.

Hard flocs are formed through polymer bridging and they have a loose, voluminous structure. They show some resistance to high turbulence for a short period. They break irreversibly after subjection to longer periods of high turbulence. When hard flocs are produced for flocculation improvement, undesirable side effects such as poor paper formation and inferior sheet quality often result due to the voluminous structure of the flocs. Neutralization and/or patch flocculation are usually the mechanism of operation of low or moderately high molecular mass, high charge density polymers[40].

2.8   Retention and the use of retention aids

The use of retention aids, (cationic and anionic polymers), as wet end additives during the production of paper and board has a great effect on machine runnability and production economy. The most important benefits are greater retention of fines and fillers leading to higher solid content after wet pressing, a lower drying steam requirement per ton of product, a more uniform moisture profile, less shrinkage and a higher dry tensile strength[34]. The application of cationic polymers is normally limited by their effectiveness at economic levels of addition and by the quality of sheet formation.

Retention aids function by inducing or accelerating the coflocculation of fibrous and non-fibrous fines into larger flocs. These larger flocs can be more readily trapped and retained by the fibrous mat formed on the wire, provided that the flocs are stable enough to resist stresses encountered during the sheet-forming process. Improper selection or application of a retention aid can cause problems even though the products may provide substantial increase in single-pass or overall retention. As an example, overflocculation of pigments can be detrimental to the optical properties for which the pigments were used. Excessive fibre flocculation can lead to poor sheet

formation, and excessive non-fibrous particle flocculation can cause deposits on the machine or spots and specks in the paper[35].

It is necessary to add water-soluble polymeric flocculants to the pulp suspension before the filtration process begins. The retention aids function by causing the colloidal filler particles to deposit as microflocs onto fiber ensuring that the filler is retained in the paper[4]. Any normal retention aid can be used in this process of coflocculation. In conventional papermaking, retention aids do not only give filler retention but also cause long fiber to coflocculate so that paper formation deteriorates. The polymer needs little time to flocculate long fibers. If too much polymer is added, the paper may be cloudy due to unnecessary strong fine-filler macrofloc formation[8].

Forseberg and Ström[34] proved that in the absence of cationic polymers, a high retention of fines reduces the drainage rate. This was attributed to the fact that retention took place through filtration in the absence of the polymer, while the presence of the polymer resulted in a colloidal retention that gave the sheet a more open structure. They also showed that high retention and fast drainage were obtained at short contact time between the added polymer and the stock. Retention and especially drainage rate decreased with increase in contact time. This decrease was explained by deflocculation in which polymer chains were broken by high shear forces and poor reflocculation. Middleton and others[36] showed that the specific surface area of fibre is a factor that is affecting the retention of fillers. The retention improved as changing wood species and beating modified the specific surface area.

2.9   Drainage

Retention and drainage are closely related to formation, sheet uniformity and flocculation. The development of a uniformly distributed web is largely dependent on the drainage characteristics of the stock. These characteristics are functions of the physical properties of the pulp, such as fines content, fibre length, and degree of fibrillation. They also depend on chemical additives (formation, retention and drainage aids). Increased production rate and reduced energy consumption in the dryers are two known main advantages of better drainage. The greatest losses of fines and filler occur within the first 5-20% of the total drainage area of a paper machine

wet end[41]. This portion of the machine contributes to more than half of the total loss through the wire.

Coflocculation of fines and pigments seems to be a major mechanism by which polymeric drainage aids improve the drainage on paper machines[35]. Good drainage properties contribute towards the runnability of the machine[42]. The micro-flocs do not block the pores like the fines particles do; instead a more open and freely draining fibrous mat is formed. Drainage will be most rapid when the wet sheet has a large pore diameter, i.e., for a thick sheet. Obstructing the pores with fines means that the flow is restricted. Therefore, for maintaining a good drainage with a high retention of fines, the structure of the sheet has to be open. The pore radius is effectively reduced when the sheet is compressed. Varieties of forces interact to affect fines retention, uniformity of formation and drainage rate. There is also some evidence that some polymers may modify fibre surface properties in a way that enhances drainage[15].

Scott[43] reported that the water retention value of secondary fibre fines was considerably higher than that of coarse fibres. This high water retention value, coupled with the high surface area of fines, accounted for the ability to reduce drainage rates drastically and to produce sheet sealing on the forming section of the paper machines. Primary fines also reduced drainage but to a lesser degree, and this was attributed to the fact that they are less swellable. Filler fines also reduce drainage rate but to an even lesser degree.

In coflocculation, it had been found that if an anionic fibre is associated with anionic fibrils and lamellas, which partly adhere to the fibre, the lamellas would spread out from the fibre surface due to electrostatic repulsion. This naturally will decrease the drainage rate on the papermaking wire. However, if the fibrils are decharged and positively recharged while the fibres are still remaining anionic, they will deposit on the fibre surface and the drainage rate will improve[9].

2.10 Anionic trash

2.10.1 Definition

Charge characteristics and the distribution of charges over the molecule are of great importance for the absorption and recharging ability of additives. Anionic trash is defined as those detrimental substances or organic materials that occur as total anionic dissolved oligomers and polymers[44, 45, 46]. These detrimental substances influence paper machine runnability by decreased fibre swelling and extended beating rates. The quantity of dissolved organic materials depends mainly on the composition of the furnish, the method of manufacture, degree of the system closure prevailing and temperature[42]. Closed or partly closed systems may contain considerable amounts of organic materials, especially when mechanical pulp is used in the furnish. The release of these organic materials varies depending on factors such as ionic strength, pH, temperature and the presence of other organics in the backwater which may induce desorption of material from the surface of the furnish solids[15].

2.10.2 The origin and control of anionic trash

Paper is a mixture of fibres and fines, to which often fillers and other additives are added. Due to their negative charge, the retention of particles of colloidal nature (fines and fillers) in a forming sheet is not efficient. The magnitude and total quantity of charge have a significant effect on the retention of pigments, dyes, internal size, on drainage and on flocculation[7, 44]. Anionic trash originates from the soluble colloids that are released from wood pulp and waste paper, which are not adsorbed and build up sticky deposits in pipelines, refiners and on wires. Coated broke and recycled fibres contain anionic residues (stickies). These residues reduce the performance of retention and sizing agents, and they form deposits. As a result the quality of the paper and runnability of the machine are adversely affected. This results in dark spots and holes in the paper sheet, reduction in quality and productivity and a fall in the efficiency of cationic additives[30, 44].

Mechanical pulping and broke handling are the main sources of anionic trash, but a reduction of effluent discharge from the system also increases its concentration.

During the production and further treatment of mechanical pulp, wood components are released into the process waters of the paper mill. Mechanical pulps are seldom washed and therefore the dissolved and colloidal substances are normally carried over to the paper machine where they interfere with papermaking[50]. Anionic trash also results from a group of organic compounds in wood, which are extracted during pulping. The addition of starch in papermaking also contributes toward higher anionic trash load. The anionic surfactants used to prepare predispersed fillers also act as interfering substances[46].

The charge measurement control is necessary to maintain the stability at the wet-end. Cationic polymers that function as charge neutralizing and fixation agents serve to counteract the negative effects that anionic contraries have on fibre surface interactions[6]. Anionic trash should therefore be recharged by addition of low molecular cationic polymers, such as PEI, or anionic trash catchers, at the point in the system, where its concentration is the highest. Minimizing the use of a furnish at high temperature or at high pH can also reduce it. A retention aid like PAM, for example, is a long-chain, low cationic charged polyelectrolyte that will flocculate suspended anionic solids. Anionic trash in comparison is a colloidal dissolved, highly anionic charged oligomer or polymer and a short-chain molecule. To neutralize and thereby to eliminate colloidal dissolved matter it is thus necessary to use chemicals of similar structure, but opposite charge. Coagulants (fixing agents), being short-chain, highly cationic charged polyelectrolytes, fulfill these requirements[30, 44]. However, it should be noted that the demand of cationic flocculants increases with an increase of fines in the suspension. Furthermore, the colloidal fraction (under 5μm) is said to adsorb 50 times more cationic flocculant than the fines fraction of 10-100μm[24]. The aggregation of anionic trash with inexpensive retention aids such as cationic starches or especially developed slightly more expensive fixatives had been found to represent a new and promising technology to remove anionic trash with the paper web. These chemicals when added to the paper making stock flocculate and possibly fixate the anionic trash to larger fibres. The anionic trash is then removed with the paper[38]. The Streaming Current Detector (SCD) has been used for measuring the charge.

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2.10.3 Effect of anionic trash on retention and drainage

High concentration of anionic trash is a source of microbial growth and frequent reasons for web breaks and lower water removal capacity because of clogging wires and felts. The blocking effect of anionic trash on beating auxiliaries and strength increasing agents leads to high-energy costs. In addition there is a loss of retention and dewatering which have bad consequences on drainage due to clogging of wires and felts[38, 44].

Due to the negative charge of pulp fibres and dispersed pigments[30, 47], the effectiveness of cationic retentionn aids is decreased in a forming neutral polymer complexes thus causing a high cationic demand. The more negative, or the higher the Zeta potential, the greater the repulsion and, therefore, the greater the stability[53]. As the Zeta potential approaches zero, the negative charge becomes less effective, as a result of the addition of positively charged chemicals, and the conditions become favourable for flocculation and consequent precipitation. It was shown that retention and drainage decreased with an increase in anionic trash[6]. This was due to the fact trash is affecting the electrokinetics of the furnish by increasing the electronegative Zeta potential. When the Zeta potential was more electronegative, retention and drainage decreased. Freeness improved with an increase in cationic addition until the end of cationic demand plateau was reached[52]. Therefore, maximum drainage usually occurs at the end of cationic demand plateau. Maximum and physical strength properties also occur at that same point. Cationic demand is found to correlate well with the amount of anionic material present[48]. Anionic trash interferes with the performance of cationic retention aids. Figure 4 illustrates the effect of anionic trash on retentionn of clay when Kraft method was used.

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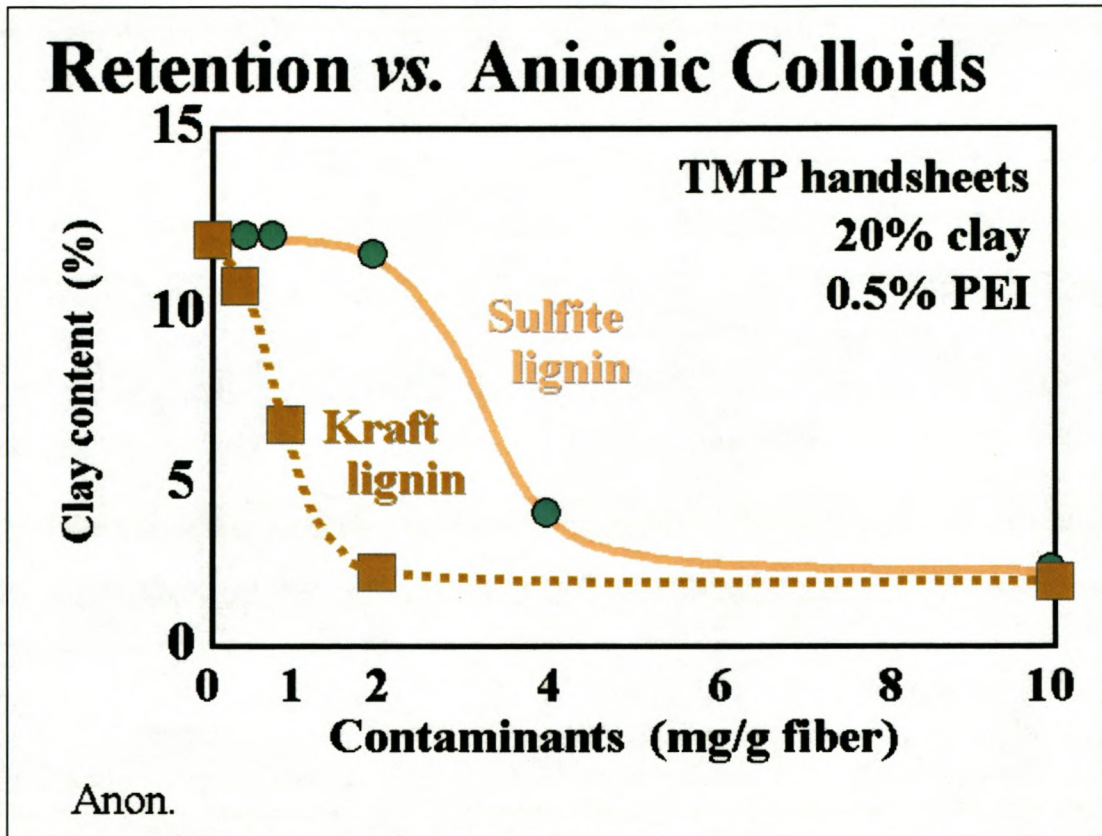
Figure 4: Effect of anionic trash on retention of clay .[49]

CHAPTER 3

EXPERIMENTAL

3.1 Raw materials

Table 3: The raw materials used

Mechanical pulp	Groundwood pulp for fines generation was obtained from Mondi Merebank in Durban.
Fibre furnish	Bleached long fibre (*Pinus patula* / *Pinus elliotii*) and bleached short fibre (*Eucalyptus grandis*).
Retention aids	Cationic PAM (Fennopol) from SA Paperkem Polydadmac from SA Paperkem
Charge neutralizer	Scavenger (Primco) from SA Paperkem
Filler	Kaolin filler grade from Serina, Noordhoek

3.2 The description of apparatuses used

3.2.1 The Lechintech Streaming Current Detector (SCD)

The SCD was used to measure the charge of fibre furnish, fines and retention aids. It is an off-line instrument. The analyzer consists of three distinct parts. These are:

1) The body that houses the cell probe

2) The mechanical drive and

3) The electronic pack.

Figure 5: The Lechintech Streaming Current Detector

3.2.1.1 Principle

The SCD works on the principle of generating a current by forcing a flow of charged particles between the two electrodes. A continuous sample is directed into an annulus, inside which a displacement piston, or probe, oscillates at a fixed frequency. The oscillating movement of the piston causes the liquid sample to flow along the wall of the cell as shown in Figure 6.

The SCD was calibrated to give a negative reading if the particles in suspension are negatively charged, and a positive reading for a positively charged system.
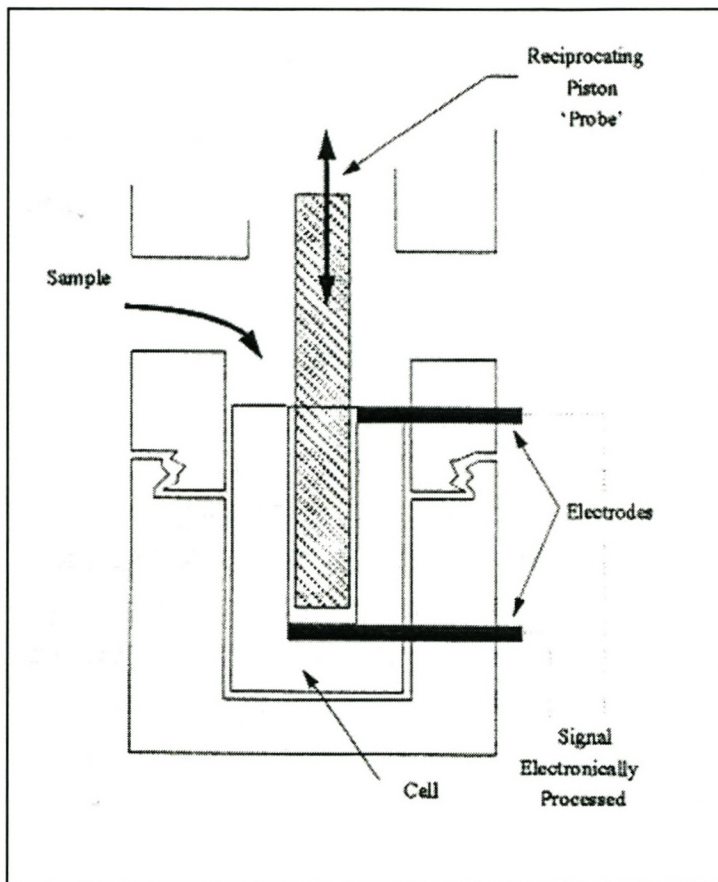
Figure 6: Schematic diagram of Streaming Current Detector
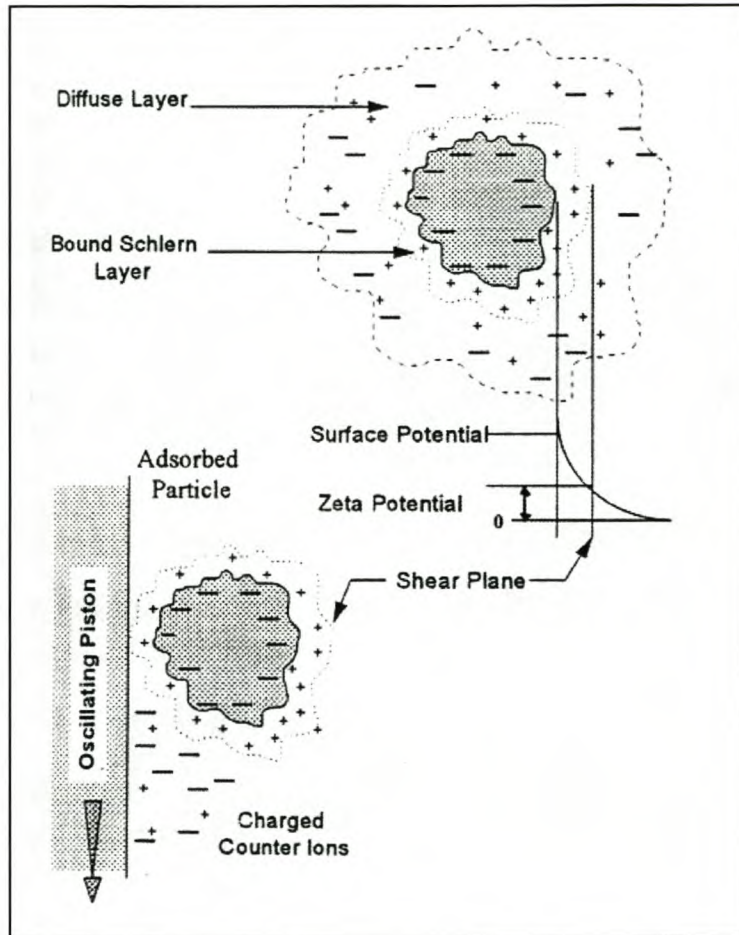
Figure 7: Development of Streaming Current Detector

The suspended particles are adsorbed onto the walls under the action of Van der Waal's forces (Figure 7). The mobile counter ions surrounding the charged particles or colloids are sheared near the surface of the particle and moved past the electrodes as the sample moves rapidly back and forth. The potential difference is induced between the two electrodes at the top and base of the cell. The resultant potential developed, proportional to charge, is electronically processed to give a reading of the streaming current in ICu (Ion Charge units).

3.2.2 The Dynamic Drainage Jar

The Dynamic Drainage Jar (DDJ) was used to separate fines and to measure the shear sensitivity of the retention aids. Shear sensitivity will determine if the retention aids will stand against strong shear forces. DDJ is described in detail by Britt *et al*.[10, 53]. It is normally used for determining the fines fraction of a paper stock sample, and the

retention of fines and filler under dynamic conditions. The Dynamic Drainage Jar is shown in Figure 8.
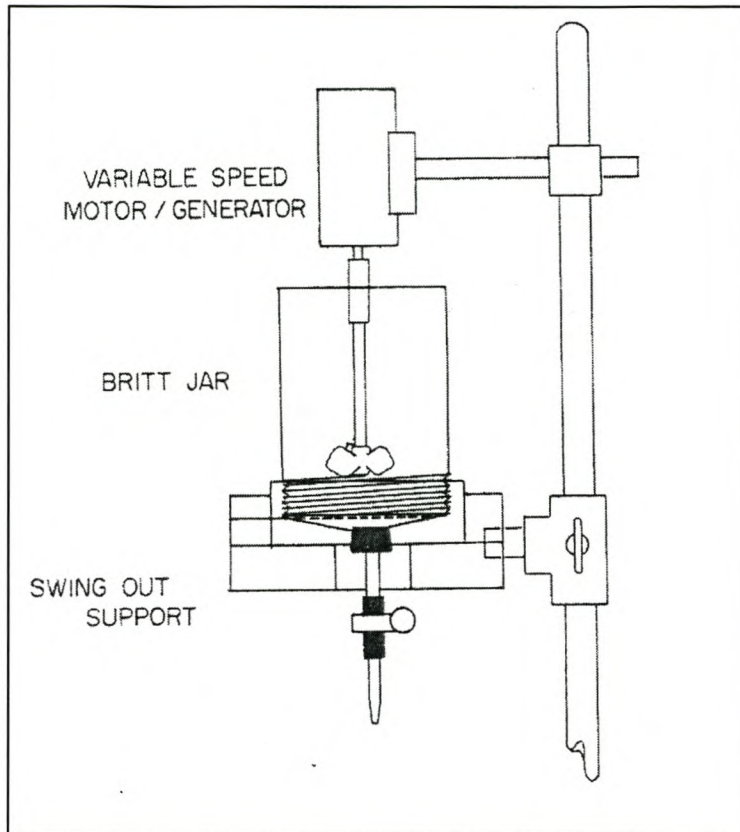
Figure 8: Schematic diagram of Dynamic Drainage Jar

3.2.3 The Frank Sheet Former

The machine combines sheet formation with wet pressing and drying. The forming section consists of a vertical filling chamber, wire part, suction chamber and water reservoir with necessary connections and controls. The filling chamber is made of Plexiglass. The filling chamber and suction chamber are separated by a wire. The water reservoir is responsible for a continuous flow of water. The dryer which consists of lid and heating chamber is used for drying the sheet formed. The Frank Sheet Former is shown in Figure 9.
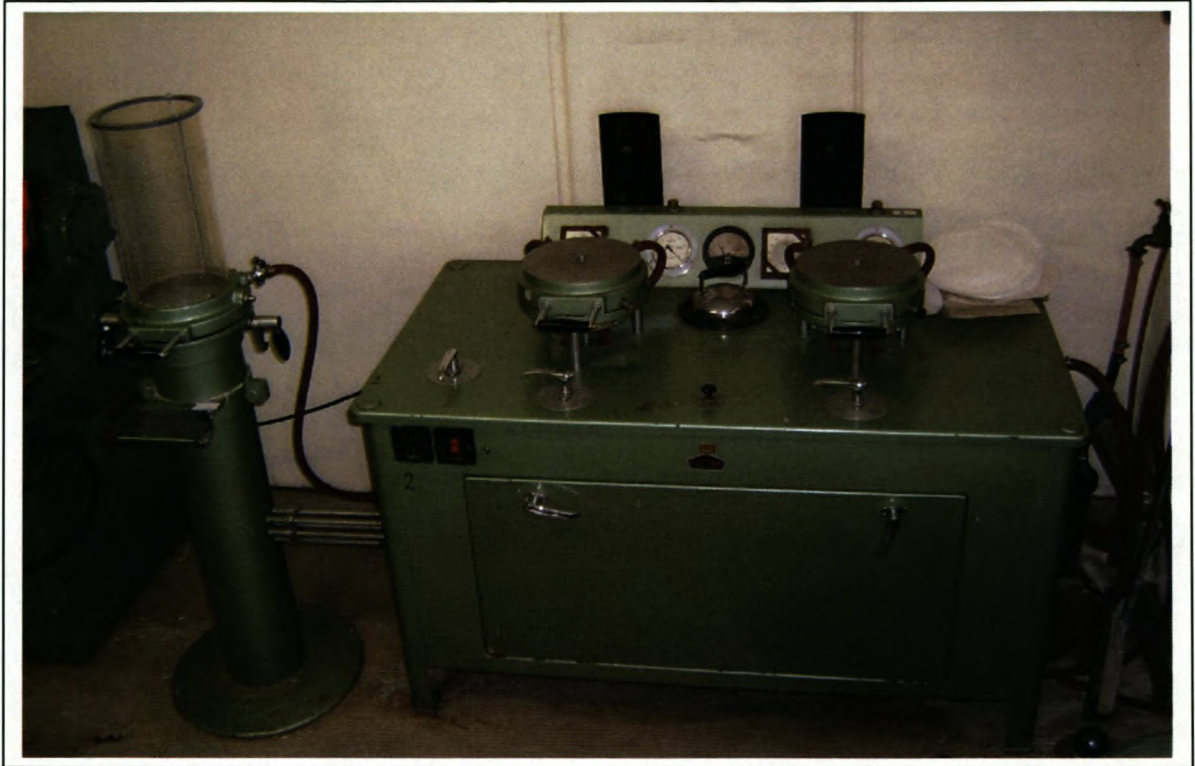
Figure 9: Frank Sheet Former

3.2.4 Other instruments used

- Metrohm pH meter, which was calibrated with buffer solutions of pH 4, pH 7 and pH9, for measuring pH of the fibre furnish, fines and retention aids.
- Scanning Electron Microscope (SEM), type LEO 1430VP, for microscopic investigation observations.
- Schoppler Riegler drainage tester for measuring the wetness of stock.

3.3 Methods

3.3.1 Evaluation of retention aids

The retention aids were evaluated as follows:

3.3.1.1 Shear sensitivity

A pulp sample was prepared at 0.4% consistency. The retention aid was dosed at 0.1% based on oven dry fibre mass. The retention aid was added to a litre of pulp and then the pulp suspension was filtered under the following three conditions:

(i) the pulp was filtered with no agitation (0 r.p.m.)

(ii) the pulp was filtered after agitation for 30 seconds at 500 r.p.m.

(iii) the pulp was filtered after 30 seconds agitation at 1000 r.p.m.

In the last two instances, the pulps were drained under continuous agitation.[52] The filtrate was collected and the solids content was determined by filtering the resulting filtrate through a membrane filter. The fines were then dried in an infra-red dryer. The amount of fines in the backwater is expressed as a percentage of the 2g oven dry fibre initially present in the fibre suspension.

3.3.1.2 Ionicity

The method of titrating the sample with an anionic polyelectrolyte was used to determine the ionicity of the retention aids. Retention aids were made up to 0.005% concentration. Starting with 10ml Polydadmac, a few drops of toluidine blue indicator were added, stirred constantly until the test solution turned to a light blue. The test solution was slowly titrated with 0,001N stock solution of polyethylene sulphide-sodium (PES-Na) until the shade changed from light blue to pale purple. The same procedure was followed for cationic PAM. For an evaluation of the titration, a reference specimen (a solution without any retention aid) was titrated and a calibration curve was plotted.

3.3.1.3 pH sensitivity of retention aids

The pH of a 0.1% solution (500 ml) of retention aid was recorded. The solution was then titrated with 0.1M HCl until the pH remained constant. The same procedure was followed with 0.1M NaOH to observe the behavior in the alkaline side. The pK_a values were calculated for each. pK_a is an extent to which cationic PAM and Polydadmac dissociated[57]. It was determined by considering the equilibrium:

$$H_2O + HPAM \quad H^+ + PAM^-$$

Then the equilibrium constant in water was given by

$$K_a = [H^+] [PAM^-]/ [HPAM]$$

K_a is the acidity constant. It is generally converted into pK_a

$$pK_a = -\log_{10} K_a$$

The K_a for cationic PAM and polydadmac were calculated to be 0.9×10^{-8} and 1.58×10^{-10} respectively. Then

For cationic PAM, $pK_a = -\log K_a$

$$= -\log (0.9 \times 10^{-8})$$
$$= 8.05$$

For polydadmac, $pK_a = -\log K_a$

$$= -\log (1.58 \times 10^{-10})$$
$$= 9.88$$

3.3.2 Fines generation

For latency removal, 40g (based on oven dry mass) of groundwood pulp was disintegrated in 1000 ml hot water 10 minutes. Then the pulp suspension was transferred to the Lampen mill and beaten for 40 minutes (10 000 rpm). The beaten pulp was then transferred to the Dynamic Drainage Jar and the particles passing through a 100-mesh screen were collected in a 1000 ml container. The separation was stopped when the particles where no longer passing through the screen (visual detection). The fine particles were allowed to settle for 3 days after which the clear water was decanted. The same procedure was repeated until a sufficient quantity of fines was collected. 800 g was collected. The charge and pH of fines were measured with SCD. Figures 10, 11 and 12 show the SEM micrographs for groundwood pulp, fines generated from groundwood pulp and fines with filler particles, respectively.
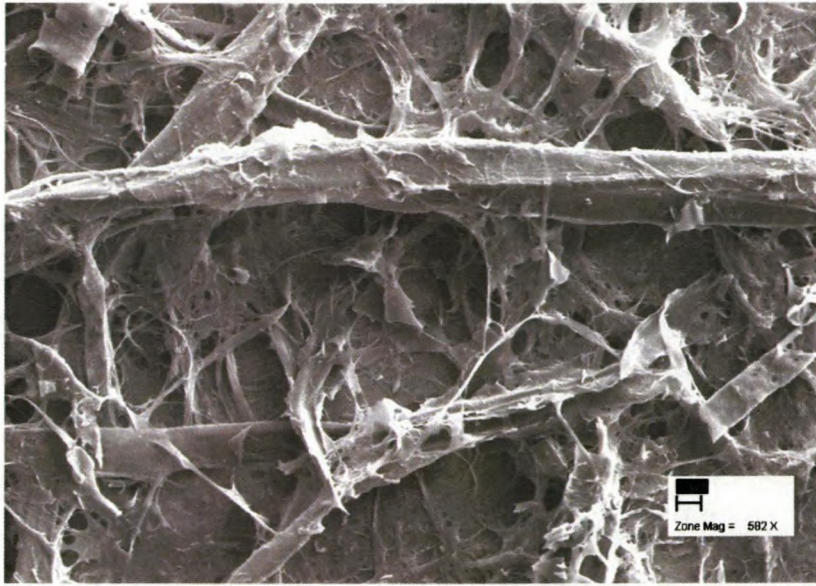
Figure 10: SEM micrograph of groundwood pulp (Magnification 582 X)
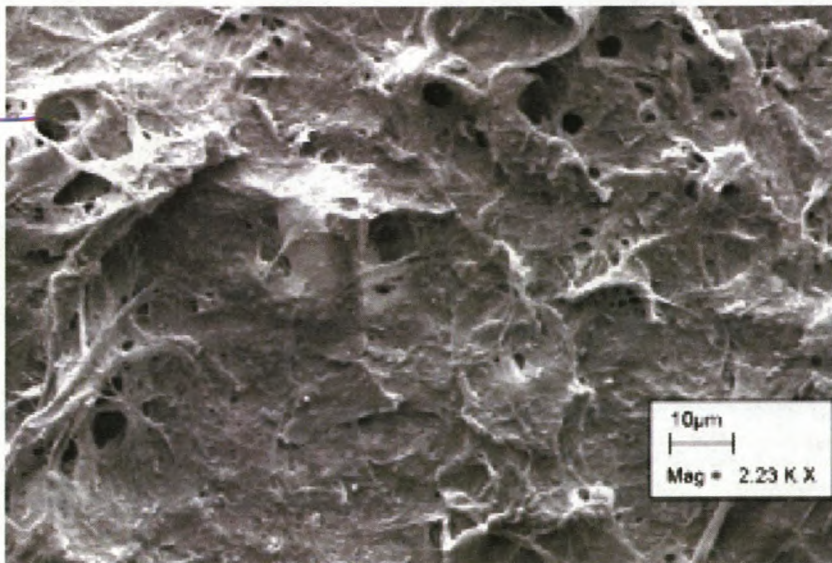
Figure 11: SEM micrograph of fines generated from groundwood pulp

(Magnification 2230 X)
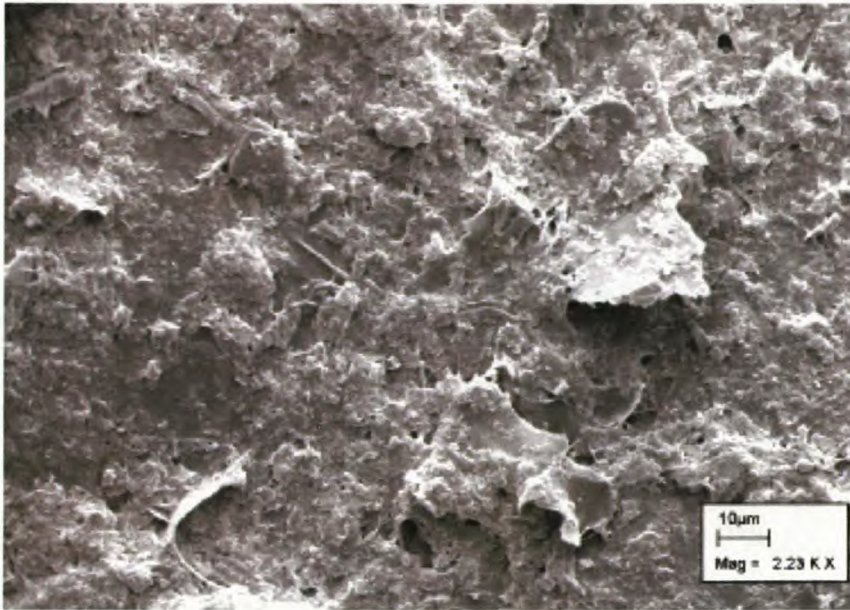
Figure 12: SEM micrograph of fines with 30% filler (Magnification 2230 X)

3.3.3 Beating and handsheet formation

The fibre furnish was beaten with a Voith overhead beater at 3.5% consistency to 30^0SR. Following this, 30g oven dry mass of 85% : 15% (hardwood / softwood mix) of the beaten fibre was disintegrated in 2000ml hot water for latency removal, after which it was diluted to 15 l with tap water to obtain a fibre suspension of 0,2 g/l solid. The dilute fibre suspension was kept agitated. Meanwhile 20g oven dry mass of fines was disintegrated in 2000 ml hot water for latency removal. It was then diluted with 5000 ml tap water. The pH, charge and °SR of the fibre suspension were measured. Following this, 10 beakers were filled each with dry 10% kaolin based on oven dry mass of the furnish. The clay was dispersed with water. The two polymers, cationic PAM and Polydadmac, were made up to solutions of 0.1% and 0.05% concentration. To each beaker 50ml of fines was added and diluted to about 100ml with water and stirred. 3 ml of each polymer solution was added to the fines-filler mixture and stirred gently for 30 seconds then added to the beaker, which contained 1*l* of pulp suspension and a handsheet was formed with Frank Sheet Former. The ^{0}SR, charge and pH were measured before the handsheet was formed. Table 4 shows the experimental variables. Ten handsheets were made for each variable.

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Table 4: Experimental variables

Variable	Levels of variable		
Filler addition	10%	20%	30%
Cat. PAM	0.05% 0.1%	0.05% 0.1%	0.05% 0.1%
Polydadmac	0.05% 0.1%	0.05% 0.1%	0.05% 0.1%
Charge (ICu)	-0.1 -1.5 -2.5	-0.1 -1.5 -2.5	-0.1 -1.5 -2.5
Fibre only	-	-	-
Filler alone	10%	20%	30%
Filler + fines	10%	20%	30%

3.3.4 Evaluation of sheet properties

All handsheets were conditioned for 48 hours at 55% relative humidity and 20°C before being tested. The handsheets for testing strength properties were cut with the aid of a die-cutter. The handsheet properties were evaluated for each set of 10 handsheets according to the following methods[55].

Table 5: TAPPI test methods used on handsheets

Test	Method
Burst strength	TAPPI standard T403 om-91
Tear strength	TAPPI standard T403 om-88
Tensile strength	TAPPI standard T 404 om-87
Opacity	TAPPI standard T 425 om-91
Air permeability	TAPPI standard T 460 om-88
Brightness	TAPPI standard T452 os-77

The ash content of the paper was determined by igniting the paper in a muffle furnace at 900^0 C for 1 hour (TAPPI standard T 413 om-85). The percentage of filler retention was calculated by expressing the ash content as a percentage of the amount of filler added initially to the stock. A correction factor of 1.163 was used in the calculation to compensate for the bound water driven off the kaolin during ignition[2].

The print quality of some of the handsheets coflocculated with fines and filler particles was evaluated by means of determining the oil penetration of the paper surface using the IGT Printability Tester. Approximately 1ml of oil was rolled into the surface of the paper under pressure to form a stain. The length of the stain was measured. The oil penetration was calculated as the reciprocal value of the stain length.

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CHAPTER 4

RESULTS AND DISCUSSION

4.1 Raw materials

The size of the charge plays a significant role on the efficiency of chemical additives and their effect on drainage and retention. Both the fines and fibre furnishes were found to have a high negative charge, -11.70 ICu and -9.82 ICu, respectively. For cationic PAM and Polydadmac, the charge was highly positive but varied with the respective solids concentrations (see Table 6). Comparing these two polymers, Polydadmac had a higher cationic charge than the cationic PAM. The fibre furnish was beaten to 30^0 SR and its pH was slightly acidic for the fibres and close to neutral for the fines. The cationic PAM was found to be more acidic than Polydadmac. At low concentrations (0.05%), both were found to be more acidic than at high concentration. The values are given in Table 6.

Table 6: Charge, pH and °SR of the raw materials

Retention aid (%)	pH	Charge (ICu)	Wetness (°SR)
Fibre furnish	6.3	-9.82	30
Fines	6.9	-11.70	-
0.05% Cat. PAM	3.9	7.18	-
0.05% Polydadmac	5.8	7.85	-
0.1% Cat. PAM	4.1	9.97	-
0.1% Polydadmac	6.7	10.65	-
Filler (clay)	5.2	-5.18	-

The charge for the fibre furnish was adjusted to -0.12 ± 0.02, -1.5 ± 0.3 and -2.5 ± 0.3 ICu. This was done in order to evaluate the effect of charge on handsheet properties and filler retention. Semnarayan[6] agreed with the fact that the running of papermaking systems near zero Zeta potential results in certain improvements. He also agreed with

the fact that the optimum retention does not necessary have to occur at the iso-electric point. The pH was adjusted to the optimum level, being around 4.7 to 5.3. This was done because at this range Semnarayan[6] proved that retention increased. pH is the most vital chemical variable that affects the quality and production performance in a paper mill. pH influences the solubility of the dissolved chemical substances in the system. At higher pHs Semnarayan[6] found that retention decreased due to the increase in the hydroxyl ion (OH⁻) concentration. This created a greater repulsion between the negatively charged fines and fibres thus impairing microflocculation. The charge, pH and SR^0 are recorded in Tables 7 – 10. Charge and pH ranges are shown in brackets.

Table 7: pH, Charge and °SR when fines were coflocculated with 10%, 20% and 30% filler (Charge is –0.12 ± 0.02 ICu and pH range: 4.7 - 5.3)

Retention aid	10% filler			20% filler			30% filler		
	pH	Charge	°SR	pH	Charge	°SR	pH	Charge	°SR
0.05% cat.PAM (filler only)	5.0	-0.11	12	4.9	-0.12	13	5.0	-0.10	18
0.05% cat.PAM(filler+fines)	5.1	-0.11	10	5.0	-0.10	10	5.1	-0.10	16
0.05% PolyD (filler+fines)	4.8	-0.11	20	4.9	-0.11	20	4.8	-0.15	20
0.1% cat.PAM (filler only)	4.9	-0.13	22	4.8	-0.11	18	4.8	-0.12	20
0.1% cat. PAM (filler+fines)	5.0	-0.12	20	5.0	-0.12	16	5.1	-0.13	21
0.1% PolyD (filler +fines)	5.1	-0.10	16	5.0	-0.13	13	5.0	-0.11	14

PolyD = Polydadmac

Table 8: pH, Charge and °SR when fines were coflocculated with 10%, 20% and 30% filler (Charge is −1.5 ± 0.3 and pH range: 4.7 - 5.3)

Retention aid	10% filler			20% filler			30% filler		
	pH	Charge	°SR	pH	Charge	°SR	pH	Charge	°SR
0.05% cat.PAM (filler only)	4.8	-1.52	14	4.9	-1.52	15	5.1	-1.49	20
0.05% cat.PAM(filler+fines)	4.8	-1.50	15	4.8	-1.53	15	4.9	-1.50	17
0.05% PolyD (filler+fines)	5.0	-1.49	16	5.0	-1.51	19	5.0	-1.51	18
0.1% cat.PAM (filler only)	4.9	-1.53	20	4.9	-1.50	19	5.0	-1.48	21
0.1% cat. PAM (filler+fines)	4.8	-1.50	17	4.9	-1.52	17	4.8	-1.52	19
0.1% PolyD (filler +fines)	5.0	-1.51	16	5.0	-1.49	15	5.0	-1.48	17

Table 9: pH, Charge and °SR when fines were coflocculated with 10%, 20% and 30% filler (Charge is −2.5 ± 0.3 and pH range: 4.7 - 5.3)

Retention aid	10% filler			20% filler			30% filler		
	pH	Charge	°SR	pH	Charge	°SR	pH	Charge	°SR
0.05% cat.PAM (filler only)	4.9	-2.51	15	4.8	-2.52	14	4.9	-2.47	13
0.05% cat.PAM(filler+fines)	5.0	-2.58	10	4.9	-2.57	9	5.0	-2.50	11
0.05% PolyD (filler+fines)	4.9	-2.50	22	5.0	-2.52	16	5.0	-2.51	17
0.1% cat.PAM (filler only)	4.8	-2.55	13	5.0	-2.53	15	4.8	-2.49	15
0.1% cat. PAM (filler+fines)	4.8	-2.53	9	4.8	-2.51	8	4.9	-2.48	8
0.1% PolyD (filler +fines)	4.9	-2.51	19	5.0	-2.54	14	5.1	-2.53	18

4.2 Evaluation of retention aids

4.2.1 Shear sensitivity

Figure 13 demonstrates the results obtained when the shear sensitivity was evaluated.
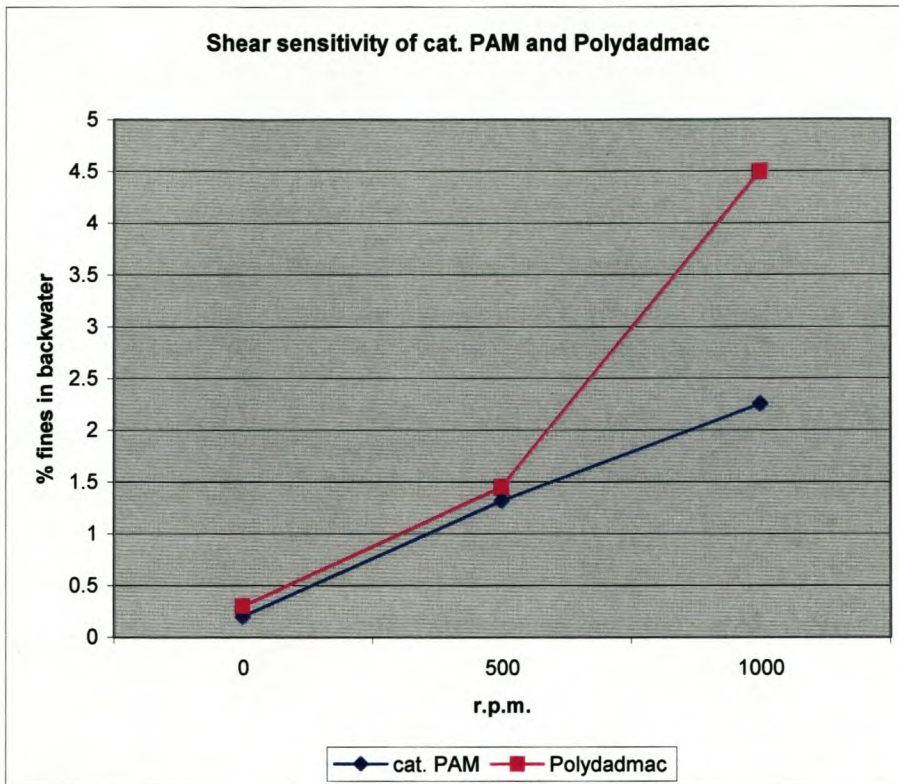
Figure 13: Shear sensitivity of cat. PAM and Polydadmac

At vigorous agitation flocculation was disturbed and a large amount of fines were found in the backwater especially when Polydadmac was used (see Figure 13). The filtration speed of backwater at high agitation was much faster. This indicated that the flocs formed by the addition of retention aid could be destroyed when submitted to strong shearing force. It was noted that the retention of fines decreased with increasing turbulence. These results agree with Britt and Unbehend[53] findings.

4.2.2 Ionicity

The ionicity results are shown in Figures 15 and 16. Figure 14 shows the calibration curve.
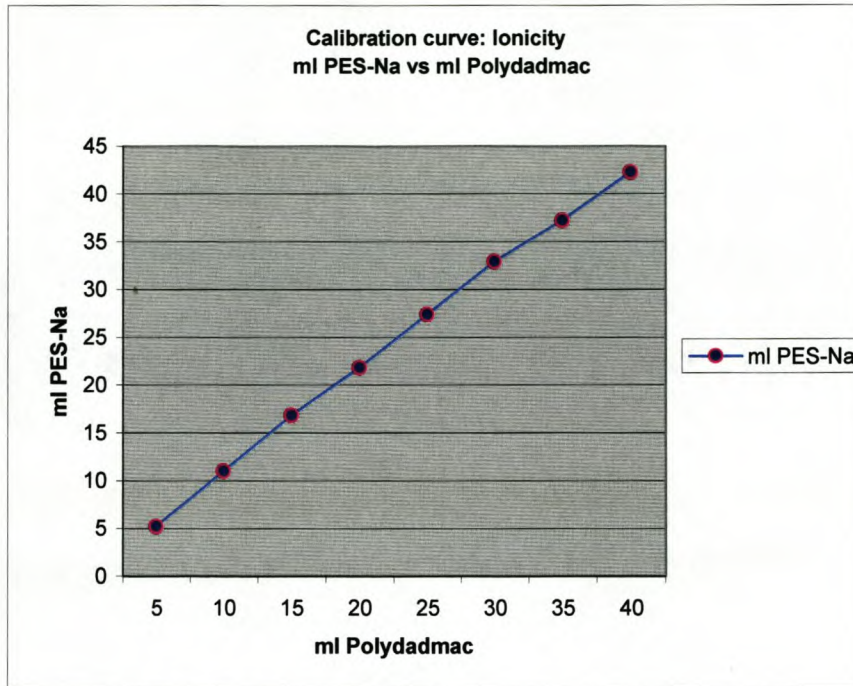
Figure 14: Calibration curve for Ionicity

Both the retention aids were of cationic in nature. At lower pH, rate of consumption of PES-Na was higher. Polydadmac showed the highest consumption of PES-Na. It was noted that the amount of PES-Na used decreased with decreasing hydrogen ion concentration $[H^+]$. Therefore it can be said that Polydadmac had a higher cationic charge than cationic PAM. Ionicity of the cationic retention aids is dependent to a certain extent on the pH of the stock suspension. The lower the pH, the more strongly cationic the retention aid generally will be. For the negatively charged cellulose, the lower the pH, the less negative is the fibre charge.
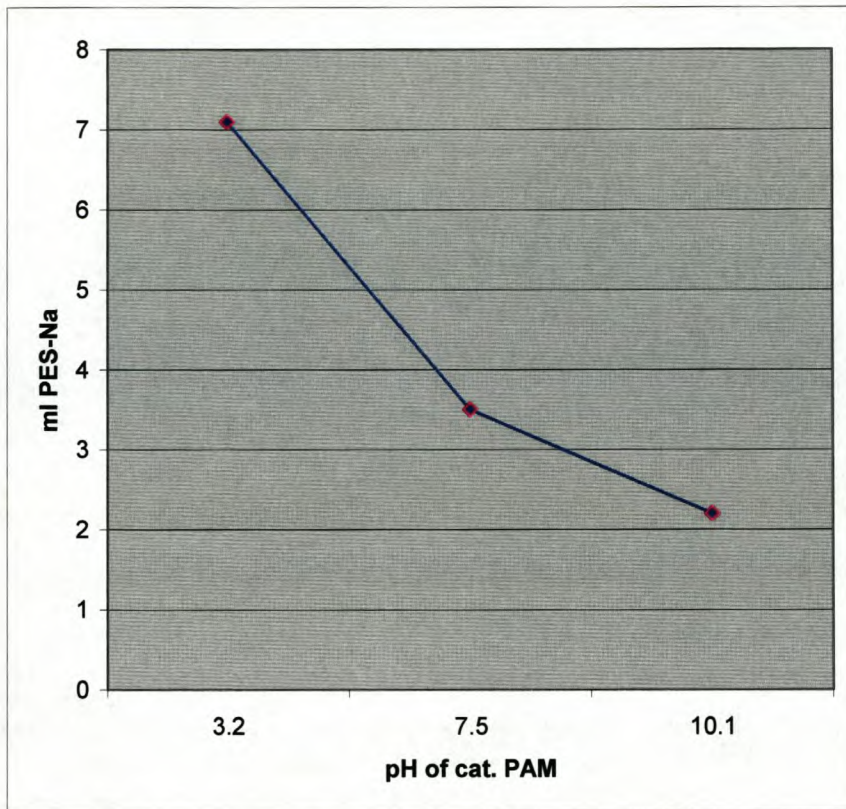
Figure 15: Ionicity of cationic PAM
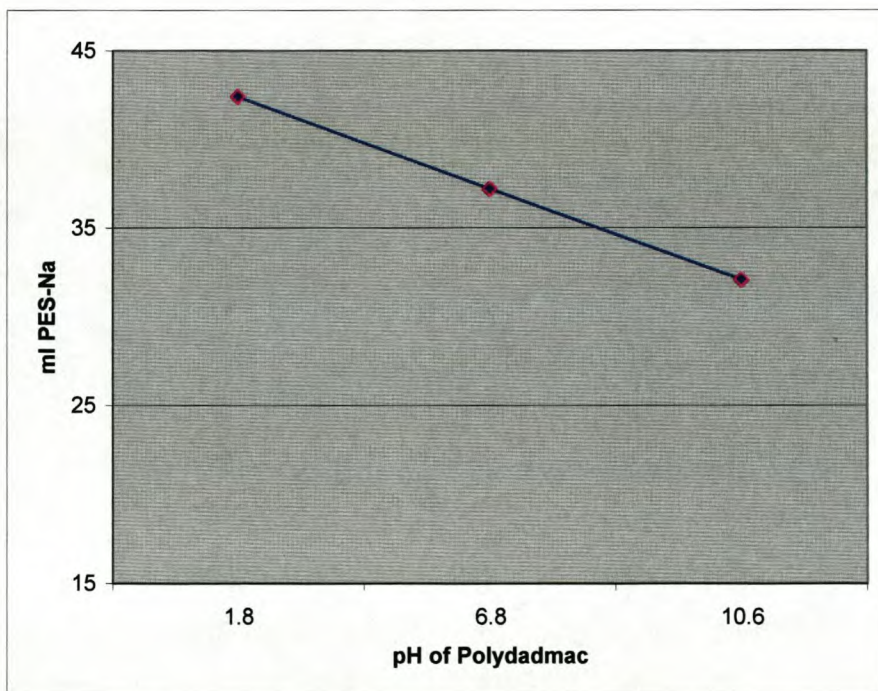
Figure 16: Ionicity of Polydadmac

4.2.3 pH Sensitivity

The smaller the numerical value of pK_a, the stronger the acid to which it refers. From the pK_a values calculated it was found that cationic PAM was a stronger acid than the Polydadmac. This means that the cat. PAM is expected to perform better than Polydadmac. pH sensitivity is shown in Figure 17.

Figure 17: pH Sensitivity for the retention aids

4.3 Evaluation of handsheet strength properties

Tables 10-18 show the values obtained for handsheet strength evaluation, filler retention, opacity, air permeability and ash content. These values are also graphically illustrated in Figures 18-23. Ten handsheets were tested for each set of variables unless otherwise stated.

Table 10: Evaluation of paper properties when fines were coflocculated with 10% filler (charge range -0.12 ± 0.02 ICu)

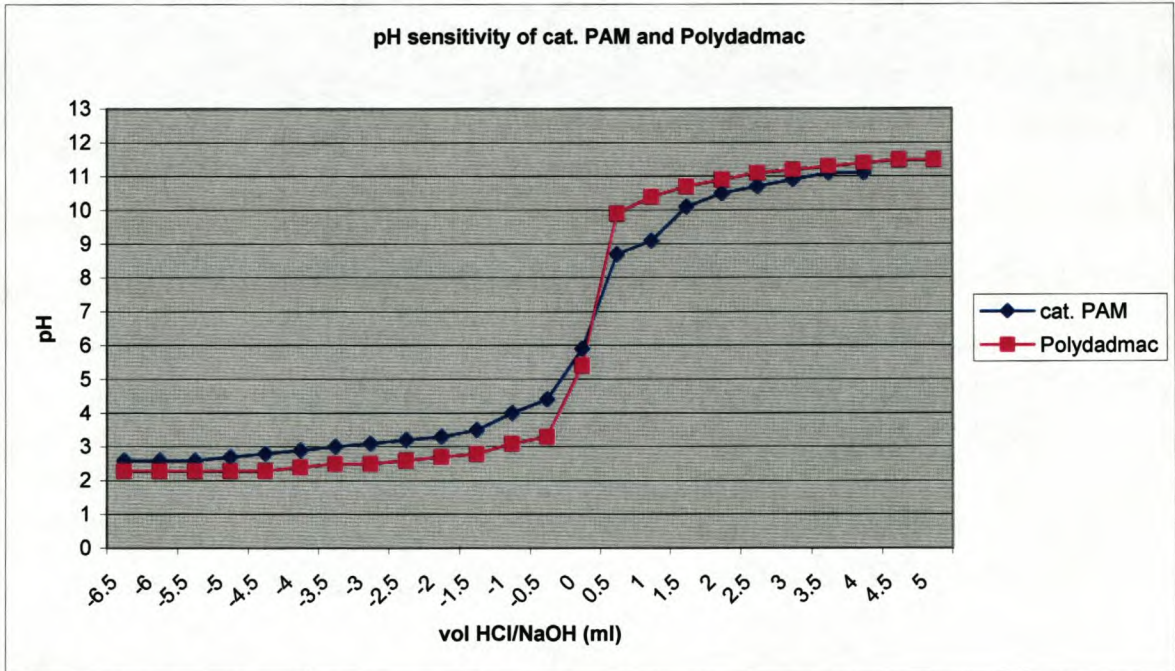| Retention aid (%) → Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	81.06	69.00	66.82	81.88	64.89	65.36
Breaking length (km)	5.95 ± 0.02	1.93 ± 0.07	4.48 ± 0.16	4.15 ± 0.17	2.33 ± 0.38	4.55 ± 0.15	4.08 ± 0.15
Burst index (kPa.m²/g)	1.50 ± 0.04	0.67 ± 0.03	1.62 ± 0.18	1.47 ± 0.09	0.79 ± 0.08	1.49 ± 0.414	1.35 ± 0.07
Tear index (mN.m²/g)	7.44 ± 0.03	4.88 ± 0.02	6.96 ± 0.17	6.06 ± 0.09	5.24 ± 0.34	6.69 ± 0.48	6.32 ± 0.72
Opacity (%)	84.97 ± 0.46	91.28 ± 0.62	90.41 ± 0.28	88.95 ± 0.55	90.78 ± 0.40	89.44 ± 0.48	88.21 ± 0.56
Air perm. (s/100ml)	3.00 ± 0.67	1.00 ± 0.04	3.00 ± 0.04	3.00 ± 0.05	2.00 ± 0.42	3.00 ± 0.04	3.00 ± 0.47
Ash content (%)	0.58 ± 0..01	7.75 ± 0.06	8.33 ± 0.042	6.01 ± 0.00	8.15 ± 0.042	7.78 ± 0.02	7.18 ± 0.03
Filler retention (%)	-	77.50 ± 0.48	83.30 ± 0.21	60.10 ± 0.00	81.5 ± 0.42	77.80 ± 0.21	71.80 ± 0.28

Standard deviation is shown as ±

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Table 11: Evaluation of paper properties when fines were coflocculated with 10% filler (charge range −1.5 ± 0.3 ICu)

Retention aid (%) → / Paper properties ↓	no fines,no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	63.65	79.68	65.64	64.09	80.10	66.99
Breaking length (km)	5.95 ± 0.02	2.62 ± 0.21	2.87 ± 0.06	1.99 ±0.09	2.35 ± 0.020	2.69 ± 0.16	1.87 ± 0.10
Burst index (kPa.m²/g)	1.50 ± 0.04	1.01 ± 0.12	0.71 ± 0.05	0.90 ± 0.03	0.88 ± 0.02	0.80 ± 0.09	0.88 ± 0.02
Tear index (mN.m²/g)	7.44 ± 0.03	4.60 ± 1.12	5.41 ± 0.55	5.29 ± 0.41	4.83 ± 0.88	5.40 ± 0.44	5.08 ± 0.15
Opacity (%)	84.97 ± 0.46	90.68 ± 0.24	90.40 ± 0.22	89.15 ± 0.49	91.38 ± 0.41	90.51 ± 0.38	88.70 ± 0.58
Air perm. (s/100ml)	3.00 ± 0.67	3.00 ± 0.01	4.00 ± 0.03	5.00 ± 0.02	4.00 ± 0.02	3.00 ± 0.02	5.00 ± 0.01
Ash content (%)	0.58 ± 0..01	7.65 ± 0.04	8.03 ± 0.04	7.09 ± 0.06	7.99 ± 0.14	7.64 ± 0.06	7.15 ± 0.07
Filler retention (%)	-	76.5 ± 0.42	80.30 ± 0.42	70.90 ± 0.57	79.90 ± 1.41	76.40 ± 0.57	71.50 ± 0.71

Standard deviation is shown as ±

Table 12: Evaluation of paper properties when fines were coflocculated with 10% filler (charge range -2.5 ± 0.3 ICu)

Retention aid (%) → Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	64.78	81.97	67.04	75.93	83.55	66.68
Breaking length (km)	5.95 ± 0.02	2.58 ± 0.06	2.69 ± 0.11	2.14 ± 0.06	2.08 ± 0.07	2.60 ± 0.06	2.29 ± 0.08
Burst index (kPa.m²/g)	1.50 ± 0.04	0.94 ± 0.02	0.77 ± 0.05	0.48 ± 0.03	0.72 ± 0.04	0.73 ± 0.04	0.61 ± 0.02
Tear index (mN.m²/g)	7.44 ± 0.03	4.54 ± 0.43	5.36 ± 0.11	5.01 ± 0.14	4.61 ± 0.19	5.45 ± 0.04	5.03 ± 0.03
Opacity (%)	84.97 ± 0.46	90.53 ± 0.03	90.43 ± 0.13	89.18 ± 0.48	91.56 ± 0.14	90.98 ± 0.25	89.01 ± 0.14
Air perm. (s/100ml)	3.00 ± 0.67	3.00 ± 0.02	2.00 ± 0.01	3.00 ± 0.01	3.00 ± 0.01	3.00 ± 0.04	3.00 ± 0.01
Ash content (%)	0.58 ± 0..01	7.15 ± 0.14	8.14 ± 0.03	7.01 ± 0.01	7.88 ± 0.03	7.55 ± 0.03	7.14 ± 0.06
Filler retention (%)	-	71.50 ± 1.41	81.40 ± 0.28	70.10 ± 0.14	78.80 ± 0.28	75.50 ± 0.28	71.40 ± 0.57

Standard deviation is shown as ±

Table 13: Evaluation of paper properties when fines were coflocculated with 20% filler (charge range -0.12 ± 0.02 ICu)

Retention aid (%) → / Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	84.88	71.83	72.02	87.55	71.36	67.05
Breaking length (km)	5.95 ± 0.02	1.51 ± 0.02	4.51 ± 0.05	4.15 ± 0.09	1.62 ± 0.03	4.68 ± 0.02	4.08 ± 0.19
Burst index (kPa.m²/g)	1.50 ± 0.04	0.50 ± 0.06	1.26 ± 0.08	1.35 ± 0.02	0.42 ± 0.05	1.28 ± 0.02	1.48 ± 0.04
Tear index (mN.m²/g)	7.44 ± 0.03	4.11 ± 0.10	6.04 ± 0.06	6.68 ± 0.09	3.58 ± 0.29	6.38 ± 0.05	6.86 ± 0.03
Opacity (%)	84.97 ± 0.46	91.97 ± 0.14	91.55 ± 0.24	90.28 ± 0.12	93.04 ± 0.34	91.98 ± 0.32	89.57 ± 0.13
Air perm. (s/100ml)	3.00 ± 0.67	1.00 ± 0.01	3.00 ± 0.01	5.00 ± 0.02	1.00 ± 0.01	4.00 ± 0.02	5.00 ± 0.01
Ash content (%)	0.58 ± 0..01	14.39 ± 0.03	14.73 ± 0.01	12.21 ± 0.09	14.01 ± 0.06	14.53 ± 0.03	12.99 ± 0.04
Filler retention (%)	-	71.95 ± 0.14	73.65 ± 0.07	61.05 ± 0.42	70.05 ± 0.28	72.65 ± 0.14	64.95 ± 0.21

Standard deviation is shown as ±

Table 14: Evaluation of paper properties when fines were coflocculated with 20% filler (charge range -1.5 ± 0.3 ICu)

Retention aid (%) → Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	83.66	72.67	72.88	84.95	72.55	70.15
Breaking length (km)	5.95 ± 0.02	1.40 ± 0.05	3.51 ± 0.04	2.09 ± 0.06	1.44 ± 0.04	3.49 ± 0.02	2.16 ± 0.05
Burst index (kPa.m²/g)	1.50 ± 0.04	0.60 ± 0.05	0.87 ± 0.04	0.56 ± 0.07	0.65 ± 0.02	0.91 ± 0.02	0.66 ± 0.02
Tear index (mN.m²/g)	7.44 ± 0.03	3.66 ± 0.06	4.01 ± 0.02	6.01 ± 0.02	3.47 ± 0.04	5.50 ± 0.22	6.33 ± 0.06
Opacity (%)	84.97 ± 0.46	91.95 ± 0.26	91.41 ± 0.18	90.18 ± 0.13	92.99 ± 0.13	91.69 ± 0.10	89.47 ± 0.12
Air perm. (s/100ml)	3.00 ± 0.67	4.00 ± 0.02	4.00 ± 0.01	4.00 ± 0.01	4.00 ± 0.01	4.00 ± 0.01	4.00 ± 0.02
Ash content (%)	0.58 ± 0..01	12.83 ± 0.03	12.98 ± 0.01	12.11 ± 0.02	12.69 ± 0.03	13.85 ± 0.02	12.35 ± 0.07
Filler retention (%)	-	64.15 ± 1.20	64.90 ± 0.07	60.55 ± 0.14	63.45 ± 0.14	69.25 ± 0.14	61.75 ± 0.35

Standard deviation is shown as ±

Table 15: Evaluation of paper properties when fines were coflocculated with 20% filler (charge range -2.5 ± 0.3 ICu)

Retention aid (%) → Paper properties ↓	no fines,no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	85.38	85.04	89.99	91.35	90.20	90.15
Breaking length (km)	5.95 ± 0.02	1.82 ± 0.07	2.54 ± 0.09	1.98 ± 0.04	1.48 ± 0.06	2.16 ± 0.03	1.65 ± 0.03
Burst index (kPa.m²/g)	1.50 ± 0.04	0.61 ± 0.05	0.67 ± 0.02	0.75 ± 0.02	0.43 ± 0.01	0.57 ± 0.05	0.69 ± 0.02
Tear index (mN.m²/g)	7.44 ± 0.03	2.38 ± 0.03	4.55 ± 0.03	4.78 ± 0.07	3.96 ± 0.02	3.83 ± 0.06	4.98 ± 0.07
Opacity (%)	84.97 ± 0.46	91.58 ± 0.15	91.38 ± 0.57	90.07 ± 0.04	91.60 ± 0.09	91.56 ± 0.19	89.11 ± 0.32
Air perm. (s/100ml)	3.00 ± 0.67	0.94 ± 0.02	3.00 ± 0.01	2.00 ± 0.01	2.00 ± 0.01	2.00 ± 0.04	2.00 ± 0.02
Ash content (%)	0.58 ± 0..01	12.78 ± 0.13	13.57 ± 0.05	11.98 ± 0.06	12.60 ± 0.42	12.69 ± 0.01	12.09 ± 0.04
Filler retention (%)	-	63.90 ± 0.64	67.85 ± 0.25	59.90 ± 0.28	63.00 ± 2.12	63.45 ± 0.07	60.45 ± 0.21

Standard deviation is shown as ±

Table 16: Evaluation of paper properties when fines were coflocculated with 30% filler (charge range -0.12 ± 0.02 ICu)

Retention aid (%) → Paper properties ↓	no fines,no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	69.86	75.70	74.81	70.42	75.56	72.94
Breaking length (km)	5.95 ± 0.02	2.04 ± 0.04	3.22 ± 0.03	3.87 ± 0.09	2.56 ± 0.03	3.81 ± 0.05	3.79 ± 0.04
Burst index (kPa.m²/g)	1.50 ± 0.04	0.91 ± 0.04	1.26 ± 0.04	1.15 ± 0.02	0.97 ± 0.02	1.11 ± 0.03	1.22 ± 0.05
Tear index (mN.m²/g)	7.44 ± 0.03	3.56 ± 0.01	5.53 ± 0.04	6.08 ± 0.04	4.92 ± 0.02	5.54 ± 0.02	6.38 ± 0.04
Opacity (%)	84.97 ± 0.46	93.26 ± 0.30	92.01 ± 0.09	92.45 ± 0.15	92.82 ± 0.12	92.78 ± 0.13	91.82 ± 0.18
Air perm. (s/100ml)	3.00 ± 0.67	4.00 ± 0.01	2.00 ± 0.01	5.00 ± 0.02	5.00 ± 0.01	4.00 ± 0.02	4.00 ± 0.02
Ash content (%)	0.58 ± 0..01	20.74 ± 0.06	19.38 ± 0.03	17.45 ± 0.03	19.58 ± 0.04	20.15 ± 0.03	19.39 ± 0.06
Filler retention (%)	-	69.13 ± 0.19	64.60 ± 0.10	58.17 ± 0.09	65.26 ± 0.14	67.17 ± 0.09	64.60 ± 0.19

Standard deviation is shown as ±

Table 17: Evaluation of paper properties when fines were coflocculated with 30% filler (charge range -1.5 ± 0.3 ICu)

| Retention aid (%) → Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	88.51	91.58	89.66	90.01	92.19	87.71
Breaking length (km)	5.95 ± 0.02	1.79 ± 0.04	2.20 ± 0.06	1.61 ± 0.08	1.61 ± 0.06	1.89 ± 0.02	1.57 ± 0.11
Burst index (kPa.m²/g)	1.50 ± 0.04	0.71 ± 0.04	0.67 ± 0.04	0.58 ± 0.04	0.73 ± 0.06	0.55 ± 0.03	0.57 ± 0.06
Tear index (mN.m²/g)	7.44 ± 0.03	2.80 ± 0.04	4.19 ± 0.04	4.28 ± 0.03	3.15 ± 0.01	4.21 ± 0.01	4.23 ± 0.02
Opacity (%)	84.97 ± 0.46	92.88 ± 0.10	92.00 ± 0.19	92.42 ± 0.13	92.65 ± 0.16	92.69 ± 0.17	91.80 ± 0.10
Air perm. (s/100ml)	3.00 ± 0.67	1.00 ± 0.02	3.00 ± 0.01	4.00 ± 0.02	1.00 ± 0.01	3.00 ± 0.03	4.00 ± 0.01
Ash content (%)	0.58 ± 0..01	19.15 ± 0.01	19.55 ± 0.01	18.81 ± 0.03	19.41 ± 0.04	19.91 ± 0.10	18.97 ± 0.03
Filler retention (%)	-	63.83 ± 0.05	65.17 ± 0.05	62.70 ± 0.10	64.70 ± 0.14	66.37 ± 2.69	63.23 ± 0.13

Standard deviation is shown as ±

Table 18: Evaluation of paper properties when fines were coflocculated with 30% filler (charge range -2.5 ± 0.3 ICu)

Retention aid (%) → Paper properties ↓	no fines, no filler, no ret. aid	0.05% cat.PAM filler only	0.05% cat.PAM filler+fines	0.05% PolyD filler+fines	0.1% cat.PAM filler only	0.1% cat.PAM filler+fines	0.1% PolyD filler+fines
Grammage (g/m²)	60.45	89.62	90.41	89.98	91.20	93.28	89.61
Breaking length (km)	5.95 ± 0.02	1.51 ± 0.03	2.09 ± 0.04	1.49 ± 0.07	1.42 ± 0.05	1.84 ± 0.05	1.53 ± 0.06
Burst index (kPa.m²/g)	1.50 ± 0.04	0.68 ± 0.04	0.55 ± 0.03	0.39 ± 0.05	0.54 ± 0.03	0.44 ± 0.04	0.41 ± 0.04
Tear index (mN.m²/g)	7.44 ± 0.03	2.20 ± 0.05	3.93 ± 0.04	3.98 ± 0.01	2.74 ± 0.02	3.81 ± 0.07	3.85 ± 0.03
Opacity (%)	84.97 ± 0.46	92.38 ± 0.16	92.04 ± 0.21	92.40 ± 0.11	92.33 ± 0.30	92.63 ± 0.15	91.80 ± 0.09
Air perm. (s/100ml)	3.00 ± 0.67	4.00 ± 0.01	3.00 ± 0.04	1.00 ± 0.02	1.00 ± 0.02	3.00 ± 0.01	1.00 ± 0.01
Ash content (%)	0.58 ± 0..01	19.08 ± 0.03	18.81 ± 0.06	18.55 ± 0.01	19.35 ± 0.04	19.42 ± 0.01	18.68 ± 0.06
Filler retention (%)	-	63.60 ± 0.10	62.70 ± 0.18	61.83 ± 0.05	64.50 ± 0.14	64.73 ± 0.05	62.67 ± 0.20

Standard deviation is shown as ±

4.3.1 Breaking length
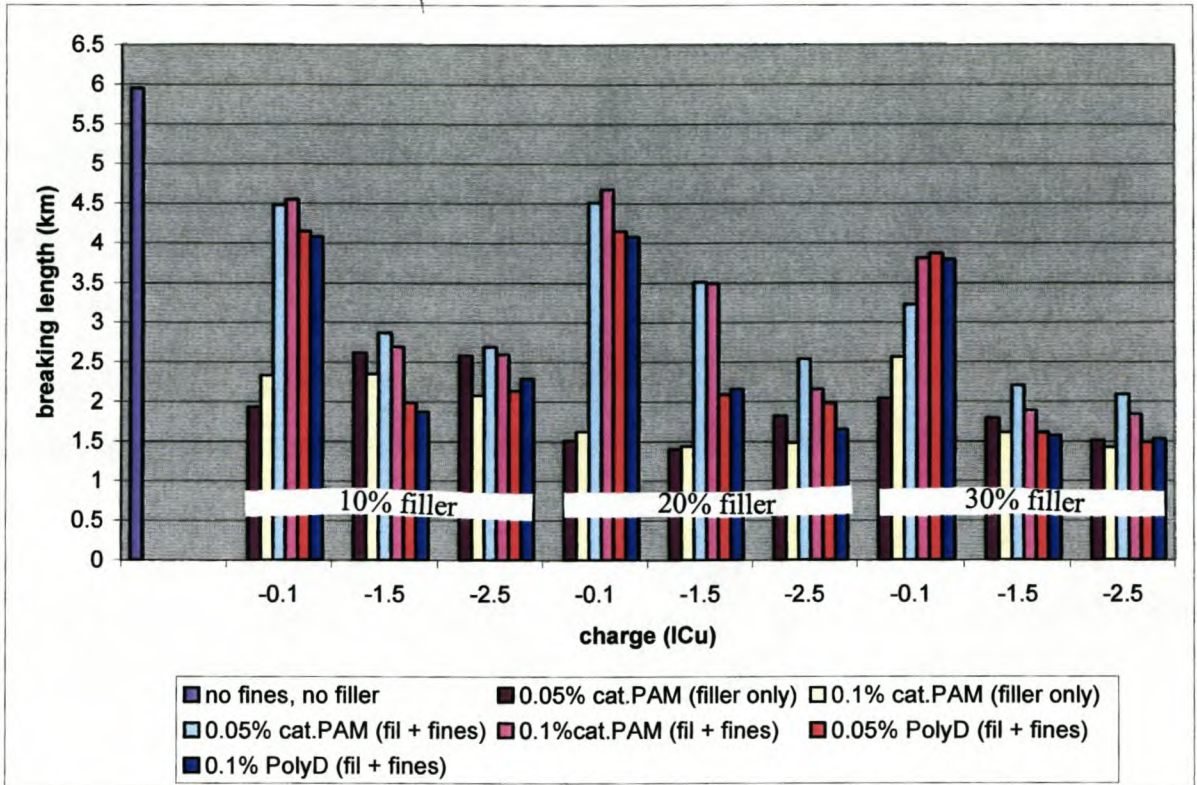
Figure 18: The effect of coflocculation on breaking length.

As expected, a high breaking length was obtained for the handsheets which contained no filler. For a 20% filler addition coflocculated with fines, at –0.1 ICu, the cationic PAM handsheets gave the best breaking length value. Figure 18 clearly shows that the breaking length dropped correspondingly as the stock charge moved further away from zero to a more negative value. Where only filler was added, the loss in breaking length was severe. This means that an increase in the amount of filler has a negative impact on strength properties. This agrees with Gerischer *et.al*[2], Eklund[28] and Hayes[29] findings. The coflocculation of filler with fines reduced the drop in breaking length as a result of the fibre-to-fibre bond protection. The chances of filler particles occupying the spaces between fibres were reduced. It is true to say that as the filler content increased, the breaking length decreased, but with coflocculation the drop in strength could be considerably reduced. The breaking length also was dependent on the nature of the stock charge.
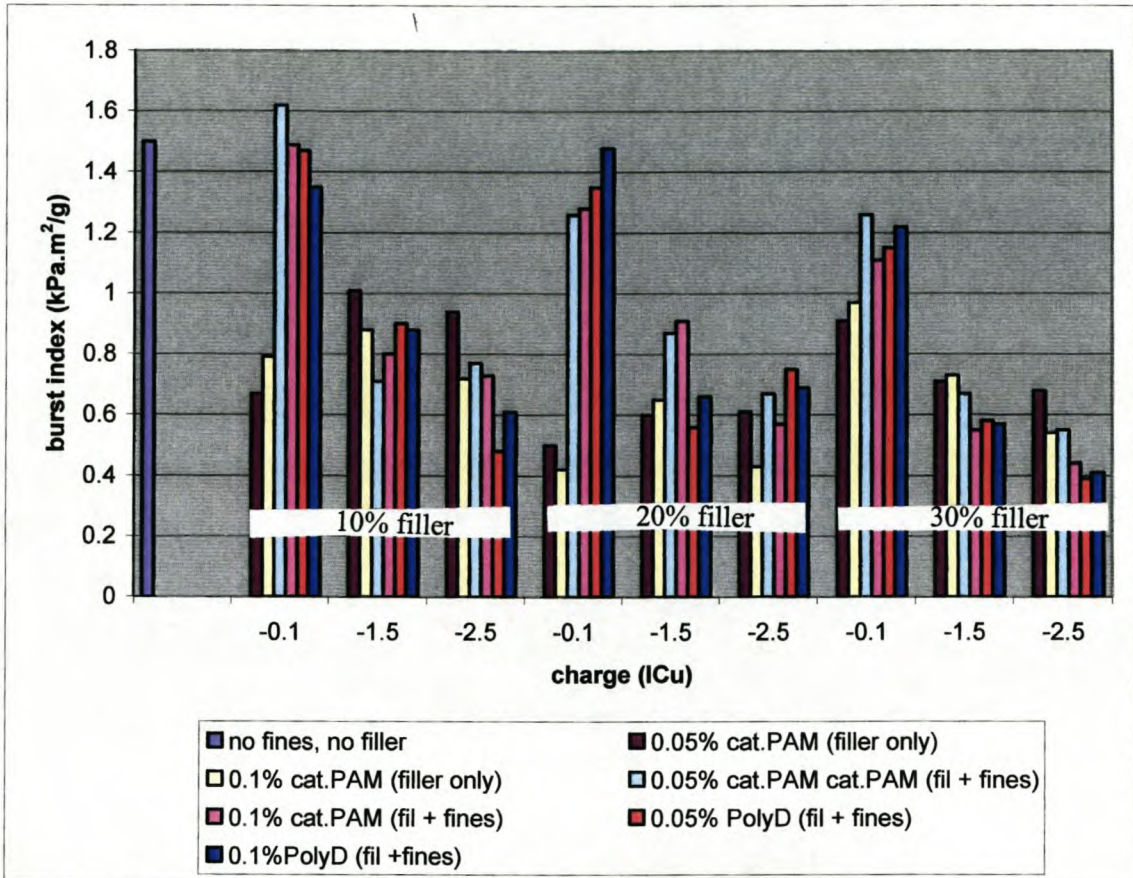
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4.3.2 Burst index

Figure 19: The effect of coflocculation on burst index.

For 10% filler addition coflocculated with fines, at –0.1 ICu, the cationic PAM gave the highest value in burst index of 1.62 kPa.m^2/g (Figure 19). For 20% filler coflocculated with fines, at –0.1 ICu, the Polydadmac handsheets recorded the highest value. For 30% filler coflocculated with fines, at -0.1 ICu, the cat. PAM handsheets gave the highest value. It was noticed that where the filler was not pretreated with fines and as the amount of filler addition increased, the burst index showed a reduction. Hayes[29] also noticed that the burst index dropped with an increase in the amount of filler added. The burst index seemed to be dependent upon the charge. As the charge moved further away from zero to the more negative side, the burst index dropped correspondingly.
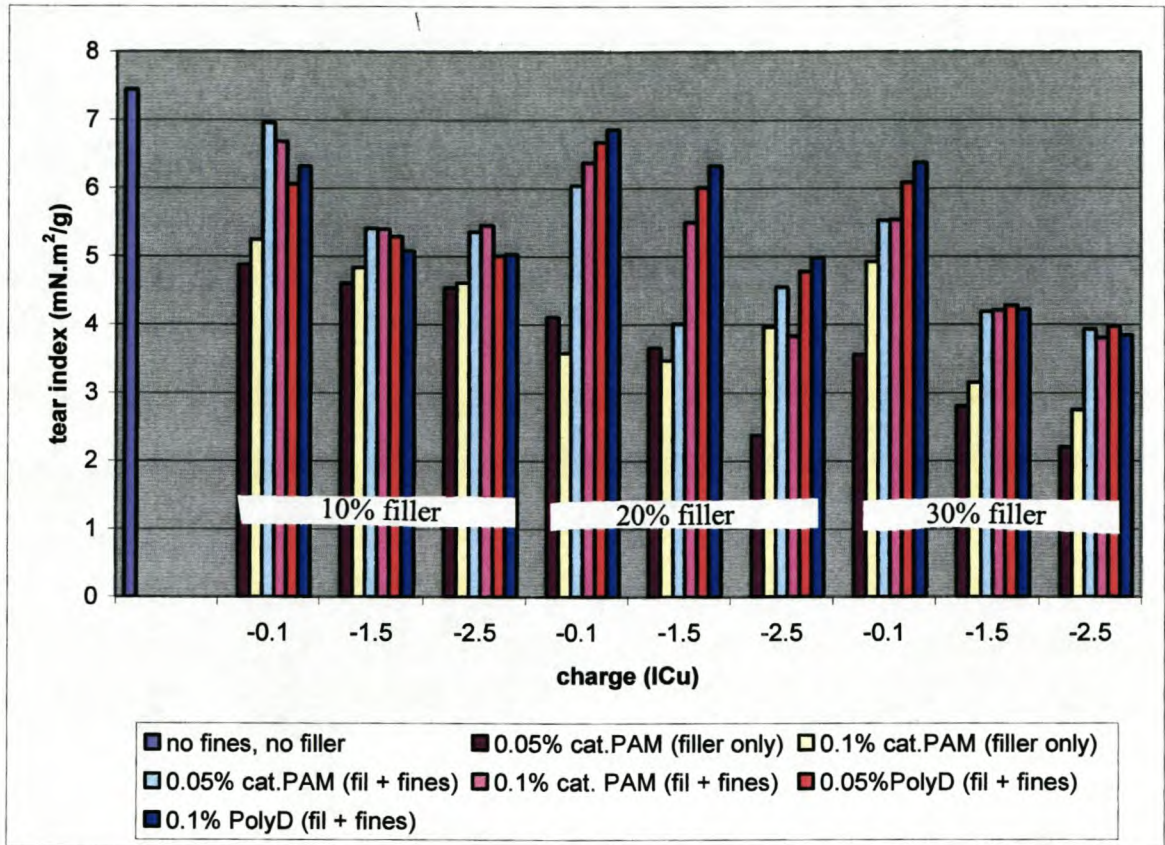
4.3.3 Tear index

Figure 20: The effect of coflocculation on tear index.

A high tear index for the stock suspension without additives is shown in Figure 20. For 10% filler addition coflocculated with fines, at −0.1 ICu, the cationic PAM handsheets gave the highest value compared to those of Polydadmac. This can be attributed to the fact that cationic PAM is a stronger acid than Polydadmac; therefore it is expected to perform better. For both 20% and 30 % filler coflocculated with fines at −0.1 ICu, the Polydadmac handsheets gave the highest values. Where only filler was added the tear index was negatively affected. Filler pre-treatment with fines (coflocculation) improved the tear index. This shows that the fibre-to-fibre bonds were protected. The tear index also seemed to be dependent upon the charge. As the charge moved close from zero to a more negative value the tear index decreased correspondingly. Controlling the charge can result in an improvement in tear index.

4.3.4 Opacity
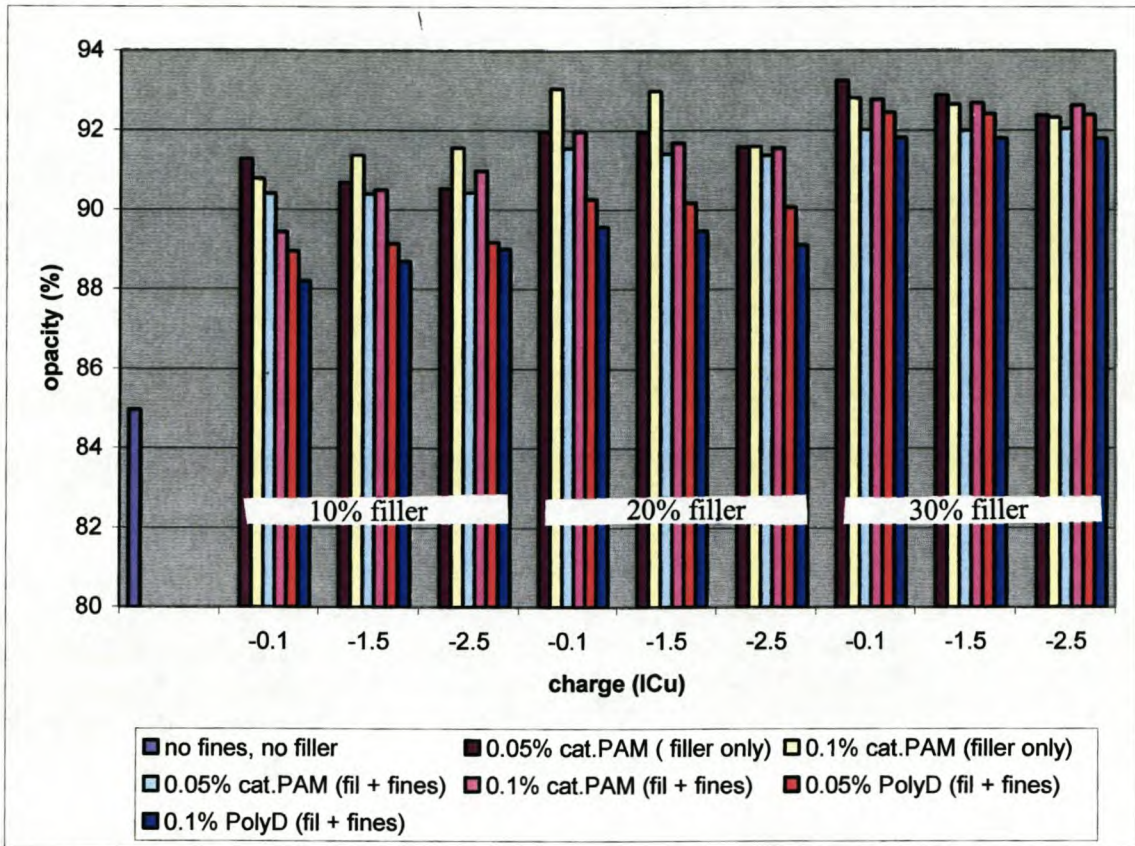
Figure 21: The effect of coflocculation on opacity.

The Polydadmac handsheets gave lower values compared to those of cat. PAM (Figure 21). One of the reasons might be the fact that cat. PAM is a strong acid compared to Polydadmac. The opacity was found to increase with an increase in filler addition. This demonstrated that the filler particles were held firmly in positions within the filler microflocs. The opacity was noticed to be lower where the filler was pre-treated with fines, i.e., with coflocculation, as compared to where the filler only was added. This can be attributed to the fact that the fines used were darker in color than the pulp used for handsheet preparation, hence the opacity appeared to be low. Opacity also seemed to be dependent on the amount of the charge. As the charge increased from -0.1 to -2.5 ICu, the opacity dropped. The opacity of a sheet is influenced by the amount and kind of filler used. It was also found that opacity improved at the expense of mechanical properties where only filler was added. This was also reported by Hayes[29] and Alince[30]. Eklund and

Lindstrom[28] reported that the decrease in mechanical properties is dependent partly on the fact that a filled sheet contains fewer fibres per unit mass and partly by the blocking of fibre-to-fibre bonds. The bond between cellulose and filler is probably good while the bonds between the filler particles are poor. They also reported that the opacity depended on the number of individual particles in the sheet structure, the grammage, the number of surfaces in the structure and the differences in refractive index between the particles and the surrounding medium. Hayes[29] reported that the decrease in strength properties occurs because fillers have no strength properties of their own and as a result they interfere with interfibre bonding. Coflocculation succeeded in keeping the fillers particles apart and thus preserving their light scattering ability in the paper.

4.3.5 Brightness
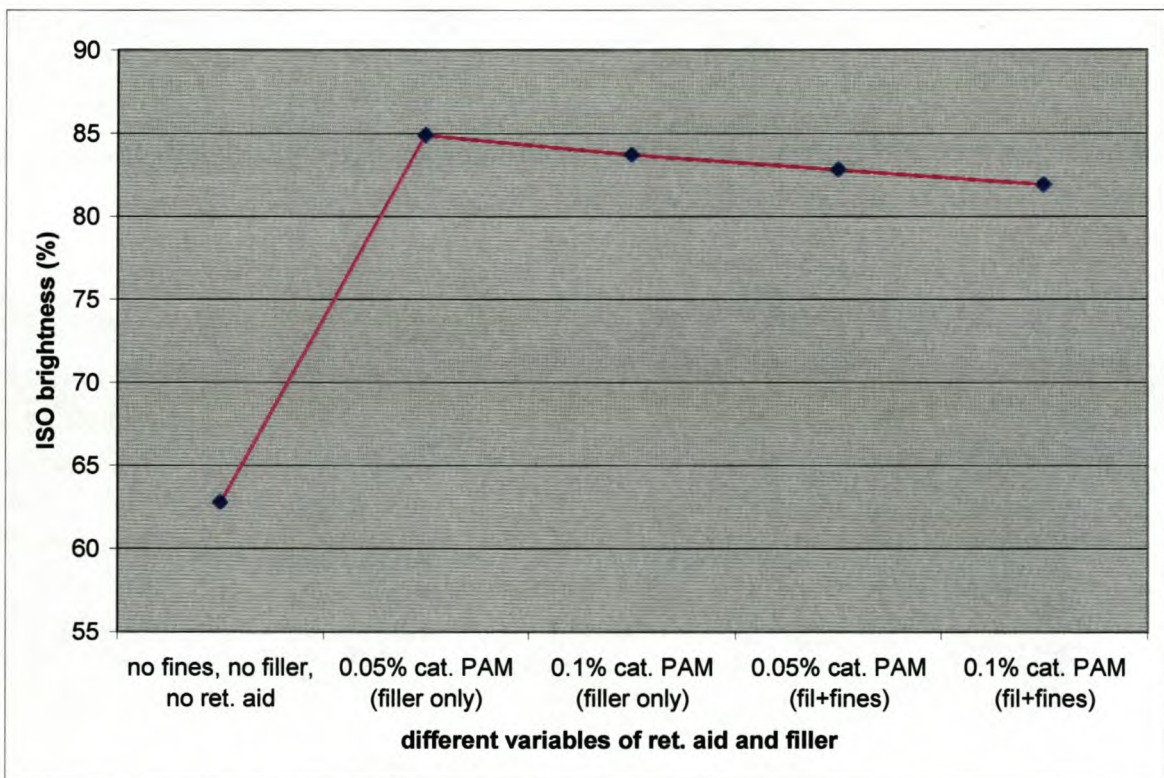
Figure 22: The effect of coflocculation on brightness.

Brightness was only measured for cationic PAM handsheets produced with 30% filler and for those produced with 30% filler and coflocculated with fines. The charge was

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adjusted to -0.1 ICu. From the results obtained (Figure 22), it appeared that the handsheets produced with coflocculation were less brighter than those produced with filler only. This could be attributed to the darker color of the added fines. It is clearly seen that the filler addition had a positive influence on the brightness.

4.3.6 Air permeability
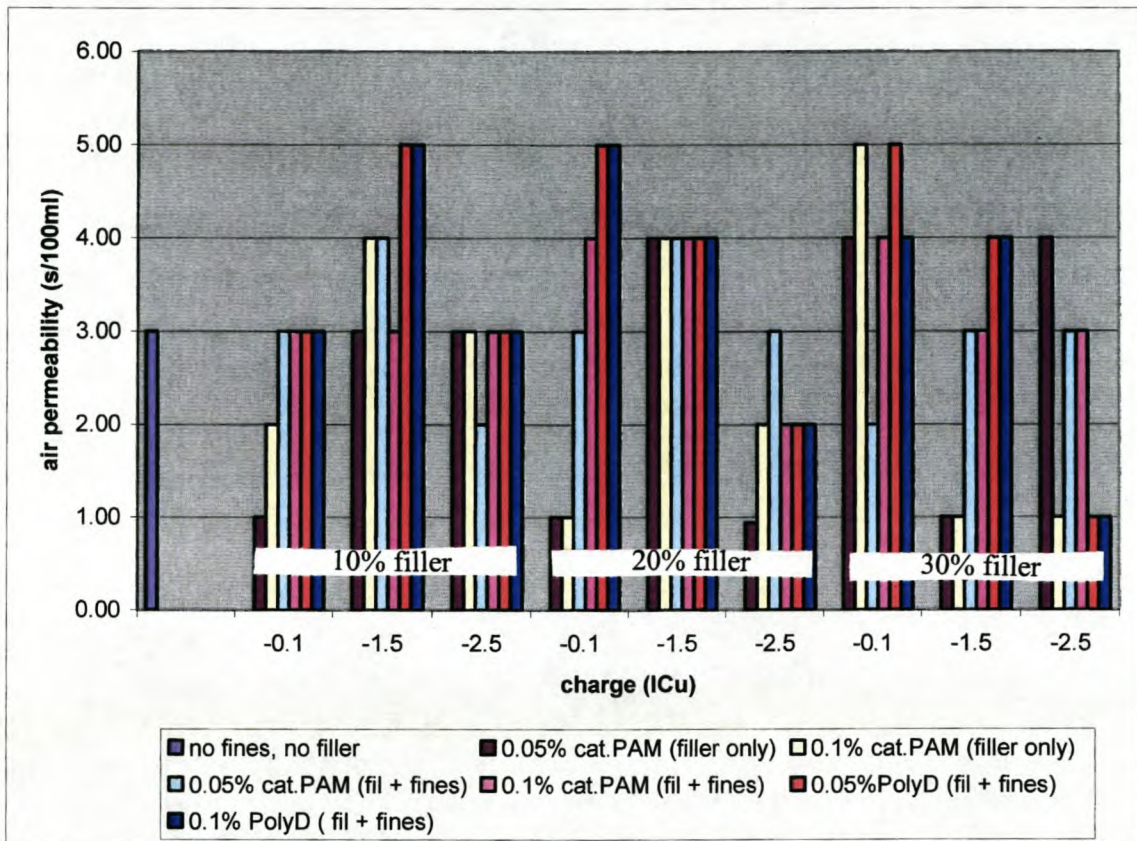
Figure 23: The effect of coflocculation on air permeability.

The slowest movement of air was found to be 5s/100ml (Figure 23). The handsheets made with the addition of cat. PAM were found to have more air spaces than those made with the addition of Polydadmac. This means that the handsheets produced with cationic PAM were more porous than those of Polydadmac. With coflocculation, less porous and denser handsheets were produced due to microflocculation. Microflocculation eliminated the repulsive negative charges, and thus caused the particles to aggregate. Where only filler was added, handsheets were more porous and less dense due to macroflocculation.

As the amount of filler increased, the handsheets became denser and less porous. This means that with coflocculation less ink would be required to achieve a given print density with the less open sheet. This agrees with Gavelin's[5] findings, the more porous the paper is, the greater is the ink consumption. The air permeability did not show to be dependent upon the charge. The filler functioned in the filling of voids between the fibres in order to produce denser, softer, brighter, smoother and more opaque sheet. This agrees with what Higham[20] and Clark[21] reported.

The air permeability of paper may be used as an indirect indicator of absorbency (penetration of oil or water). The oil penetration depends on the number and sizes of pores within the paper structure and is a relevant property for printing and in tissue grades. Both the internal structure and the surface finish of paper will influence it. A paper with more air spaces is known to be bulky or of lower density. As the paper becomes denser, air spaces decrease. The more absorbent the paper is, the faster will be the ink drying by penetration. Air permeability is also influenced by the type and amount of filler used.

4.3.7 Ash content
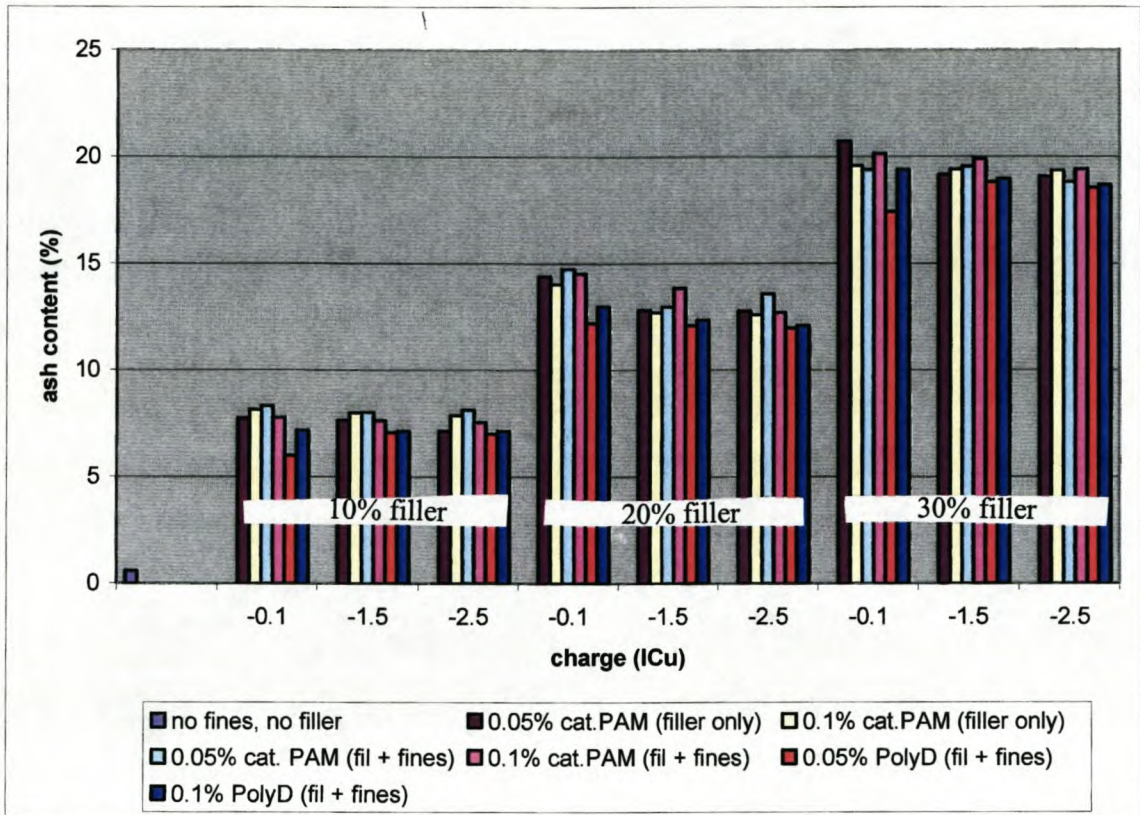
Figure 24: The effect of coflocculation on ash content.

A correction factor of 1.163 was used to compensate for the material lost during the ashing.[2] As expected ash content increased with an increase in filler addition (Figure 24). Coflocculation and the use of cationic PAM gave handsheets with the highest ash content. The charge was found to have an effect on the amount of filler retained. As the charge increased from -0.1 to -2.5 ICu, the ash content decreased. This can be attributed to the fact that the filler retention became poorer as the charge increased from -0.1 to -2.5ICu. Semnarayan[6] also reported that filler retention and drainage decreased with an increase in charge towards the negative side.

4.3.8 Filler retention

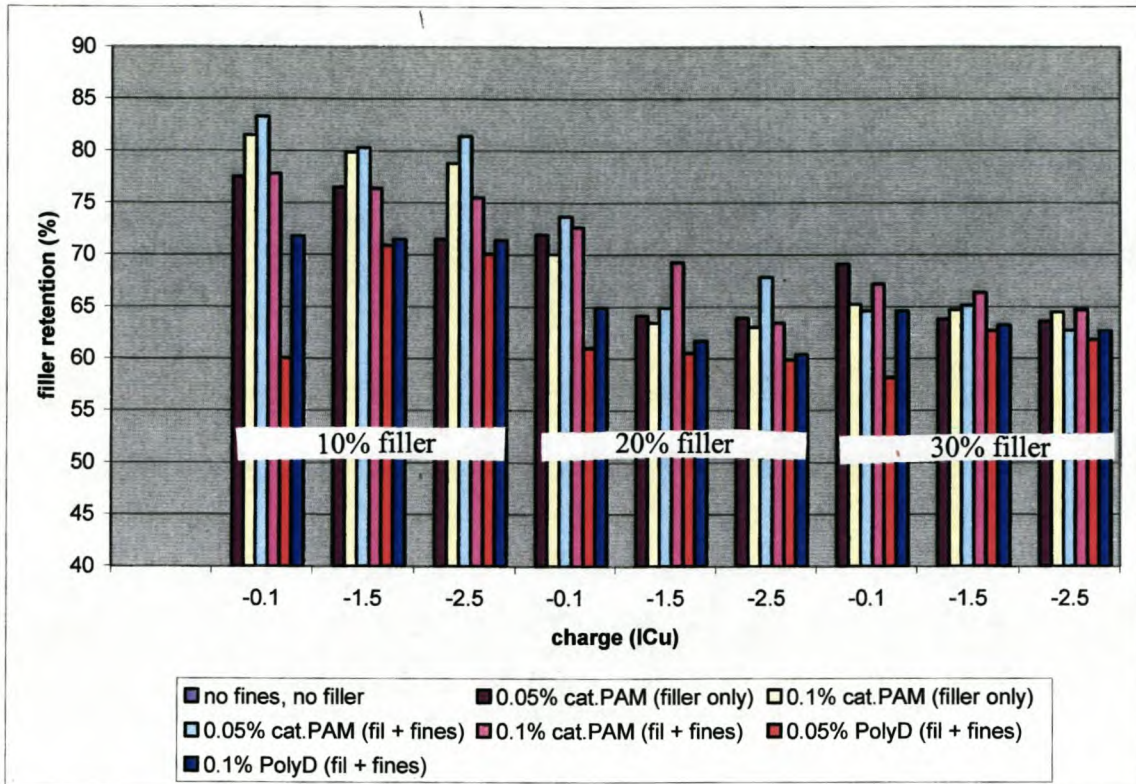**Figure 25**: The effect of coflocculation on filler retention.

The filler retention is a reciprocal of ash content (compare Figures 24 and 25). With coflocculation of fines, the filler particles were well retained and the strength properties showed an improvement (Figure 25). Where only filler was added all the strength properties were negatively affected especially the burst index even though the filler retention was high. Increasing the filler content reduced the sheet strength because the filler interfered with fibre-to-fibre bonds, thereby occupying the space that might otherwise have been occupied by fibres. This agrees with what Gavelin[5], Eklund *et.al.*[28], Hayes[29] and Alince[30] reported.

The handsheets produced with cationic PAM gave the highest filler retention values as can be seen in Figure 25. The handsheets produced with coflocculation also appeared to be less two-sided than those produced without coflocculation, but this was not measured. The effect of filler presence on the mechanical / strength properties paper depends on

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how the filler is distributed in the fibre network structure. One can say that, where there was filler only, the filler was distributed as an expansion material. Eklund *et.al.*[28] reported that expansion leads to an increase in the number of potential stress concentration sites, such as cracks, notches, pores, etc, which is a disadvantage for the development of mechanical strength properties. The charge also played an important role on filler retention. As the charge moved away from close to zero to the more negative side, the filler retention became poorer. This agrees with Semnarayan[6] and Durgueil[7] findings that the amount of charge should be controlled for optimum filler retention. Fillers make the paper surfaces to be less hydrophilic and thus more receptive to oily printing inks, thereby improving the printability. It also means that if the filler is well retained, ink will be saved because the filler particles will fill the voids that were going to take up additional ink. Coflocculation helped in keeping the filler particles apart and preserved their light scattering ability in the paper, and at the same time held them more securely so that they did not migrate through the fibre network and being lost during sheet drainage. Coflocculation promoted the hydrogen bonding capacity. This agrees with what Gavelin[5] and Gerischer et.al.[2] reported. The amount of filler retained also had an influence on opacity and air permeability of the paper.

4.3.9 Scanning Electron Microscopy (SEM) Observations

Figures 26 and 27 (different magnifications) show the SEM micrographs of a handsheet made with 30% filler, which was coflocculated with fines at a charge of -0.1 ICu. It can be clearly seen from the two micrographs that the filler was well precipitated and distributed over the fibre surfaces. Filler pre-treatment with fines assisted in holding fillers more securely in the fibre network.
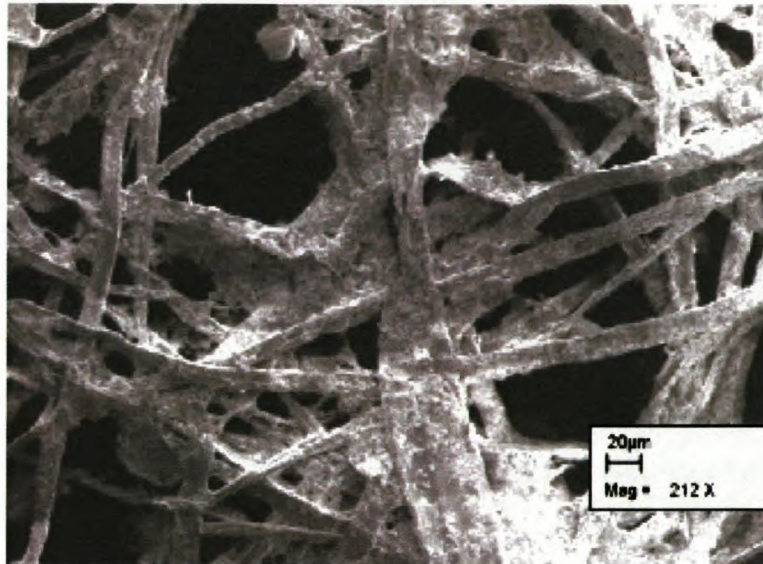
Figure 26: SEM micrograph of handsheet containing 30% filler coflocculated with fines for cationic PAM at a charge of -0.1 ICu. (Magnification 212 X)
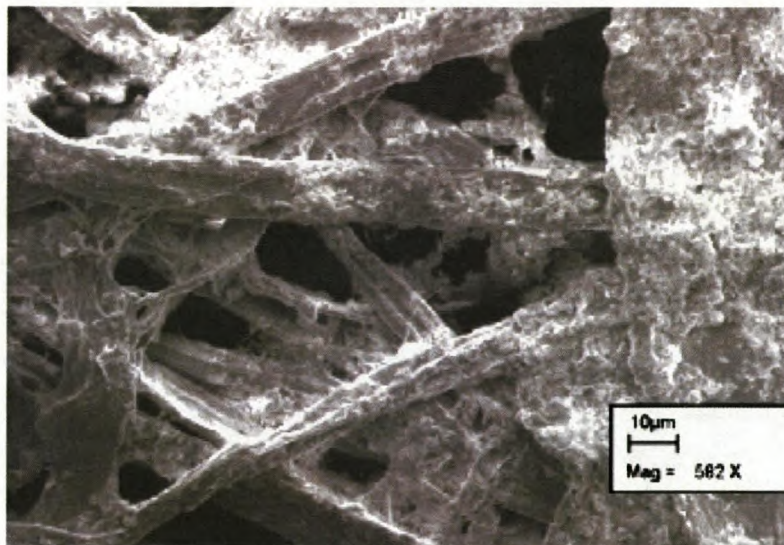
Figure 27: SEM micrograph of handsheet containing 30% filler coflocculated with fines for cationic PAM at a charge of -0.1 ICu. (Magnification 582 X)

Figures 28 and 29 (different magnifications) show SEM micrographs of a handsheet containing filler only, i.e., without coflocculation. The filler precipitated but the

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distribution was not uniform, having a patchy appearance. Uneven distribution of filler resulted in both two-sidedness and poor optical properties which had a negative impact on sheet quality. This clearly demonstrated that coflocculation played a significant role in the distribution and precipitation of filler.

Figure 28: SEM micrograph of handsheet containing 30% filler without coflocculation for cationic PAM at a charge of -0.1 ICu (Magnification 582 X)
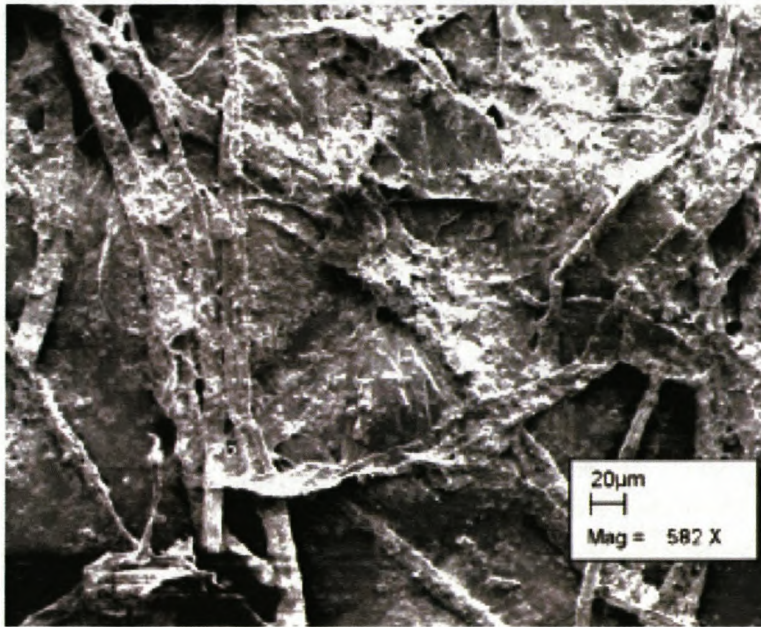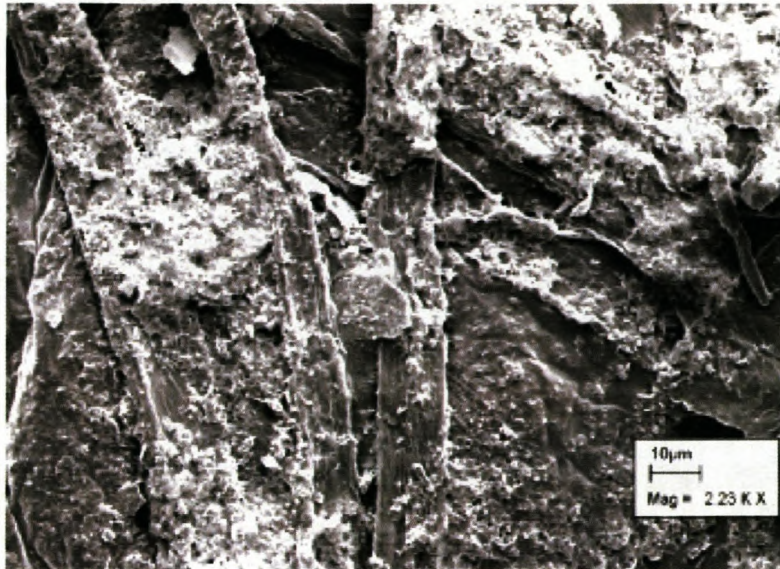
Figure 29: SEM photograph of handsheet containing 30% filler without coflocculation for cationic PAM at a charge of -0.1 ICu (Magnification 2230 X)

4.3.10 Print evaluation
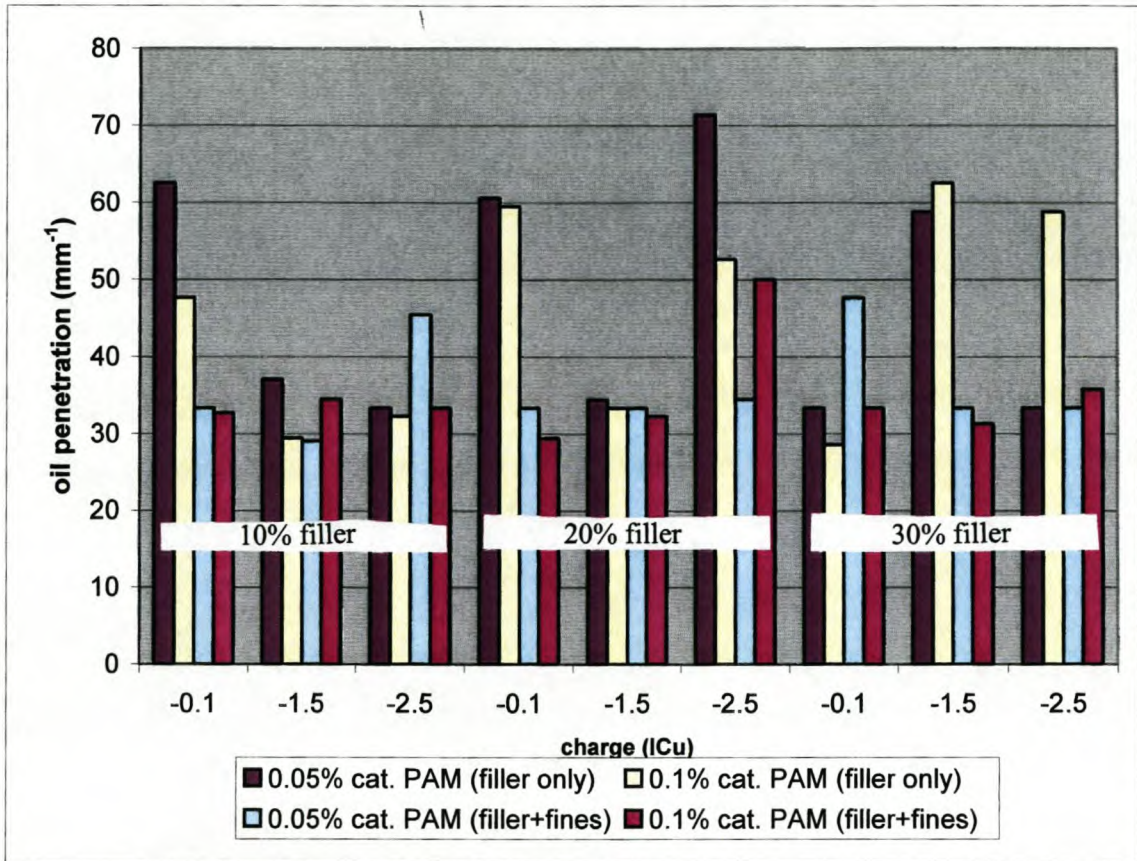
Figure 30:The effect of coflocculation on oil penetration.

Only the cationic PAM handsheets were tested for oil penetration. Only five handsheets were tested for each variable. From the results obtained (Figure 30), it appeared that the charge did not substantially influence the oil penetration. Oil penetration was calculated as the reciprocal value of the stain length: 1000 / stain length (mm).

At -0.1 ICu, the oil penetration for all coflocculated handsheets ranged between 28.99 and 34.95 mm^{-1} with the only exception being the handsheets made with 0.05% cationic PAM which gave much higher oil penetration value. The values for 0.1% cationic PAM were lower than those of 0.05% cationic PAM. Oil penetration depends on the number and sizes of pores within the sheet structure and is a relevant property for printing and tissue grades. A short stain may point to a greater roughness and a higher degree of absorbency. The stain length depends on the penetration of oil into the pore structure of

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the paper during printing. As the paper becomes smoother and less absorbent the length of the stain becomes larger. The handsheets made with coflocculation were found to be denser and smoother than those made without coflocculation. Thus it appeared that coflocculation would reduce ink consumption during printing. Tables 18-20 show the values for stain lengths and oil penetration. The print penetration values for filler only addition, appeared to be higher as compared to those of filler and fines addition. This means that the handsheets produced with filler only are more porous and less dense than those produced with coflocculation. Therefore, it can be said that handsheets produced with filler only will absorb more ink.

Table 19: IGT print penetration (charge range -0.12 ± 0.02 ICu)

Ret. Aids	10% filler		20% filler		30% filler	
	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})
0.05% cat. PAM (filler only)	16	62.50	16.5	60.60	30	33.33
0.1% cat. PAM (filler only)	21	47.62	16.8	59.52	35	28.57
0.05% cat. PAM (filler+fines)	30	33.33	30	33.33	21	47.62
0.1% cat. PAM (filler+fines)	30.6	32.68	34	29.41	30	33.33

Table 20: IGT print penetration (charge range –1.5 ± 0.3 ICu)

Ret. Aids	10% filler		20% filler		30% filler	
	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})
0.05% cat. PAM (filler only)	27	37.03	29	34.48	17	58.82
0.1% cat. PAM (filler only)	34	29.41	30	33.33	16	62.50
0.05% cat. PAM (filler+fines)	34.5	28.99	30	33.33	30	33.33
0.1% cat. PAM (filler+fines)	29	34.48	31	32.26	32	31.25

Table 21: IGT print penetration (charge range –2.5 ± 0.3 ICu)

Ret. Aids	10% filler		20% filler		30% filler	
	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})	Stain length (mm)	Oil penetration (mm^{-1})
0.05% cat. PAM (filler only)	30	33.33	14	71.43	30	33.33
0.1% cat. PAM (filler only)	31	32.26	19	52.63	17	58.82
0.05% cat. PAM (filler+fines)	22	45.45	29	34.48	30	33.33
0.1% cat. PAM (filler+fines)	30	33.33	20	50.00	28	35.71

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CHAPTER 5

CONCLUSIONS

Coflocculation resulted in handsheets with improved opacity and sheet strength properties were maintained even when the filler was added. Coflocculation is a method that can be used to optimize or maximize filler retention and opacity whilst at the same time improving (maintaining) handsheet strength properties. In general the results were positive.

- The filler was well retained without coflocculation but was not well distributed as a result of macro-flocculation. With coflocculation, the filler was well retained and distributed as micro-flocs. The coflocculation promoted the formation of fibre-to-fibre hydrogen bonding, thus promoting a better sheet strength development.

- The SEM micrographs clearly demonstrated that coflocculation played an important role in the even distribution of filler particles. Where only filler added, a patchy flocculation appearance was observed.

- All the strength properties (breaking length, burst and tear) were negatively affected when the filler was not mixed with fines, i.e., without coflocculation. With coflocculation, the strength improved. The fibre-to-fibre bonds were thus protected. The charge influenced the paper strength properties. The more negative the charge was, the poorer the paper strength properties.

- Opacity depended on the amount of filler added. Coflocculation increased the opacity. It assisted in keeping the filler particles apart and thus preserving the light scattering ability of the paper. The charge also influenced the opacity. As the charge increased from less negative to the more negative side, the opacity dropped.

- Coflocculation made the handsheets to be less porous and more dense; which would affect paper printability positively. The charge did not influence the air permeability.

- The ash content increased with an increase in the amount of filler added. Coflocculation increased the amount of filler retained in the handsheets. The charge

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influenced the ash content. As the charge increased from less negative to the more negative side, the ash content of the paper dropped.

- This study showed that the most beneficial effect of the coflocculation of filler particles with fines was obtained when the electric charge of the furnish was maintained at −0.1 ICu with the 0.1% addition of cationic PAM retention aid.

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