12-1980

A Study of the Models Describing Fines and Filler Retention by Utilizing Cationic Starch as the Retention Aid

Nen-Sen Chen
Western Michigan University

Recommended Citation

Chen, Nen-Sen, "A Study of the Models Describing Fines and Filler Retention by Utilizing Cationic Starch as the Retention Aid" (1980). *Masters Theses*. 1878.
https://scholarworks.wmich.edu/masters_theses/1878

A STUDY OF THE MODELS DESCRIBING FINES AND FILLER RETENTION BY UTILIZING CATIONIC STARCH AS THE RETENTION AID

by

Nen-Sen Chen

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

Western Michigan University
Kalamazoo, Michigan
December 1980

A STUDY OF THE MODELS DESCRIBING FINES AND FILLER RETENTION BY UTILIZING CATIONIC STARCH AS THE RETENTION AID

Nen-Sen Chen, M.S.

Western Michigan University, 1980

Fines and filler retention under dynamic conditions was studied in this thesis work. Zeta potential of samples are also measured. Dynamic Retention/Drainage Jar and Lazer-Zee Meter were used to accomplish this work. The results have been analyzed by statistical methods. When cationic starch was utilized as a retention aid the pH affected its efficiency, probably because the charge of cationic starch was dependent on pH. This effect was detected by utilizing two-way analysis of variance to find the sources of its interactions with molecular weight and agitation rate. The mechanism was thus determined. At pH 3 and 4, charge neutralization appeared to be the main mechanism for fines retention. And from pH 5 to 8, the mechanism became more dependent on polymer bridging. The charge neutralization mechanism did not appear involved in improving fines retention while the bridging mechanism did. The reason was concluded to be mainly due to the difference in charge between cationic starch and fiber fines.

ACKNOWLEDGEMENTS

Many people have contributed directly or indirectly to the completion of this thesis work. The author is indebted to their assistance.

My highest appreciation is given to the chairman of the thesis advisory committee, Dr. Raymond L. Janes. With his constant encouragement, this thesis was successfully completed. Mr. James E. Kline and Mr. John M. Fisher also served on the committee and provided necessary assistance.

I thank the Department of Paper Science and Engineering sincerely for helping me financially. Also, the policy of this Department provided facile equipment and individual space. This environment assisted in my improvement in concept and skill.

My friend, Dr. David C. Haung of Upjohn Company, also merits my thanks for his unselfishness on the discussion of statistical methods after his busy days. Finally, the efficient system of the University Computer Center accelerated the data management in this work.

Nen-Sen Chen

INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.
2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in "sectioning" the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University
Microfilms
International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1316199

CHEN, NEN-SEN
A STUDY OF THE MODELS DESCRIBING FINES AND FILLER RETENTION BY UTILIZING CATIONIC STARCH AS THE RETENTION AID.

WESTERN MICHIGAN UNIVERSITY, M.S., 1980

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

TABLE OF CONTENTS

(cont.)

(cont.)

LIST OF TABLES

INTRODUCTION

The use of polymers in the flocculation of colloidal dispersions has been widely utilized in industry. Cationic polymers are now extensively employed in water clarification, sewage treatment, ore recovery and paper manufacture. In the paper industry, the polymers are utilized to improve fines retention, drainage rate, sheet strength, chemical recovery and effluent clarification.

The mechanism of aggregation of negatively charged particles by cationic polymers has been explored by a great deal of research. Three major postulations for the mechanisms involved are: charge neutralization, polymer bridging and electrostatic patch formation. The main purpose for the application of cationic polymers is to aggregate particles. Somehow, the effect of agitation may cause the aggregated particles to redisperse. Much research focuses on the mechanism of reflocculation after the disruption. Nevertheless, in some circumstances, such as on the wire part of the paper machine, the disruption does not recover to a stable state for reflocculation to occur. The ability of the flocs to resist agitation is thus a main topic for such an environment.

LITERATURE REVIEW

ELECTROKINETIC EFFECTS IN COLLOIDAL SYSTEMS

BRIEF DESCRIPTION

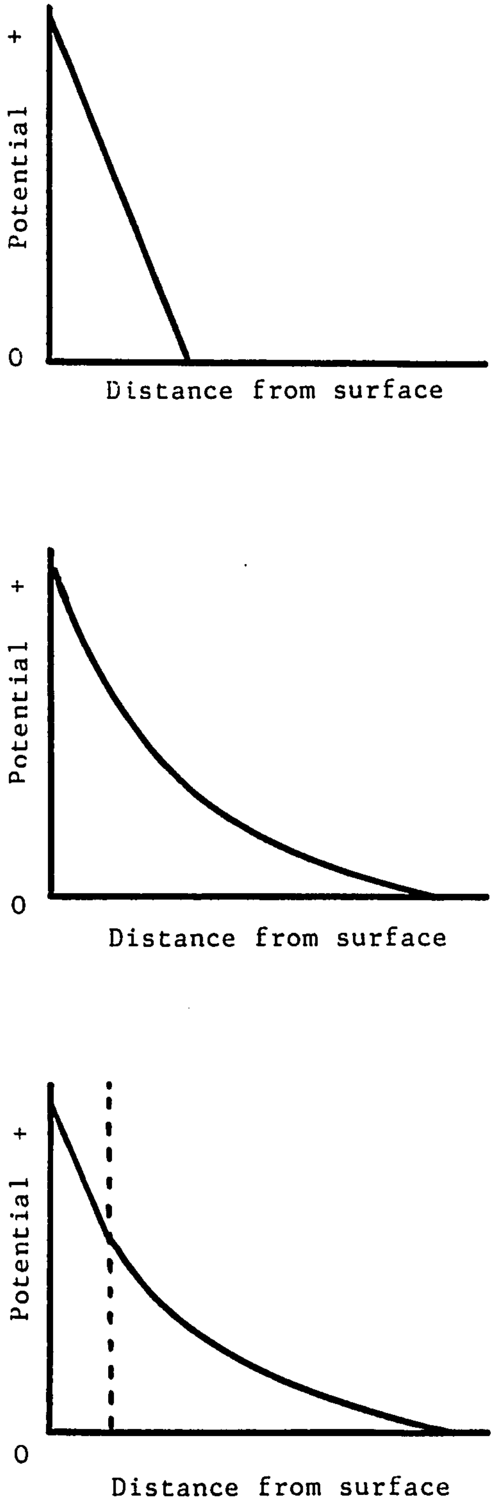
In papermaking systems, it is common to deal with dispersed solids in water. The particles in a dispersed system may be classified as: gross dispersion, colloidal dispersion and ionic dispersion; generally defined in terms of size alone (1). For certain purposes it is sometimes necessary to control the electrokinetic environment of the papermaking system. The fiber fines and filler which pass through wire could be reduced by means of flocculation. This reduces additional loading on savealls and improves the quality of paper.

HISTORICAL DEVELOPMENT (1)

In the middle of nineteenth century, the development of electro-osmosis potential measurement led to the discovery of electrical potential generated by flowing liquid in a capillary tube, where the e.m.f. developed was called streaming potential. This led to the hypothesis that the effects were caused by the presence of electrically charged layers of opposite sign at the solid/liquid boundary. The streaming potential was the result of a charge displacement by the forced flow of liquid along the solid interface. A further investigation described that when suspended particles are forced to move through liquid in response to gravitation a potential gradient also is generated. This sedimentation potential can also be explained by the hypothesis of solid/liquid boundary interface. The concept of an electric double layer was then proposed and the phenomenon of adding electrolytes in a colloidal system to make its environment unstable was also reported. At the turn of this century, the experiment of migrating particles within a colloidal suspension in response to an applied electric field was accomplished. This behaviour of colloids is now called electrophoresis. The experiment of electrophoresis potential again supported the assumption of an electric double layer at the solid/liquid boundary.

DISCUSSION OF ELECTRIC DOUBLE LAYER (2)

In 1879, Helmholtz first proposed the model of the electric double layer at the phase boundary. He related mathematically the velocity of electroosmotic flow to charge separation on the double layer. Helmholtz envisioned all the counterions as being lined up parallel to the charged surface at a distance of about one molecular diameter (3). According to this capacitor model, Figure 1-a, the electric potential should fall rapidly to zero within a very short distance from the charged surface. The effect such as thermal agitation of counterions which causes a distribution of counterions near the surface is not considered by this model. A model which described a diffuse layer of counterions was later proposed independently by Gouy and Chapman, as shown in Figure 1-b. They envisioned a diffuse distribution of the counterions. This model is useful for planar charged surfaces with low charge densities, or for distances not too close to the surface. In 1924, Stern modified the Gouy-Chapman model



a. Helmholtz model

b. Gouy-Chapman model

c. Stern model

Figure 1. Models of Electric Double Layer.

to include an immobile, inner region of adsorbed ions (Figure 1-c). This layer (Stern layer) of strongly held counterions adsorbed close to the charged surface plus a mobile, diffuse outer layer (Gouy-Chapman or diffuse layer) is presently accepted as the basic concept of the electric double layer.

Recent modifications of the double layer theory, including the model described by Levine et al. (4), propose a thin layer of firmly adsorbed ions which lie in the inner Helmholtz plane (I.H.P.), and followed by a layer of hydrated counterions which lie in the outer Helmholtz plane (O.H.P.). The diffuse layer thus extends from the O.H.P. out to the bulk solution. Figure 2 illustrates the main features of the electric double layer including the concept of the O.H.P. The terms in Figure 2 are listed below:

ψ_o = the potential at the surface

ψ_δ = the potential at the O.H.P.

δ = thickness of the immobile Stern layer

ζ = experimentally determined potential at the hydrodynamic shear plane, i.e. Zeta potential

κ = Debye-Huckel constant ($1/\kappa$ is the effective thickness of double layer)

The discussion of double layer provides the idea of Zeta potential. Assuming that the experimental measurement of the potential at hydrodynamic shear plane coincides with the potential at outer Helmholtz plane, then $\zeta=\psi_\delta$. However, some differences have been found between values calculated for ζ and ψ_δ. More detailed knowledge about Zeta potential will be discussed in the latter section.

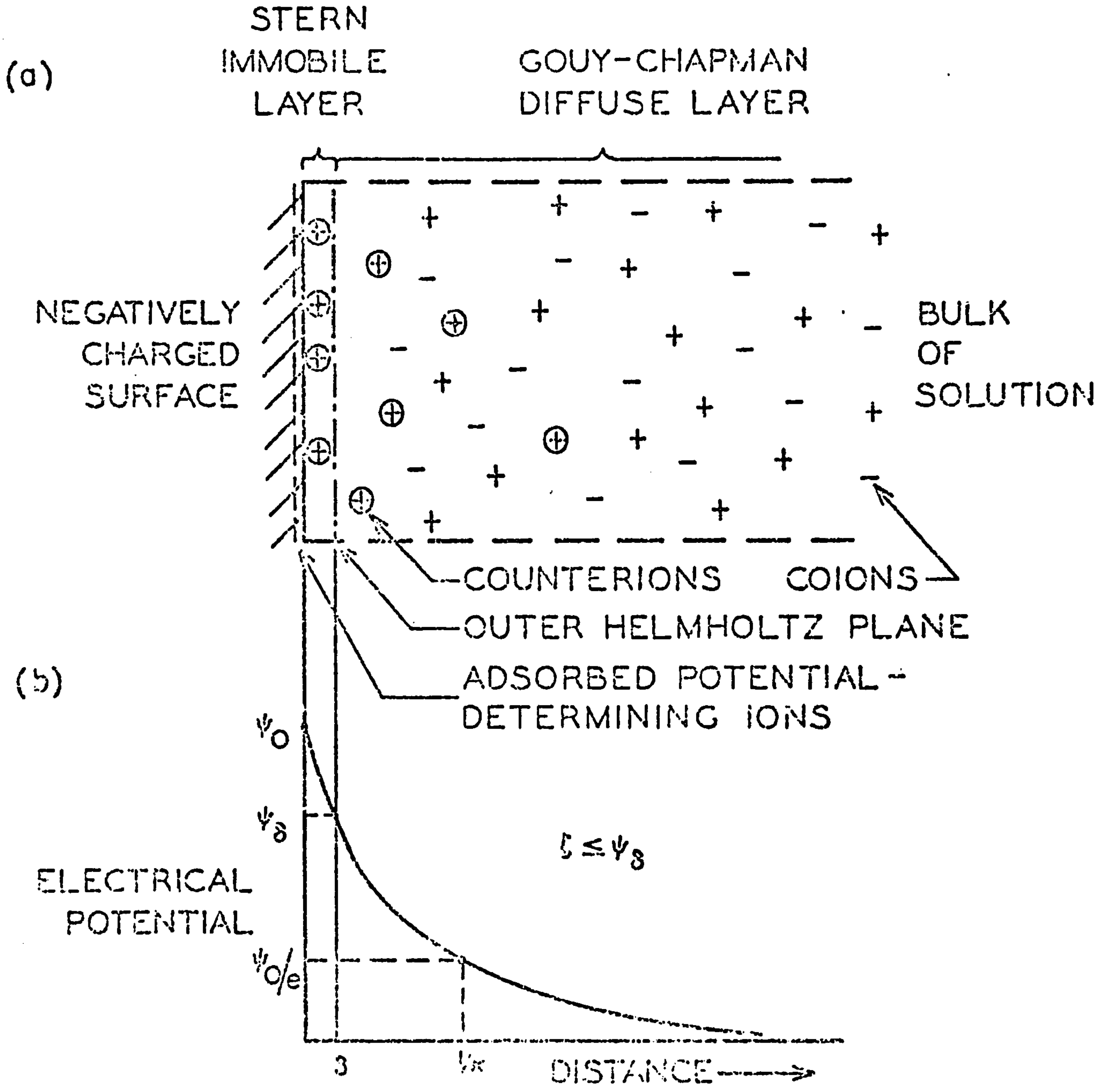


Figure 2a. Model of the Electric Double Layer

Figure 2b. Potential Distribution in the Double Layer

The concept of Debye-Huckel constant, k, leads to a closer look of the electric double layer. Usually, the reciprocal of k, the effective thickness, is applied to describe the distance from the charged surface into the solution within which the electrical interactions with the surface can be considered to occur. The effective thickness, usually called Debye length, is given by the expression (3):

$$1/\kappa = \left(\frac{\epsilon_r \, \epsilon_o \, R \, T}{4 \, \pi \, F^2 \, \Sigma \, C_i \, Z_i^2} \right)^{1/2} \qquad (1)$$

where ϵ_r = ϵ/ϵ_0 : the relative dielectric constant of the solution (ϵ : of the solution, ϵ_0: of a vacuum)

R = the gas constant

T = the absolute temperature

F = the Faraday constant

C_i = the molar concentration of any ion in the solution phase

Z_i = the valence of the ions in the solution phase

From the preceding relationship, it is apparent that with high dielectric constants of the solution, such as water, the electrical effects would extend much further into the solution. And also, in the presence of electrolytes, electrical effects have shorter ranges than in their absence; that is, the electric double layer is compressed. The concept of coagulation due to the existence of ions and the effectiveness of coagulation changing due to the valence is known as the Schulze-Hardy rule.

THE MEASUREMENT OF DOUBLE LAYER POTENTIAL

The potential of a charged particle can not be measured directly by any instrument. It is usually calculated from evaluations of electrokinetic phenomenon: electroosmosis, streaming potential, sedimentation potential, and electrophoresis. The calculated potential, Zeta potential, is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other. Since the relative motion develops at a slip plane, the Zeta potential is then evaluated within fluid region (diffuse layer) and is not necessarily at the O.H.P. or at the edge of Stern layer. The Zeta potential is consequently equal or smaller in magnitude than the Stern potential. Still, Zeta potential is the most convenient to evaluate the double layer potential.

Sennett and Olivier (1) present equations to calculate Zeta potential for each of the measuring methods.

COLLOIDAL STABILITY

The colloidal stability in a system is the direct consequence of the interactions between electric double layers. Energy barriers must be overcome before two particles can collide. The interaction energies between charged particles in aqueous solution are described by the Derjaguin-Landau, Verwey-Overbeek (DLVO) theory of colloidal stability.

$$V_t = V_a + V_r \qquad (2)$$

The total potential energy of interaction V_t is the sum of the potential energy of attraction V_a and that repulsion V_r. A detailed discussion of the DLVO theory may be found in the presentation by Adamson (5).

The potential energy of attraction for similar spherical particles of radius a and centers separated by distance R is given by Hamaker's expression (3):

$$V_a = \frac{-Aa}{12H} \qquad (3)$$

Where A is the Hamaker (van der Waals) constant and H is the nearest distance between the surface of the particles.

The potential energy of repulsion V_r depends on the size and shape of the dispersed particles (Lyklema equation) (3):

$$V_r = \left(\frac{\epsilon\ a^2\ \psi_o^2}{R}\right)E \qquad (4)$$

where ϵ = dielectric constant of the liquid

a = radius of particles

ψ_o = the potential at the surface

R = separation distance of two particles

E = e^{-kH} for $ka \ll 1$

= $\ln(He^{-kH})$ for $ka \gg 1$

Jaycock (6) discussed the interaction between spherical particles and plates by referring to the equation of Hogg et al. (50). This could approximate the interaction between filler (spherical particle) and fiber (flat plate).

Figure 3 illustrates the dependence of the total interaction energy on the distance between particles. The additive method is up to now the best way to estimate the total energy of interaction. However, Jaycock (7) warned in his paper that care must be taken while precise calculations are dealt with for both V_a and V_r.

ADSORPTION AT THE SOLID/LIQUID INTERFACE

The adsorption of polymers at the solid/liquid interface is influenced by a number of factors: the surface nature of adsorbate, the surface nature of polymer and the environment of the liquid phase. Mechanisms of adsorption have been described by Rosen (3), which include the orientation of polymers either on similarly or oppositely charged surfaces, hydrogen bonding, van der Waals forces and hydrophobic bonding.

ADSORPTION ISOTHERMS

The adsorption isotherm is mainly interested in determing the efficiency and effectiveness of polymer molecules adsorbed on a surface. Practically speaking, the measurement of efficiency deals with that concentration of adsorbent required to produce a given surface concentration and the measurement of effectiveness deals with the concentration at saturation. The mechanisms of adsorption may affect the shape of an adsorption isotherm. Onabe (8) found that

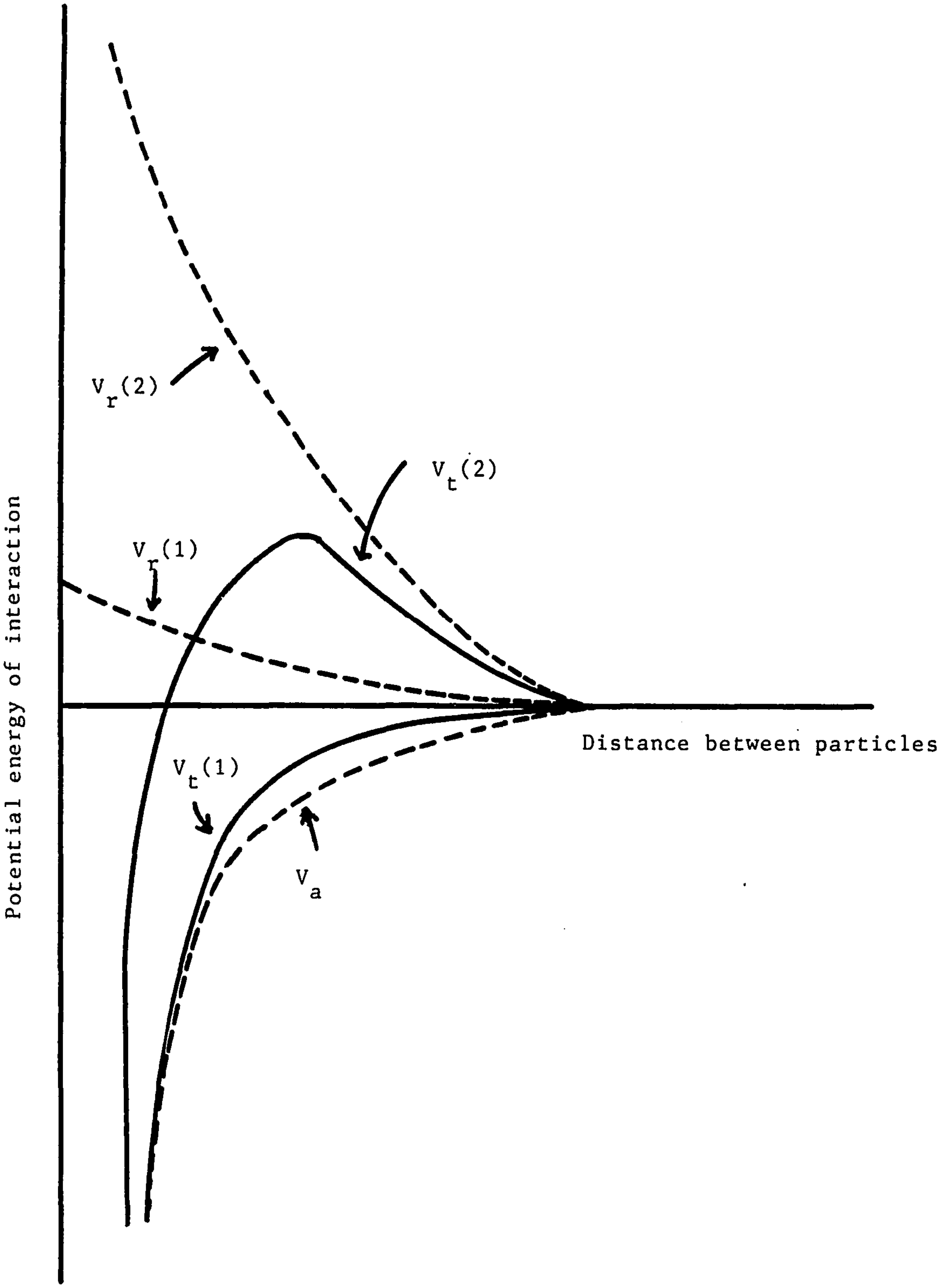


Figure 3. Total Interaction Energy Curves

fiber with a lower density of carboxyl groups forms monolayers of adsorbent and multilayers with higher density. In his experiments, he added polymer with low and high molecular weights into separate systems which contained fiber of low carboxyl group density. The adsorption isotherm showed that efficiency was dependent on the molecular weight and effectiveness was not. At the same time, he also showed that for polymers with different molecular weight adsorbing on fiber with high carboxyl groups density, the effectiveness was dependent on molecular weight whereas the efficiency was not.

Kindler (9) measured the adsorption isotherms as a function of polymer molecular weight, polymer concentration, ionic strength, and pH. He found that the smaller molecules of Polyethyleneimine were sorbed to a greater extent than the larger ones. And due to ion-exchange reaction involving ionized hydroxyls on the fiber, the maximum in polymer retention was observed at pH 10.9. Das and Lomas (10) showed the same results.

For polymers with different degrees of substitution the effectiveness of adsorption can also be affected. Lindstrom et al. (11) showed that the higher the degree of substitution of polymeric molecules, the lower was the cationic demand for a fiber-cationic polymeracrylamide system. Strazdins (17) proposed that the dimensions of adsrbate would also change the adsorption isotherm. He postulated that cationic demand was directly proportional to the hydrodynamic surface area of the adsorbate.

CONFIGURATION OF ADSORBED POLYMERIC MOLECULES

Generally, polymer molecules are adsorbed on a solid surface more or less as random coils. Three basic configurations of adsorbed polymeric molecules are train, loop and tail.

The main factor determining the configuration of polymeric molecules adsorbed on a solid surface is the charge density of either the solid surface or the polymer (12). For relatively lower charge density polymer molecules, segments may extend to the solution as tails and unadsorbed portions may form loops. It is clear that the tails extending to the solution have more available sites for further adsorption than loops and trains. This is the reason why retention aids in papermaking system are preferably polymers with medium charge density. Some highly charged surfaces or polymers would form multilayer configurations of adsorpent due to the excess sites (13, 14). Also, multilayers of aggregated alumina on fiber surfaces have been found by Alince and Robertson (15). They postulated that positively charged alumina strongly adsorbed with fiber surfaces and that the formation of multilayers of alumina was due to the homoflocculation of alumina rather than the excess sites of fiber surfaces.

FACTORS AFFECTING RATE OF ADSORPTION

If polymer retention is plotted versus time, the slope of the line shows adsorbing rate of the polymer. Factors which affect the rate of adsorption are charge density of polymer, amount of polymer addition, degree of agitation, molecular weight of polymer and the nature of adsorbate. Lindstrom and Soremark (16) took temperature to be an experimental variable and found that increased temperature increased only the adsorbed amount. They also showed that polymers with lower degrees of substitution had higher rates of adsorption to reach equilibrium state, and less added amount of polymer had higher rate of adsorption. Kindler (9) found that changes in agitation speed have insignificant differences in polymer adsorbing rate. He proposed that the type of agitation in his experiment could not produce significant change in the degree of agitation inside the apparatus, and conclusive agitation-dependence of adsorption kinetics in his experiment required a different form of agitation.

ADSORPTION AND ELECTRIC DOUBLE LAYER

People have studied the adsorption mechanism by looking at electrokinetic effects (17, 18, 19). Britt (20 suggested that charge adjustment of fiber may be required so that the polymer and charged surface approach each other closely enough for attractive forces to cause adsorption. Still, the main initiation of polymer adsorption is either through the interaction of oppositely charged electric double layers or through the engagement of strong physical forces (17). The main factor is dependent upon the electrical nature of polymer or adsorbate. A study of adsorbing rate showed that in a system with polymer adsorbed on fiber fines, mobility of fines would be reversed from positive to negative after one percent of long fiber had been added (16). This indicated that the rate of adsorption may be affected by the dimensions of the adsorbate.

COAGULATION AND FLOCCULATION

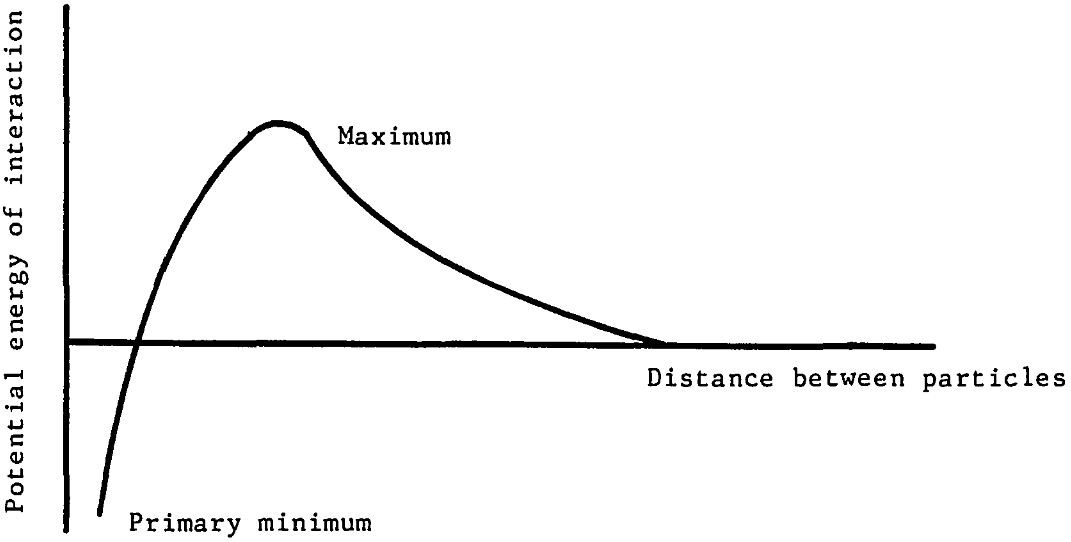
The previous section has discussed the total potential energy of interaction among particles. The final interaction energy has a very close relationship with the product of Deby-Huckel constant and particle radius (ka). When ka $>>$ 1, that is, the ratio of particle size to thickness of the electric double layer is very large, the curve for total energy (Figure 4) shows a secondary minimum at a relatively large distance of separation between the particles in addition to the primary minimum (3). Particles may therefore aggregate at a relatively large distance from each other and this type of aggregation is called flocculation to distinguish it from that in the primary minimum, which is termed coagulation (when ka $<<$ 1). The actual mechanisms of aggregation of particles are divided into three categories: charge neutralization, polymer bridging, and electrostatic patch formation.

CHARGE NEUTRALIZATION

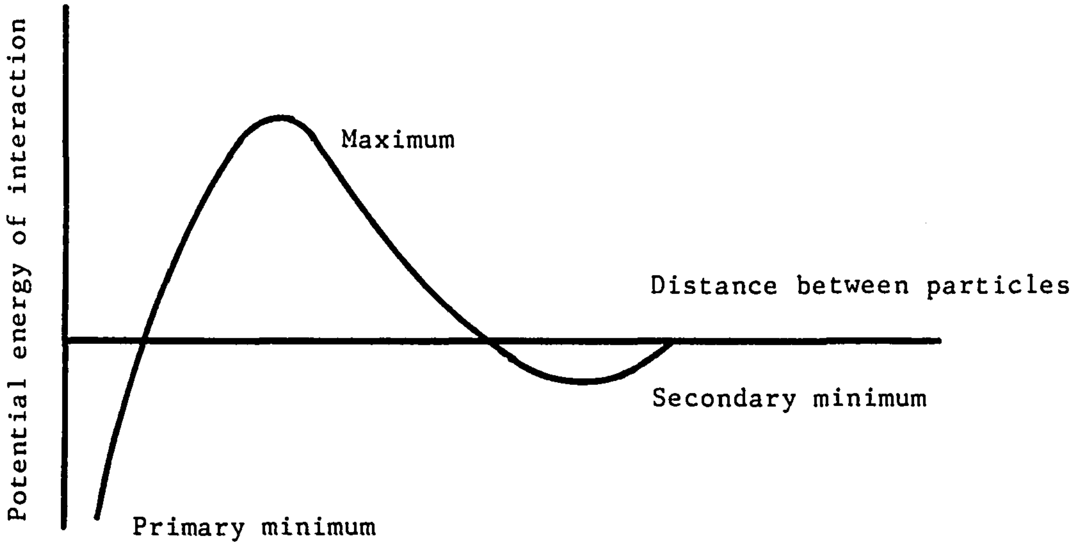
From the equation for Debye length (eq. 1), the addition of electrolyte to a colloidal suspension causes a compression of the electric double layer. This increases the concentration of ions in the Stern layer and lowers the Stern potential (Schulze-Hardy rule). Walkush and Williams (21) showed that electrophoretic mobility of fines approached zero near the critical coagulation concentration (concentration of counterion where rapid coagulation occurs). Strazdins (22) showed that electrolytes had the same performance.

POLYMER BRIDGING

The bridging mechanism, first postulated by Ruehrwein and Ward



$(a)\ ka \ll 1$



$(b)\ ka \gg 1$

Figure 4. Potential Energy of Interaction.

(23), has become an accepted explanation for flocculating colloidal particles by high molecular weight polymers. La Mer and Healy (24, 25) suggested that polymer molecules adsorbed on the particle surface at one or more sites have segments extending into the solution. These extended segments provide free sites and adsorb on the other particles surface forming a three dimensional network. The network is affected by the shear gradient imposed from external agitation. The ability of the network to endure a certain degree of agitation without breaking down is an important requisite of the bridging mechanism. Once the networks are broken down, by definition, it is not possible to reform a floc similar to the original one. Unbehend (26) called this type of aggregation a "hard floc". Polymers to form this type of flocculation could either be moderately charged cationic polymers or non-ionic polymers. For non-ionic polymers to form bridging-type floc, the electric double layer should first be compressed by adding electrolytes (27).

The disruption rate of the network is a function of the dimension of the units. La Mer and Smellie (28) proposed that the rate of disintegration of spherical particles in the network is inversely proportional to the surface area of the particle. King and Williams (29) had the same results in their experiments. They found that smaller fines particles experience a smaller degree of disrupting shear forces from slurry agitation than do the larger fiber particles. This results in less floc disruption, at the same degree of agitation, for the fines-to-fiber system than for the fiber-to-fiber system. From an electrokinetic viewpoint, Sandstrom (30) proposed that the polymer bridging type mechanism could be maximized even if the electrical mobility was still on the negative side. Britt et al. (18) showed that over 90% fines was retained with negative Zeta potential of the furnish.

ELECTROSTATIC PATCH FORMATION

The electrostatic patch mechanism was first proposed by Kasper (31). When the interaction forces between colloid and polymer are large, the polymer molecules adsorb in the form of patches on the adsorption surface. Since the adsorption mechanism is not a one-to-one association between negatively charged sites on the adsorbate and the strongly positively charged groups on the polymer, it results in a distribution of positive patches adsorbed on the particle surface. The overall charge on the patches, nevertheless, is still positive. These patches are then interacting with other particles to form flocs. Thus, for aggregation to occur, the total net charge of the particle need not approach zero, because the net interaction force is dependent on the localized patch charges. This model may be studied by evaluating either the distance between particles of the aggregate (32) or the surface coverage of polymer on the particle (12).

RUPTURE OF AGGREGATES

It is known that when the velocity gradient is appreciable, an aggregate may be disrupted. If an aggregate is formed by charge neutralization, the ability to reform following disruption is almost instantaneous after the shear gradient is removed (26). In a system with polyelectrolytes, La Mer and Healy (25) postulated that rupture of bridging type flocs occured on desorption of the polymer under shear gradient. Goosens and Luner (19) found that with increasing time of agitation and also the degree of agitation, the cationic demand increased. This was attributed to cationic ions diffusing into pores of the particles.

Unbehend (26) concluded in his experiments that upon redispersion of bridging type flocs, a "primary flocculation" was reached. He regarded this phenomena as a result of "flattened" cationic patches caused by shear gradients on the original adsorbed particle and by uncovering anionic areas of the particles. Beck, et al. (33) found that bridge type flocs broken by shear forces reflocculated slowly and less effectively than the original flocculation. Sikora (32) showed that dispersed patch flocs have the ability to reflocculate almost reversibly while bridging type flocs do not recover well. In his experiments he found that at pH 3 and 9, polyvinylamine formed patch flocs in the aggregation of polystyrene latics; whereas at pH 10 bridging flocs were formed. The difference of mechanisms is due to the charge density of polyvinylamine which changes at various pH levels. High charge density polymer formed patch flocs whereas low charge density polymer formed bridging flocs.

ZETA POTENTIAL AND APPLICATIONS

It has been mentioned in the previous section that thickness of the electric double layer of a colloid determines the stability of system. Zeta potential measurement is the most convenient and popular way to estimate colloidal environment. People have strongly supported Zeta potential to be a guide to colloidal stability in papermaking systems (34, 35). Strazdins (22) has shown that near the isoelectric condition optimum one-pass retention, faster drainage and production rate were obtained. For fines and filler retention Britt and Unbehend (36) found that the mechanism of aggregation would sometimes determine the importance of Zeta potential measurement. Zeta potential was only one of several important factors that determined the degree of the tenacity of bridging.

EFFECTS OF FINES

The electrical charge on the surface of cellulose is negative which is believed to be due to carboxyl groups. Britt and Unbehend (36) found that small amounts of cationic polymer can neutralize the charge of pulp with negligible carboxyl groups while pulp high in carboxyl groups needed a relatively large quantity. This proved the carboxyl groups have a main effect on electrokinetic behavior. Strazdins pointed out that fiber fines which pass through a 200-mesh screen possess approximately three times higher electronegative Zeta potential than those of long fibers (37). In his experiments, he supported the hypothesis that fiber fines as measured by electrophoresis were representative of the fiber surface as a whole. It was done by changing the degree of refining on fiber. While degree of refining increased, this added the quantity of fines to the system. Increments in electronegativity of the entire system and also the increment in the cationic demand due to refining effect proved the importance of the role played by fiber fines. Jaycock and Pearson tried to find the electrokinetic effect of pH on a system of fines plus filler. The results showed that filler had no effect on electrokinetic characteristics. By utilizing streaming potential technique they could distinguish the mobilities of filler and fines separately (38). They concluded that the insignificance of filler character was due to the surface of the filler being modified by adsorbed fines and this led to a shift of apparent isoelectic point of filler (38, 16). More discussion about the electrokinetic characteristics of fillers will be found in a later section.

EFFECTS OF MULTIVALENT IONS

Alum when added to the papermaking systems act as a flocculating agent. By the Schulze-Hardy rule, addition of counterions compresses the electric double layer. Theoretically, the degree of compression is inversely proportional to the sixth power of the valence. Under this circumstance, a Zeta potential condition approaching zero is the best for aggregation to occur. Jaycock and Pearson (39) studied the effect of alum and pH on the retention of filler with stock suspension loaded with inorganic filler. Results showed that at the same alum addition level, retention increased from pH 4 to 8. This was attributed to the electrokinetic interaction between fiber and filler. The Zeta potential measurement of various fillers showed that with the existence of alum, the isoelectric point of the fillers had only small variation between pH 5 and 8. While the Zeta potential of fiber remained at a low negative level, the increment in retention was predominately due to the electrokinetic effect of filler. Since the Zeta potential of filler with the existence of alum had the lowest value at pH 4, they also showed that the maximum in electronegativity occuring from pH 3.7 to 4.0 caused the lowest filler retention. A minimum in retention of titanium dioxide in paper has been reported at pH 4.5 to 4.7 with the existence of alum (40). Moore (41) found in system treated with polymeric cationic drainage aids that the presence of alum at pH 4.5 to 5.0 was detrimental to the activity of cationic polymers. Waklush and Williams (21) showed that the build-up of sulphate ion affected the retention effect due to its interaction with aluminum ion. Since fines have higher surface area than fibers, Marton (45) found that nonuniform distribution of adsorbed alum on fines and fiber would cause uneven distribution of rosin size and certain dyestuffs.

EFFECTS OF POLYMERIC MOLECULES

Ancient Chinese papermakers had introduced seaweed extract into handcraft papermaking early in the third century (42). From the electrokinetic viewpoint, the addition of similarly charged polymer (seaweed extract) is mainly for a better dispersing effect. For fines and filler retention purposes, application of polymeric molecules has been widely accepted. The effect of charge of polymeric molecule on the efficiency of retention is still a subject for much research. Whether the polymer charge or the electrokinetic environment of the system determined the efficiency of retention aid has been argued (43, 44).

Sandstrom (30) reported a maximum retention effect occured at Zeta potential of -6mV. This showed that with high molecular weight cationic retention aids the system need not necessarily be neutralized. Penniman (34) suggested that the difference in retention effect was not apparent with the range of Zeta potential from 0 mV to -8 mV. He also proposed that the difference would show up when the Zeta potential was more negative than -8 mV. Valette (35) approached maximum retention by first neutralizing the fiber with alum and then adding in the non-ionic polymer. It is clear that both the electrokinetic environment and characteristics of polymer should be taken into consideration to reach optimum conditions for flocculation.

NATURE OF FILLERS

Jaycock and Pearson conducted a series of studies on different inorganic fillers (38, 39). They found that fillers showed various electrokinetic properties at different pH levels. Nevertheless, the isoelectric point of the filler had no effect on its retention characteristics. The reason for this was surface modification by cellulose fines. This has been discussed in the previous section. In their experiments they found that the isoelectric point of anatase was far away from literature values while rutile was not. They attributed the shift to phosphate ions coated on the anatase surface and proved that a washed sample had the isoelectric point of the literature value. In an early study, Rogols and High (46) reported that anatase gave little change in retention due to the variation of pH; whereas the effect on rutile was dependent on the change of pH. Pummer (47) found that titanium dioxide was retained more than kaolin. From all these reports, it is obvious that interaction of filler and fines on retention must be carefully treated.

FILLER RETENTION AND OPTICAL PROPERTIES OF PAPER

Changes brought about by chemical additives at the wet end affect the optical properties of paper. The scattering coefficient of the Kubelka-Munk theory is applied to analyze the relationships. Schiesser (48) found that over-flocculation, which usually does not happen in a practical sense, decreased opacity of paper. Pummer (49) reported that retention of titanium dioxide by means of coagulation gave better optical properties than did flocculation, and suggested that the size of filler agglomerates affected the scattering power.

PRESENTATION OF THE PROBLEM

Factors affecting fines and filler retention have been discussed in the previous sections from various angles. Theoretically, each factor has its own character and is predictable for its effect. Nevertheless, the interactions among them are not known. Researchers have seldom worked on evaluating the interaction by statistical techniques. Milichovsky (51) discussed the retention effect with mathematical models, and showed that the terms involved in the effect can sometimes be eliminated. However, his discussion about interaction terms was omitted.

The aggregation mechanism of particles has been proposed to be dependent on the charge density of a polymer (32). For fines and filler retention, the interactions with shear and molecular weight due to the effects of polymer charge have not been determined. In a recent experiment, the results showed that the charge of cationic starch is dependent on pH. By varying the pH the charge level of cationic starch can thus be changed. Since the degrees of interaction among polymer charge, polymer molecular weight and shear in the bulk flow are different from case to case, a three way factorial design is thus needed. It is proposed that from the responses the effect of polymer charge on retention and its interaction with shear and molecular weight can be determined.

EXPERIMENTAL DESIGN

Factors such as velocity gradient of the bulk solution and the molecular weight of cationic starch will affect fines and filler retention. This had been confirmed by some previous experiments (57). The role that charges of cationic starch play in retention and the degree of interaction among these factors have not been studied. From the previous section it is known that the charge of this particular cationic starch is dependent on the pH of system. An experimental design which included pH, shear and starch molecular size was selected to develop the model for this study.

The levels of each variable were carefully selected based on the previous experiences. This 6X4X4 factorial design with three replicates in each cell is listed in Table I. Where the units of conversion are represented by the amount of enzyme addition (SKB) and that of shear is the rate of agitation (RPM). In each cell there are three, four-digit numbers. The first digit (1 to 6) represents the level of pH (3 to 8). The second digit (1 to 4) represents the shear level (200, 500, 1000, 1500 RPM). The third digit stands for starch conversion level (0, 100, 200, 300 SKB); where SKB is the added amount of amylose. The fourth digit indicates the replicate in this cell. For easier data management, the control (no cationic starch) was arranged to store in the computer as the fifth level of conversion, although it had nothing to do with conversion.

TABLE I

EXPERIMENTAL DESIGN

	SKB	0				100				200				300			
pH	RPM	200	500	1000	1500	200	500	1000	1500	200	500	1000	1500	200	500	1000	1500
3		1111	1211	1311	1411	1121	1221	1321	1421	1131	1231	1331	1431	1141	1241	1341	1441
		1112	1212	1312	1412	1122	1222	1322	1422	1132	1232	1332	1432	1142	1242	1342	1442
		1113	1213	1313	1413	1123	1223	1323	1423	1133	1233	1333	1433	1143	1243	1343	1443
4		2111	2211	2311	2411	2121	2221	2321	2421	2131	2231	2331	2431	2141	2241	2341	2441
		2112	2212	2312	2412	2122	2222	2322	2422	2132	2232	2332	2432	2142	2242	2342	2442
		2113	2213	2313	2413	2123	2223	2323	2423	2133	2233	2333	2433	2143	2243	2343	2443
5		3111	3211	3311	3411	3121	3221	3321	3421	3131	3231	3331	3431	3141	3241	3341	3441
		3112	3212	3312	3412	3122	3222	3322	3422	3132	3232	3332	3432	3142	3242	3342	3442
		3113	3213	3313	3413	3123	3223	3323	3423	3133	3233	3333	3433	3143	3243	3343	3443
6		4111	4211	4311	4411	4121	4221	4321	4421	4131	4231	4331	4431	4141	4241	4341	4441
		4112	4212	4312	4412	4122	4222	4322	4422	4132	4232	4332	4432	4142	4242	4342	4442
		4113	4213	4313	4413	4123	4223	4323	4423	4133	4233	4333	4433	4143	4243	4343	4443
7		5111	5211	5311	5411	5121	5221	5321	5421	5131	5231	5331	5431	5141	5241	5341	5441
		5112	5212	5312	5412	5122	5222	5322	5422	5132	5232	5332	5432	5142	5242	5342	5442
		5113	5213	5313	5413	5123	5223	5323	5423	5133	5233	5333	5433	5143	5243	5343	5443
8		6111	6211	6311	6411	6121	6221	6321	6421	6131	6231	6331	6431	6141	6241	6341	6441
		6112	6212	6312	6412	5122	6222	6322	6422	6132	6232	6332	6432	6142	6242	6342	6442
		6113	6213	6313	6413	6123	6223	6323	6423	6133	6233	6333	6433	6143	6243	6343	6443

EXPERIMENTAL MATERIALS AND METHODS

TESTING MATERIALS

The stock to be used throughout the whole experiment was first prepared, air dried and stored in a constant humidity room. For every batch of dispersed pulp the consistency and fines content were evaluated separately to avoid sampling variation. Generally, the consistency was controlled at 0.5% ± 0.02% and fines content was 32% ± 1%. The detailed preparation method is listed in Appendix I.

Cationic starch was chosen as the retention aid because of its multifunctional application in papermaking (52). Because of its strong adsorption on fibers (53), starch in effuent can thus be reduced. For environmental control purpose the trend should be favorable to cationic starch as a multifunctional additive. The cationic starch with charge densities of 1X and 3X used in this experiment was supplied by the starch manufacturer in granule form. The molecular weights of the starches were controlled by utilizing enzyme conversion. The conversion levels were differentiated by time and enzyme concentration. For preventing retrogradation all prepared starch solutions were stored in a hot water bath of 150° F. Each prepared solution was consumed within eight hours to minimize changes with time of storage. For every batch of starch the fluidity was evaluated and recorded as reference. A detailed description of starch preparation is listed in Appendix II.

RETENTION TESTING METHOD

There are many methods to evaluate fines and filler retention. The Dynamic Retention/Drainage Jar was selected because of its convenience for adjusting dynamic conditions and also the easy handling of the apparatus in the laboratory. The credibility of this measuring instrument has been reported (54, 55). The agitator drive unit in this device is a motor generator with a servo feedback control which provides speed control from 0 to 3000rpm. The filtering media is a screen made of electrodeposited nickel and has holes with conical cross section. By positioning the small end of the cones upstream, plugging was minimized and non-aggregated particles passed through the 76μm diameter holes (200 mesh). Filtrate collected from the jar was then dried to evaluate the corresponding retained part. Please refer to Appendix III for the procedure and calculation methods.

DATA MANAGEMENT

For every retention test the data were all recorded and stored in a computer data file. A FORTRAN program (Appendix IV) was written to accomplish storage, calculation, sorting and output by a random-access procedure. The benefits of the random-access procedure were: space saving in core memory, easy input-output handling, and only limited data loss during unexpected system failures.

ZETA POTENTIAL MEASUREMENT

For a better understanding of the electrokinetic properties involved in the experiment, the Zeta potential was measured with Laser-Zee meter. Since the turbidity of sample may sometimes interfere with the accuracy, readings were only taken whenever the situation permitted. Although workers have reported that diluting with "mother liquor" would not change the electrokinetic environment (56), "mother liquor" made in the laboratory by centrifuge was found to affect Zeta potential reading of the system which was diluted.

ELECTROKINETIC NATURE OF STOCK

Zeta potential was measured for stock diluted with distilled water while the pH was adjusted with HCl and NaOH. Since the stock was a combination of fibers and anatase, the measured Zeta potential should be interacted by the electrokinetic natures of these two material. By comparing Figure 5 with literature values (38), the curve was similar to the response of fiber fines. The Zeta potential of fines represented the whole pulp as proposed by Jacock (38).

ELECTROKINETIC NATURE OF CATIONIC STARCH

The cationic starch (charge density 3X) solutions with three conversion levels were prepared. These three levels were: control (no conversion), medium and high conversion, the fluidities were 3.63, 1.20, 0.51 centistokes respectively at 150° F. Then small amounts of fiber fines were added and the mixture was diluted. Zeta potential was measured after the pH of the system was adjusted. The results (Figure 6) showed that charge of cationic starch would vary with pH. The peaks of the curves shifted toward lower pHs as the degree of conversion increased. The reason for this shift is

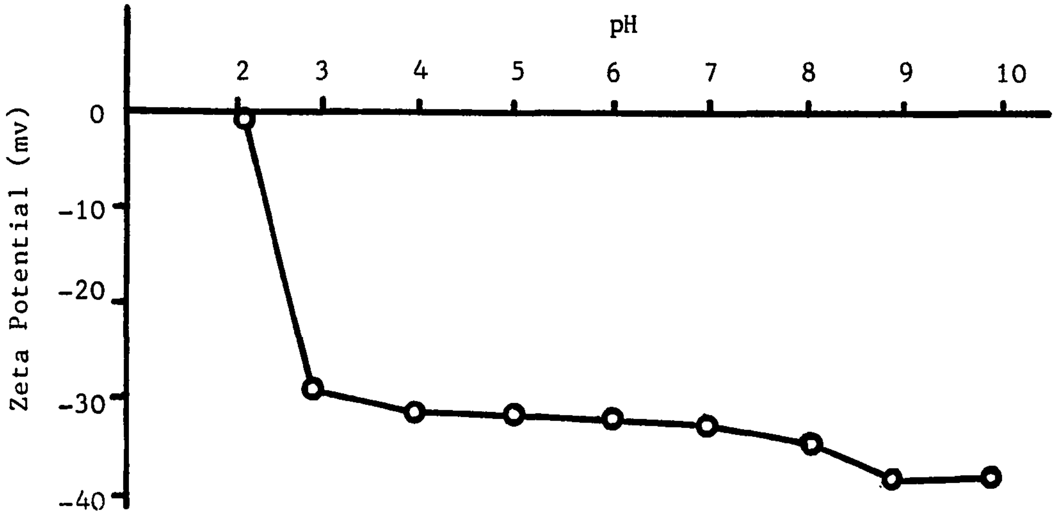


Figure 5. Zeta Potential of the System; Fiber Fines with the Existence of TiO_2 and Long Fiber.

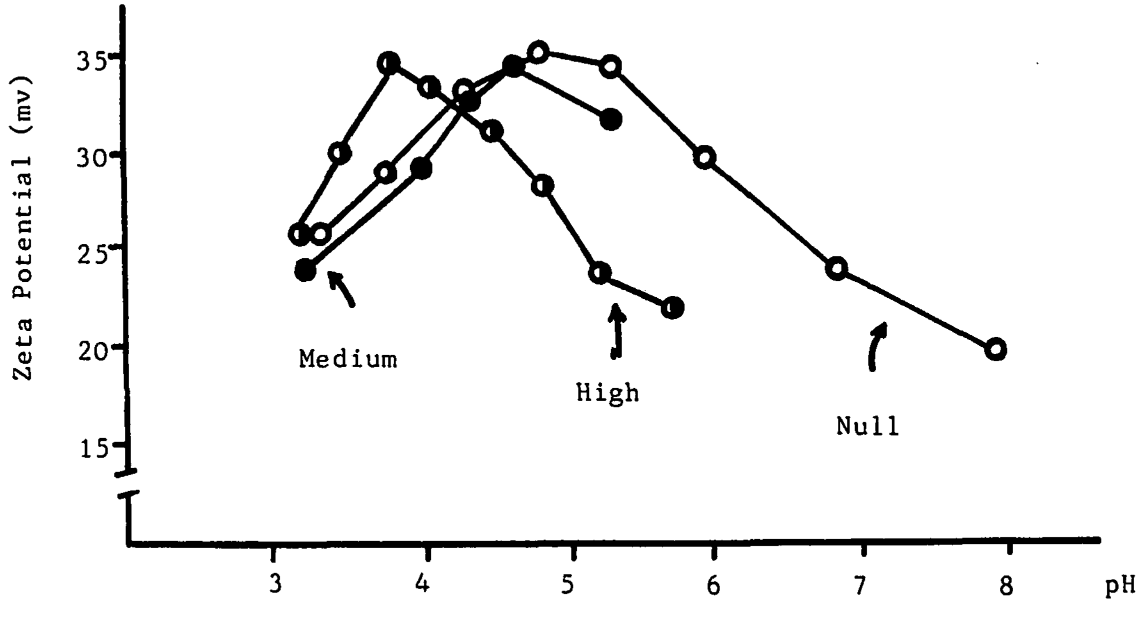


Figure 6. The Effects of pH and Degree of Enzyme Conversion on Zeta Potential of Cationic Starch (3X).

not known. It is suspected that the existence of enzyme affected the electrokinetic behavior of cationic starch.

CATIONIC DEMAND OF STOCK

For determination of cationic demand of stock two non-converted cationic starches with charge density of 1X and 3X were evaluated at pH 7. The results (Figure 7) showed that the plateau regions of cationic demand fell in the positive Zeta potential side rather than the negative as emphasized by Penniman (34).

REACTION RATE

The purpose of this experiment was mainly to find out how the reaction rate would affect the retention of fines and filler. The reaction rate in this experiment was defined as an overall effect of variations which affected the fines and filler retention at different time periods. The experiment was carried out on the Dynamic Retention/Drainage Jar and the results of retention were taken as references for judgement of reaction rate. Since the adsorption rate of polymer and the collision frequency of particles are the main factors which determine the configuration of adsorbed polymer as noticed by Goossenes and Luner (19), care must be taken on setting the rate of agitation while adsorption rate was involved. Also, the agitation speed in this test should set on an acceptable level where bridges could be formed and floc rupture prevented. Thus, when the test was carried under dynamic condition, both polymer adsorption rate and particle flocculation rate would be affected

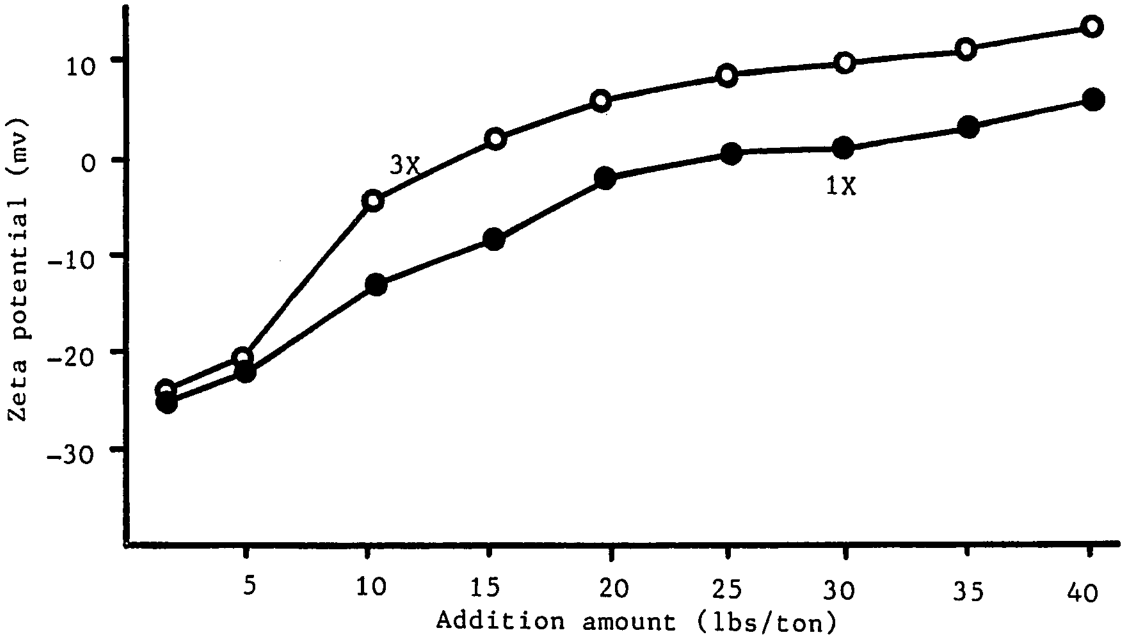


Figure 7. Cationic Demand. Cationic Starch with Charge Density 1X and 3X.

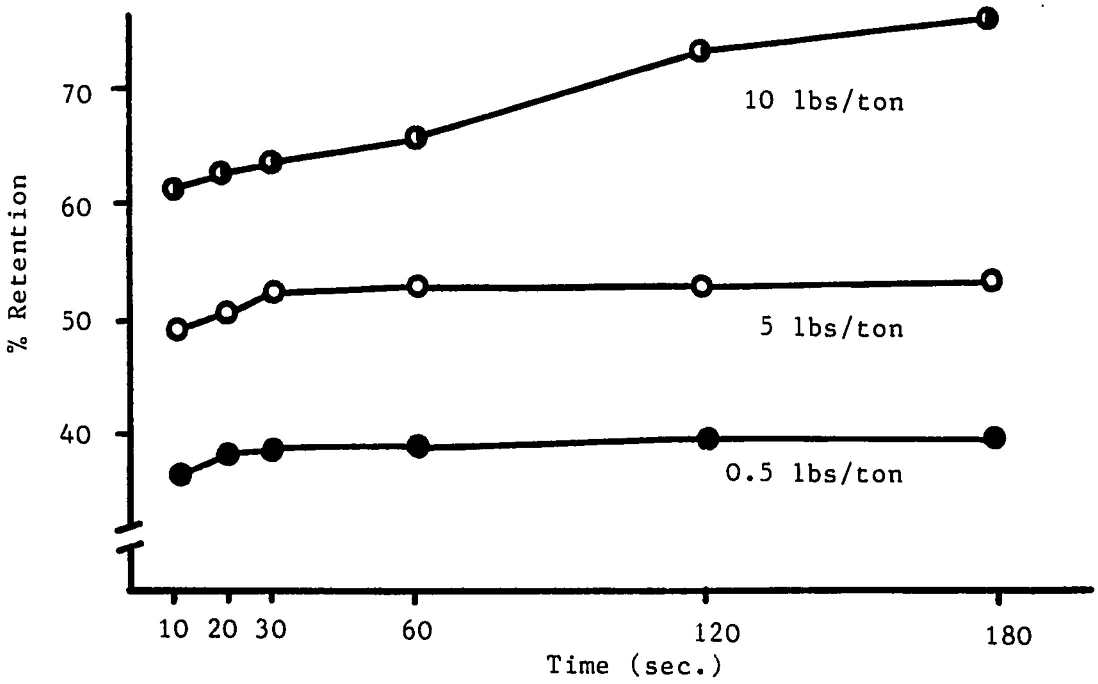


Figure 8. Reaction Rate Indicated by % Retention at Three Addition Levels: 0.5, 5, 10 lbs/ton.

by agitation. The reaction rate was then determined by the overall effects of adsorption rate and flocculation rate. Rotation speed of 100, 200, and 300rpm were tried to observe the relative motion of bulk flow. It was found that when rotating speed exceed 200rpm the dead corner was omitted.

A retention test for three levels of dosage showed that the retention rate was dependent on both time of agitation and the amount of polymer addition (Figure 8). The higher the dosage the longer was the time needed for retention to reach its maximum. This indicates that as far as retention at low velocity gradient was concerned, the higher the dosage the longer the time needed for the system to reach equilibrium.

Further testing was focused on trying to determine when the retention would reach its maximum under mild agitation. 10 lbs/ton cationic starch was selected and the agitation speeds were set on 200 and 300rpm. The results in Figure 9 showed that at 300rpm the retention neither increased nor decreased for different agitating periods. Whereas at 200rpm, the retention reached equilibrium only after at least 30 minutes of agitation. This means that under lower agitating speed fines retention should not be prematurely determined before the reaction reaches equilibrium state.

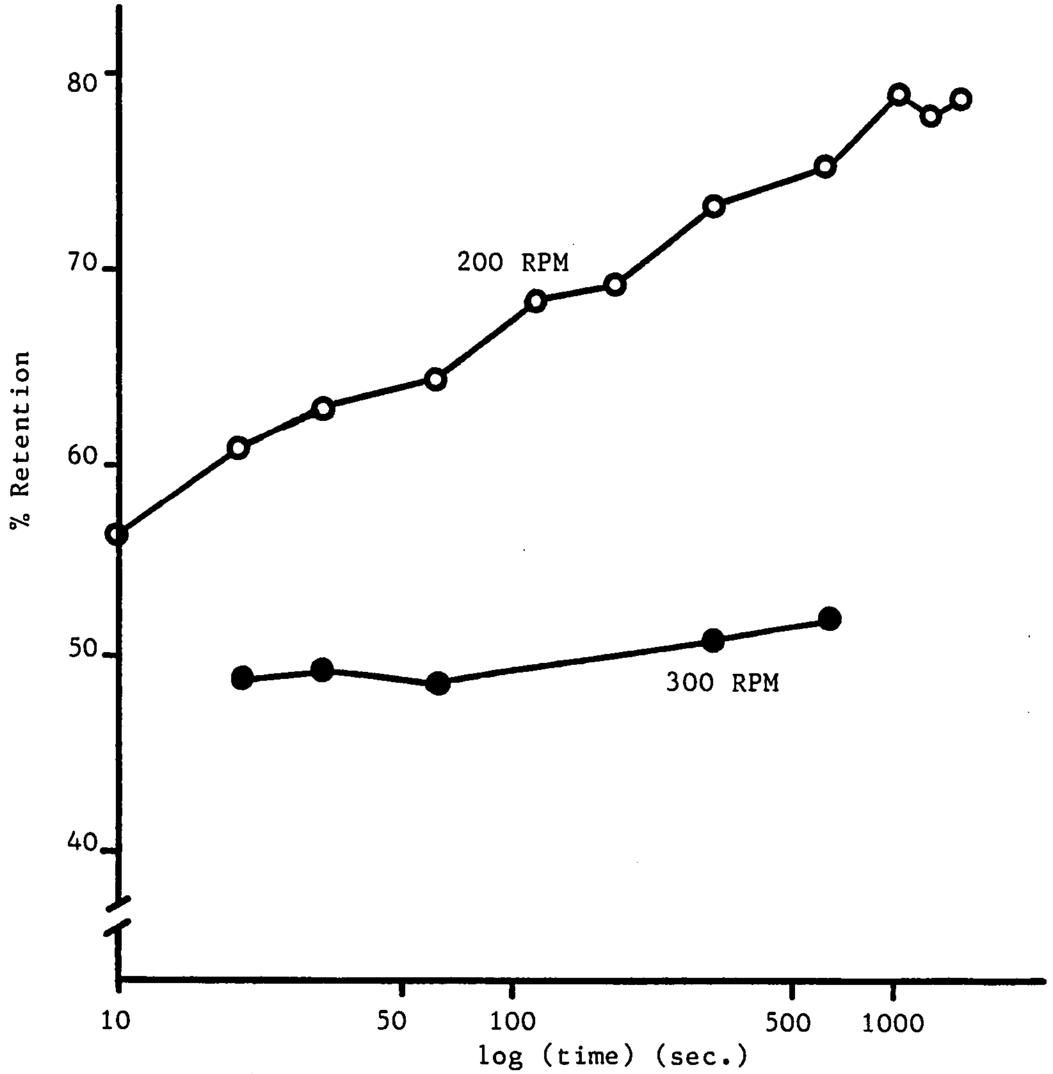


Figure 9. Reaction Rate Indicated by % Retention at Two Shear Levels: 200, 300 RPM.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental design in this work if formed by three variables with several levels. For clear visualization the comparison of these variables is broken down to a degree where phenomena can be explained. First, the mathematical models which describe the experimental data were tested by two-way analyses of variance (ANOVA). These tests are called primary, two-way ANOVA in this work. In the results of two-way ANOVA, models eliminating interaction terms are the simpler ones and responses can be inspected by the variation among levels of all variables. For those models where interactions were significant, attempts were made to break down the levels of every variable and the possible reasons for the interactions were explored. These tests are called group-wise, two-way ANOVA.

DEFINITION OF MATHEMATICAL MODELS

Variables concerned in this experiment were pH, shear and extent of starch conversion. The data of any two of these variables was combined into a A by B two dimensional table with mxn levels, wherein each cell there were three replicates. Take the columns in Table I for example. For each level of conversion there is a pH by shear factorial design (6X4). Totally, there are four levels of conversion that make up four pH by shear designs. Similarly, with six levels of pH there are six shear by conversion factorial designs and four levels of shear make another four combinations.

Consider a mathematical model that might describe such a set of data in each combination. If Y_{ijk} represents the response variable for the kth replicate given the jth B level and ith A level. The model for this design is as follows:

$$Y_{ijk} = N + P_i + Q_j + W_{ij} + E_{ijk}$$

$$i = 1 \text{ to } m$$
$$j = 1 \text{ to } n$$
$$k = 1 \text{ to } 3$$

where

N = a general mean

P_i = a A effect, i.e., the mean increment in retention with the ith A level

Q_i = a B effect

W_{ij} = the interaction effect of A and B

E_{ijk} = an error

If A and B act additively, i.e., no A and B interaction (denoted as AXB), the model is reduced to:

$$Y_{ijk} = N + P_i + Q_j + E_{ijk}$$

This can be distinguished by statistical testings. In a two-way analysis of variance (ANOVA), a non-significant ($p > 0.05$) AXB interaction leads to the inference that the A effect and B effect are additive. Under this condition we can thus determine the effect of each variable while eliminating the effects of the others. When the effect of the variable is statistically significant ($p < 0.05$), this means the increment of response is partially or completely due to its effect. Generally, if there is non-significant AXB interaction, the phenomenon may only be explained by one of the following reasons:

1. Both A and B have no effect on retention: by changing the level of both A and B the response does not change.

2. One of A or B has effect on retention: only by changing the level of one of these variables would the response change; while the other has no effect on response.

3. Both A and B have effects on retention: by changing either level of A and B the response will always change, and their effects are additive.

In Figure 10, the three cases are illustrated.

The determination of which level of each variable has the best result for the response is generally done by posteriori comparison. Basically, for posteriori comparison the means of all levels are first sorted in order and then the difference is tested statistically. There are many procedures to accomplish posteriori test. The Duncan's procedure (59) was selected in this entire analysis work. It provides a protection level of alpha for the collection of tests and also it is less conservative than the others.

If there is interaction between A and B, care must be taken for illustrating the results. Generally, there are two conditions as shown in Figure 11. In condition 1, the interaction between A and B only occured at level A1 and A2, where on level A2 and A3 there might not be any interaction. Under this condition group-wise break down

1. Both A and B have no effect on R.
2. One of A and B (B) has effect on R.
3. Both A and B have effect on R, but they are additive.

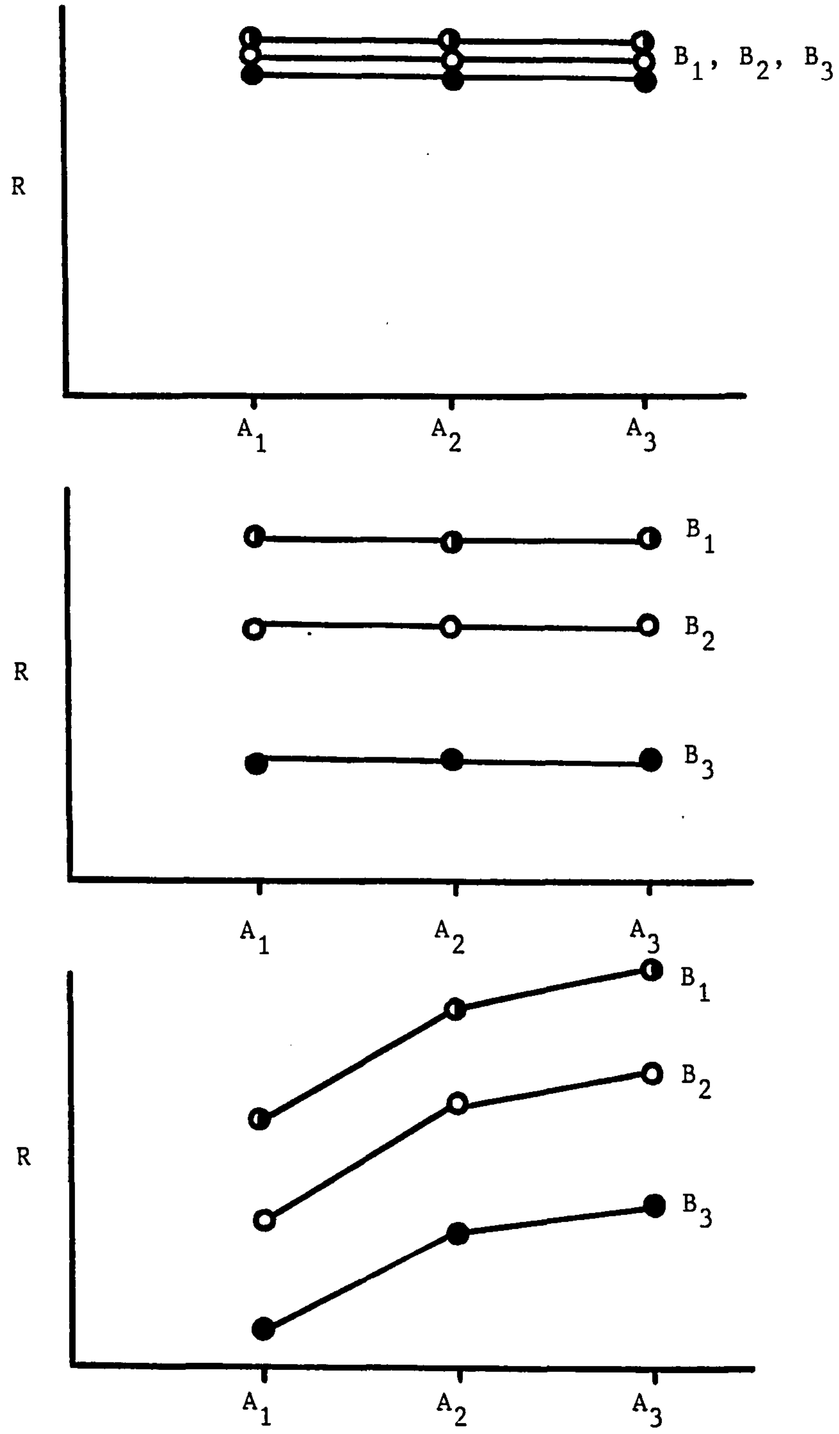
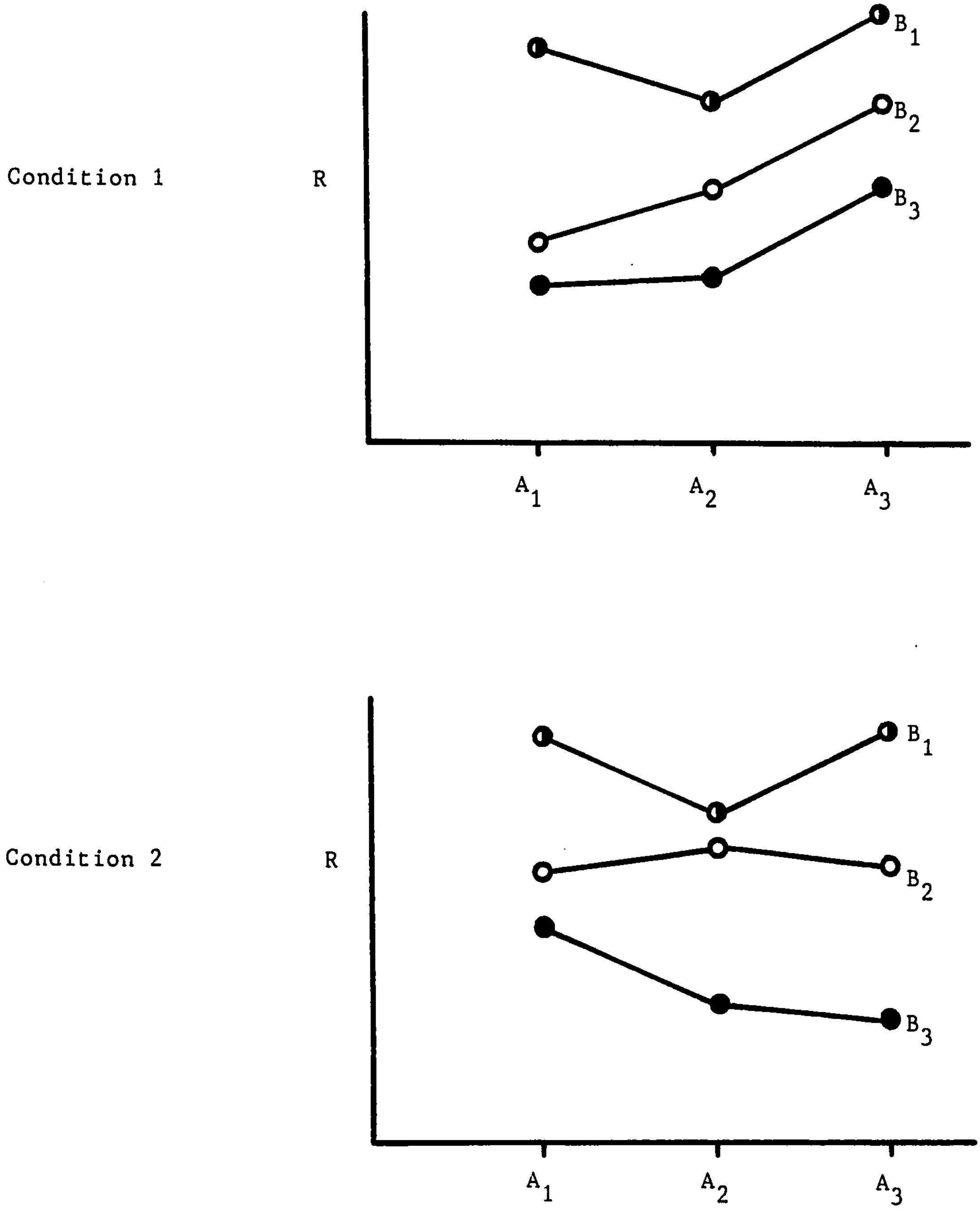


Figure 10. Conditions for Effects of A and B on R.



Condition 1

Condition 2

Figure 11. Conditions for AXB Interaction.

sometimes can explain the phenomenon separately; i.e., A1-A2 by B regarded as a model and that A2-A3 by B another. If there is not a (A2-A3)XB interaction, the general model then can further be reduced to:

$$Y_{ijk} = N + P_i + Q_j + E_{ijk}$$

$$\begin{aligned} i &= x \text{ to } m \\ j &= 1 \text{ to } n \\ k &= 1 \text{ to } 3 \end{aligned}$$

This phenomenon can be explained by the reasons mentioned previously. If the result showed as condition 2 in Figure 11, conditions should be explained individually. For a detailed description of the implementation of two-way ANOVA please refer to Appendix V.

In this research, the group-wise two-way ANOVA has been tested. First, some description of the methods to illustrate the tables of results must be made. In the break-down tables, interaction is not significant for those levels which have the same letter. Also, in the results of posteriori comparison, all means having the same letter are not significantly different within the specific level.

One example may be helpful to visualize how these tables work. Suppose a two-way ANOVA for all the points in Figure 12, 13 results in significant interaction, and if the group-wise break down ANOVA gives the table as:

(A) X (B); B break down		(A) X (B); A break down	
B1	E	A1	E
B2	F	A2	F
B3	F	A3	F

Figure 12.

Example:

AX(B1, B2)

Interaction is

Significant.

AX(B2, B3)

Interaction is

Insignificant.

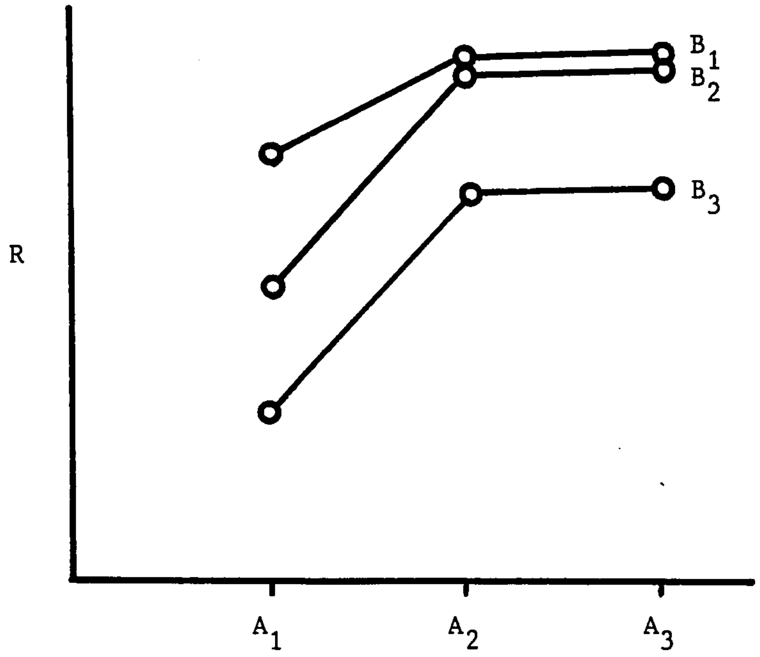


Figure 13.

Example:

(A1, A2)XB

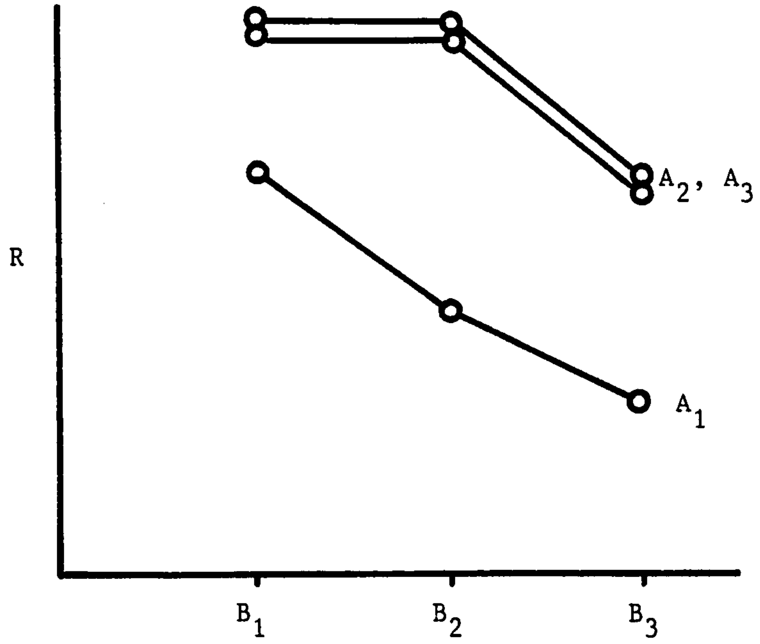
Interaction is

Significant.

(A2, A3)XB

Interaction is

Insignificant.



The interpretation is then: AX(B1,B2) interaction is significant while AX(B2,B3) is not; similarly, (A1,A2)XB interaction is significant while (A2,A3)XB is not.

And if the posteriori comparison results are as follows:

	A1	A2	A3
B1	3.4 E	4.3 E	4.3 E
B2	2.1 F	4.2 E	4.2 E
B3	1.4 G	3.1 F	3.2 F

	B1	B2	B3
A1	3.4 F	2.1 F	1.4 F
A2	4.3 E	4.2 E	3.1 E
A3	4.3 E	4.2 E	3.2 E

Then one can interpret it as: under A1 condition, B1, B2, B3 are significantly different. Under both A2 and A3 conditions, B1 and B2 are not significantly different but are different from B3.

Complete tables of posteriori comparison for this thesis work are listed in Table II, III, and IV. There are three combinations and the comparisons are done by Duncan's procedure.

PRIMARY TWO-WAY ANALYSES OF VARIANCE

The results of the analyses of variance for testing the interaction of (pH)X(conversion), (shear)X(conversion), and (pH)X(shear) are listed in Table V.

(PH)X(CONVERSION) TESTING

The results showed that for four different shear levels the interaction was insignificant only at 1500RPM. The response due to the pH effect was not significant (p=0.204) while there was a conversion effect (p=0.009). In a practical sense this means that at the high shear condition, when pH changes from 3 to 8 the effect of mole-

TABLE II

COMPARISON OF THE CONVERSION EFFECT ON RETENTION AT DIFFERENT pH AND SHEAR LEVELS

		pH					
SHEAR	SKB	3	4	5	6	7	8
200	0	91.26 A	94.92 A	96.14 A	95.52 A	96.26 A	94.90 A
	100	90.21 A	91.98 A	79.44 A	63.89 B	54.32 B	51.40 B
	200	92.01 A	84.82 A	57.70 B	52.72 B	50.09 B	49.30 B
	300	89.65 A	87.03 A	60.59 B	55.55 B	50.45 B	55.30 B
500	0	49.03 B	65.60 A	68.88 A	69.02 A	64.50 A	61.16 A
	100	56.80 A	54.14 AB	44.45 B	39.37 B	37.58 B	36.64 B
	200	58.62 A	49.46 B	37.55 B	31.49 B	31.73 B	30.97 B
	300	56.30 A	50.56 AB	35.41 B	31.98 B	31.04 B	30.19 B
1000	0	26.72 A	36.77 A	37.31 A	36.00 A	34.25 A	32.91 A
	100	33.20 A	33.01 A	25.20 B	20.79 B	20.82 B	19.58 B
	200	33.82 A	29.46 A	23.92 B	23.33 B	22.76 B	22.38 B
	300	33.59 A	30.26 A	23.61 B	21.48 B	21.16 B	22.97 B
1500	0	21.92 A	29.16 A	30.73 A	28.98 A	26.39 A	25.40 A
	100	25.05 A	25.29 A	21.05 A	19.22 AB	19.12 A	19.10 A
	200	24.36 A	24.77 A	21.68 A	21.40 AB	21.48 A	20.87 A
	300	26.66 A	25.82 A	23.08 A	21.11 B	21.08 A	20.37 A

TABLE III

COMPARISON OF SHEAR EFFECT ON RETENTION AT DIFFERENT CONVERSION AND pH LEVELS

		CONVERSION (SKB)			
pH	RPM	0	100	200	300
3	200	91.26 A	90.21 A	92.01 A	89.65 A
	500	49.03 B	56.80 B	58.62 B	56.30 B
	1000	26.72 C	33.20 C	33.82 C	33.59 C
	1500	21.92 C	25.05 C	24.36 D	26.66 C
4	200	94.92 A	91.98 A	84.82 A	87.03 A
	500	65.60 A	54.14 B	49.46 B	50.56 B
	1000	36.77 C	33.01 C	29.46 C	30.26 C
	1500	29.16 C	25.29 C	24.77 C	25.82 C
5	200	96.14 A	79.44 A	57.70 A	60.59 A
	500	68.88 B	44.45 B	37.55 B	35.41 B
	1000	37.31 C	25.20 BC	23.92 C	23.61 C
	1500	30.73 C	21.05 C	21.68 C	23.08 C
6	200	95.52 A	63.89 A	52.72 A	55.55 A
	500	69.02 B	39.37 B	31.49 B	31.98 B
	1000	36.00 C	20.79 BC	23.33 C	21.48 B
	1500	28.98 C	19.22 C	21.40 C	21.11 B
7	200	96.26 A	54.32 A	50.09 A	50.45 A
	500	64.50 B	37.58 AB	31.73 B	31.04 B
	1000	34.25 C	20.82 B	22.76 C	21.16 B
	1500	26.39 C	19.12 B	21.48 C	21.08 B
8	200	94.90 A	51.40 A	49.30 A	55.30 A
	500	61.16 B	36.64 AB	30.97 B	30.19 B
	1000	32.91 C	19.58 B	22.38 C	22.97 BC
	1500	25.40 C	19.10 B	20.87 C	20.37 C

TABLE IV

COMPARISON OF THE pH EFFECT ON RETENTION AT DIFFERENT SHEAR AND CONVERSION LEVELS

SHEAR (RPM)

	pH	200		500		100		1500	
	3	91.26	A	49.03	B	26.72	A	21.92	A
	4	94.92	A	65.60	A	36.77	A	29.16	A
0	5	96.14	A	68.88	A	37.31	A	30.73	A
	6	95.52	A	69.02	A	36.00	A	28.98	A
	7	96.26	A	64.50	A	34.25	A	26.39	A
	8	94.90	A	61.16	A	32.91	A	25.40	A
	3	90.21	A	56.80	A	33.20	A	25.05	A
1	4	91.98	A	54.14	A	33.01	A	25.29	A
0	5	79.44	AB	44.45	A	25.20	B	21.05	A
0	6	63.89	BC	39.37	A	20.79	B	19.22	A
S	7	54.32	C	37.58	A	20.82	B	19.12	A
K	8	51.40	C	36.64	A	19.58	B	19.10	A
B									
	3	92.01	A	58.62	A	33.82	A	24.36	A
2	4	84.82	A	49.46	B	29.46	B	24.77	A
0	5	57.70	B	37.55	C	23.92	C	21.68	A
0	6	52.72	B	31.49	C	23.33	C	21.40	A
	7	50.09	B	31.73	C	22.76	C	21.48	A
	8	49.30	B	30.97	C	22.38	C	20.87	A
	3	89.65	A	56.30	A	33.59	A	26.66	A
3	4	87.03	A	50.56	A	30.26	A	25.83	A
0	5	60.59	A	35.41	B	23.61	A	23.08	A
0	6	55.55	BC	21.98	B	21.48	A	21.11	A
	7	50.45	BC	31.04	B	21.16	A	21.08	A
	8	55.30	C	30.19	B	22.97	A	20.37	A

TABLE V

PRIMARY TESTING OF INTERACTION BETWEEN TWO VARIABLES

	SHEAR LEVEL			
	200	500	1000	1500
(pH)X(CONVERSION)	YES[*]	YES	YES	NO[**]

	pH					
	3	4	5	6	7	8
(SHEAR)X(CONVERSION)	NO	NO	YES	YES	YES	YES

	CONVERSION LEVEL			
	0	100	200	300
(pH)X(SHEAR)	NO	YES	YES	YES

[*] YES: Means the Interaction is Significant.

[**] NO: Means the Interaction is Insignificant.

cular weight of cationic starch is predominant.

(SHEAR)X(CONVERSION) TESTING

Insignificant interaction of shear and starch molecular weight occurred at both pH 3 and 4. Since both effects of shear and conversion are significant, this leads to a proposal that the effects are additive. Posteriori comparison showed that in all cases retention decreased as the shear increased. At pH 4, the conversion of cationic starch decreased the retention, whereas for pH 3 conversion had the opposite effect on retention. In other words, the non-converted cationic starch retained less fines than the converted ones did. A back-up experiment was then set up to measure the Zeta potential of stock with the addition of non-converted cationic starch at different pH levels. The results in Figure 14 suggest that the positive Zeta potential at pH 3 and 4 caused by the addition of cationic starch dispersed fine particles and, thereby, caused lowered retention.

(PH)X(SHEAR) TESTING

Insignificant interaction only occurred with the non-converted starch. Comparing the total means showed that retention was reduced with the increasing shear, and also reduced by the effect of pH while pH changed from 4 to 3. This reduction can be explained by the reason mentioned in the previous section.

GROUP-WISE TWO-WAY ANLYSES OF VARIANCE

(PH)X(CONVERSION) GROUP-WISE BREAK DOWN TESTING

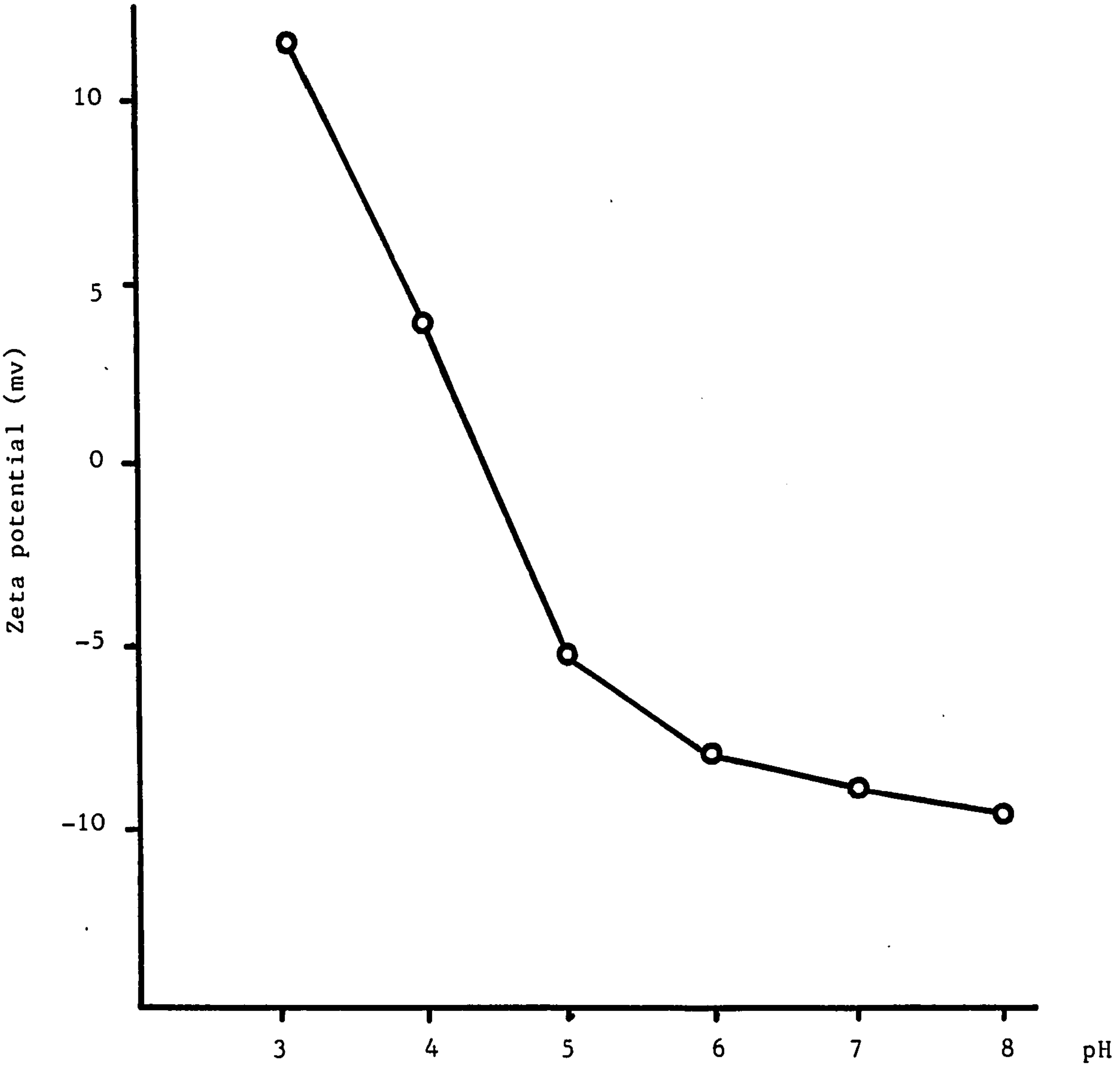


Figure 14. Zeta Potential of the System, One Hour after the Addition of Non-Converted Cationic Starch.

A typical interaction between pH and conversion may be seen in Figure 15.

PH break down:

Table VI shows the interactions between pH and conversion were less apparent as the shear increased. And eventually, at highest shear level the responses have the same model. All the interactions occurred on the upper left corner on the table indicating that at low shear levels the retention is not predictable by the effects of pH and conversion; especially for those of low pH levels.

Conversion break down:

Table VII shows that at high shear level there was no pH and conversion interaction. Whereas, at low shear levels the dimensions of the cationic starch molecules may cause differential action.

Inference and discussion:

It is obvious that the interactions between pH and conversion occurred most frequently at low shear levels. Also, these interactions occurred predominantly at low pH and low starch conversion levels. In the upper two rows (200, 500RPM) of Table II, where retention is almost independent of conversion at pH 3 and 4, the conversion effect occurred only at higher pH levels. This indicates that at pH 3 and 4, dimensions of the cationic starch molecules did not affect retention. In other words, particles flocculated by the polymer did not act as the mechanism of aggregation in this case. The phenomena of high Zeta potential occuring at pH 3 and 4 have been illustrated in Figure 15. The high Zeta potential may over-

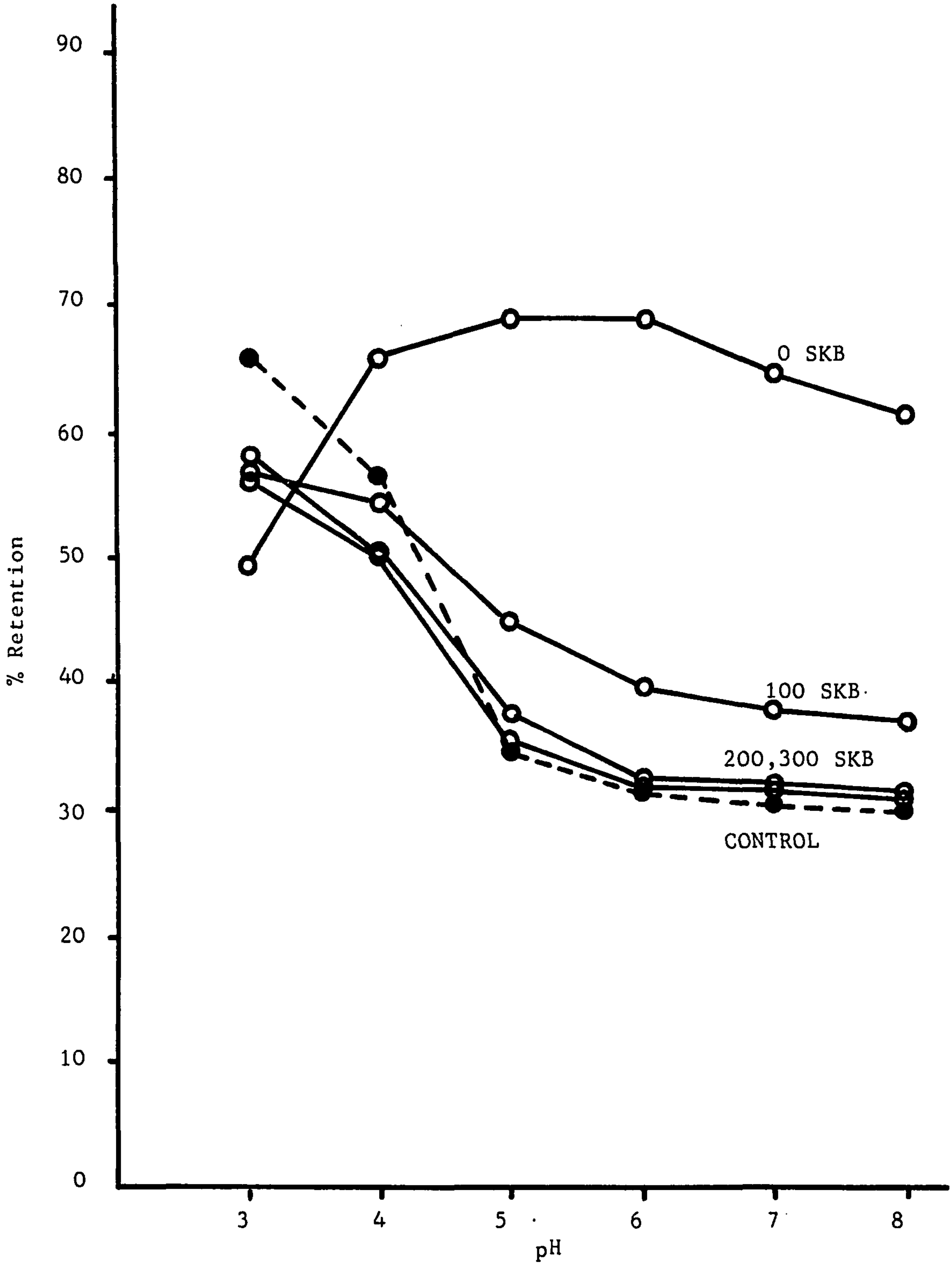


Figure 15. The Effect of pH on Retention. Shear Level: 500 RPM. Different Starch Conversion Levels Plus Control are Compared.

TABLE VI

(pH)X(CONVERSION) INTERACTION TESTING; PH BREAK DOWN AND FOUR SHEAR LEVELS ARE COMPARED

	SHEAR LEVEL			
pH	200	500	1000	1500
3	A	A	A	A
4	A	B	B	A
5	B	C	C	A
6	C	D	C	A
7	C	D	C	A
8	C	D	C	A

TABLE VII

(pH)X(CONVERSION) INTERACTION TESTING; CONVERSION BREAK DOWN AND FOUR SHEAR LEVELS ARE COMPARED

	SHEAR LEVEL			
CONVERSION LEVEL	200	500	1000	1500
0	A	A	A	A
100	B	B	B	A
300	C	C	B	A
300	C	D	B	A

shadow the bridging effect of non-converted cationic starch.

For the role of conversion the first two columns (200, 500RPM) of Table IV (p. 46) show that the effects of pH were differentiated when conversion increased. But for the non-converted starch system, retention of fines was not affected by the changes in pH. That is, charge of cationic starch did not affect retention in this case. Thus, it can be inferred that the effect of bridging by non-converted cationic starch overshadowed the effect of Zeta potential. As conversion increased, as shown in Figure 16, the bridging effect appeared to become less important and the electrokinetic environment became the main factor determining retention. Figure 15 also shows that when conversion levels exceeded 200 SKB, the dimensions of the starch molecules apparently had no effect on fines retention.

(SHEAR)X(CONVERSION) GROUP-WISE BREAK DOWN TESTING

In the primary two-way ANOVA testing, the interactions between shear and conversion occurred across the pH range of 5 to 8 (Table V) (p. 47). According to previous studies (57) the response was sensitive to both variables. This means that from level to level the extent of change in retention is high and thus causes interactions.

Conversion break down:

Table VIII shows that for pH 3 and 4 there were no interactions between shear and conversion. And in the first two columns (pH 3. 4) of Table II, it appears that at 500 RPM the effect of retention aid acted somewhat differently, where at pH 4, non-converted cationic

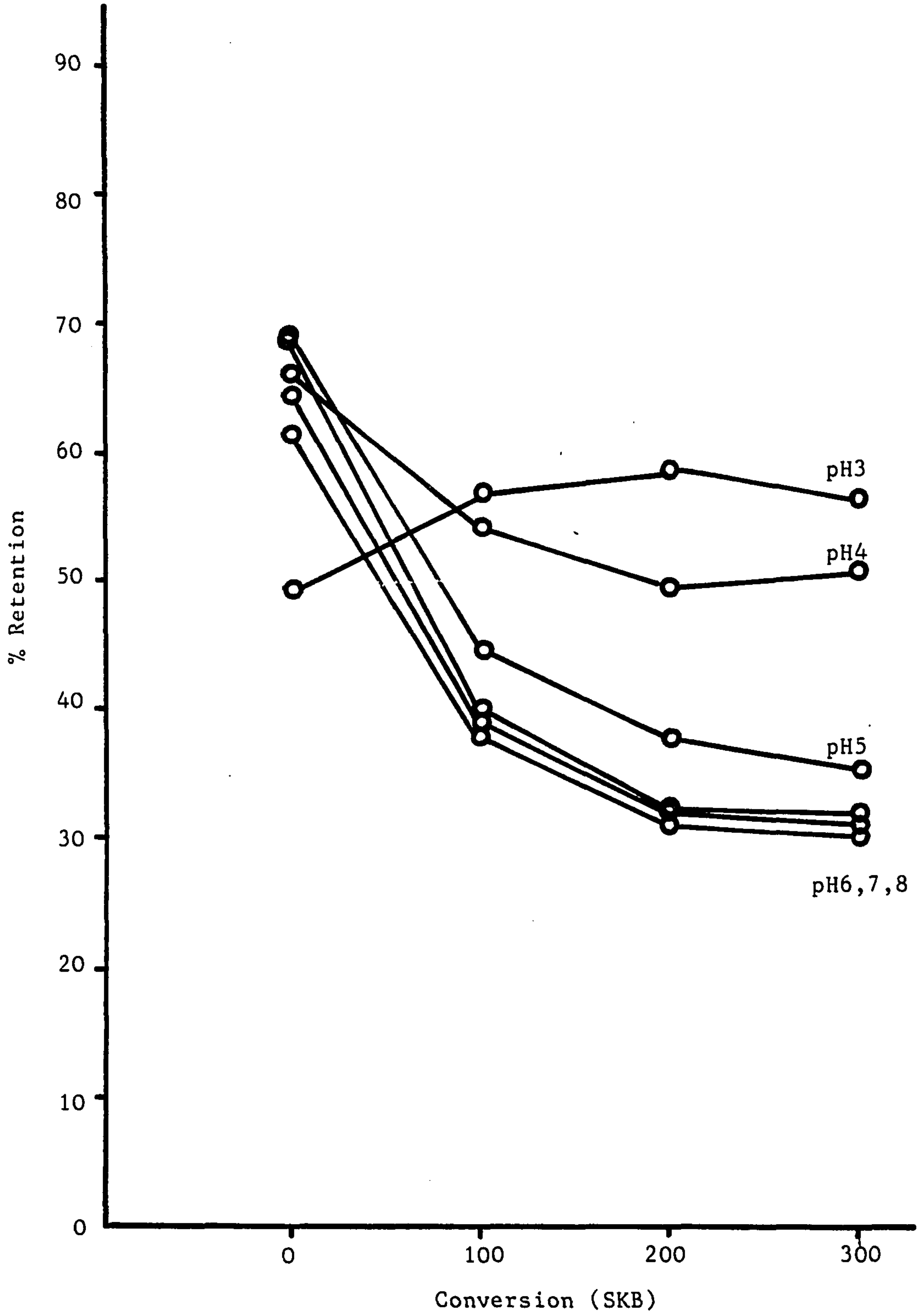


Figure 16. The Effect of Starch Conversion Level on Retention, Shear Level: 500 RPM; Different pH Levels are Compared.

TABLE VIII

(SHEAR)X(CONVERSION) INTERACTION TESTING, CONVERSION BREAK DOWN AND SIX pH LEVELS ARE COMPARED

	pH					
CONVERSION LEVEL	3	4	5	6	7	8
0	A	A	A	A	A	A
100	A	A	B	B	B	B
200	A	A	C	C	B	B
300	A	A	C	C	B	B

starch retained significantly more fines, and at pH 3, it retained less fines. There was probably a slight bridging effect at pH 4 as opposed to the counteracting effect at pH 3 (also consulting figure 15).

In the lower right corner of Table VIII the trend shows while pH increased the converted cationic starch tends to act by the same mechanism. This means that the model is less interacted by the effects of shear and conversion within this range. From the results of posteriori comparison, Table II (p. 44) shows there was insignificant difference in retention among the converted levels. Then the change in shear should take the full responsibility for the interaction between shear and conversion. For the reason of model shifting due to pH effect, the sensitivity of response to the shear effect is considered. In Figure 17, while pH increased the sensitivity (slope) of

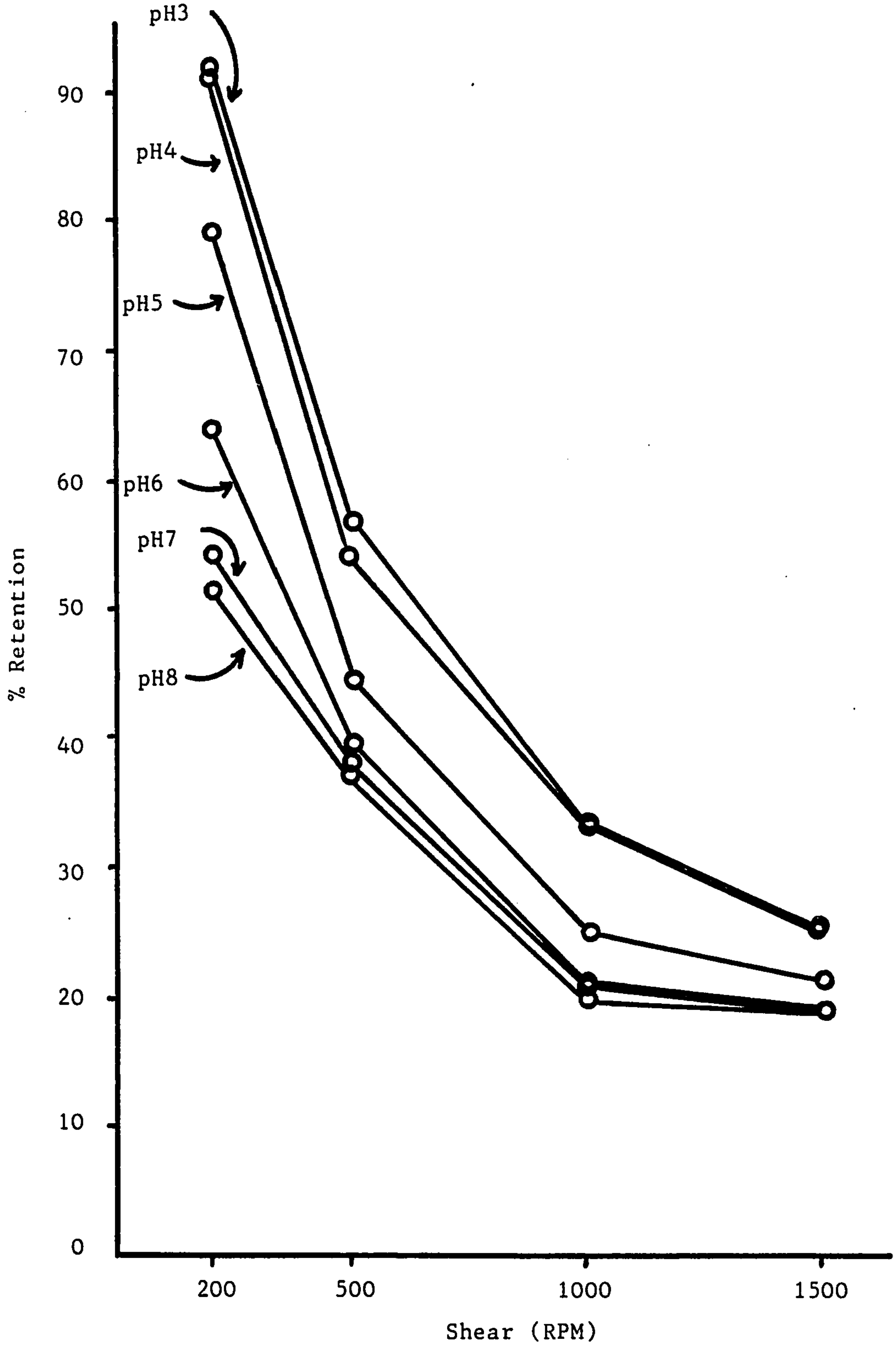


Figure 17. The Effect of Shear on Retention. Conversion Level: 100 SKB. Different pH Levels are Compared.

response due to the effect of shear reduced. And at high pH levels the models tend to be similar.

Shear break down:

Table IX shows a different trend as compared with the previous part; the change in pH from 5 to 8 does not shift the model. Since the posteriori comparison (Table III) (p. 45) does not give us any hint for explaining the cause of interaction, the sensivity of response at different starch conversion levels to the shear effect was then tested. Figure 18 shows that as conversion increased the retention was less sensitive to the conversion effect. This explains part of the reasons why shear and conversion effect were interacted.

Inference and discussion:

In the previous part we concluded that when pH changed from 5 to 8, the degree of influence of rate of shear decreased. This im-

TABLE IX

(SHEAR)X(CONVERSION) INTERACTION TESTING.
SHEAR BREAK DOWN AND SIX pH LEVELS ARE COMPARED

	pH					
SHEAR LEVEL	3	4	5	6	7	8
200	A	A	A	A	A	A
500	A	A	B	B	B	B
1000	A	A	C	C	C	C
1500	A	A	C	C	C	C

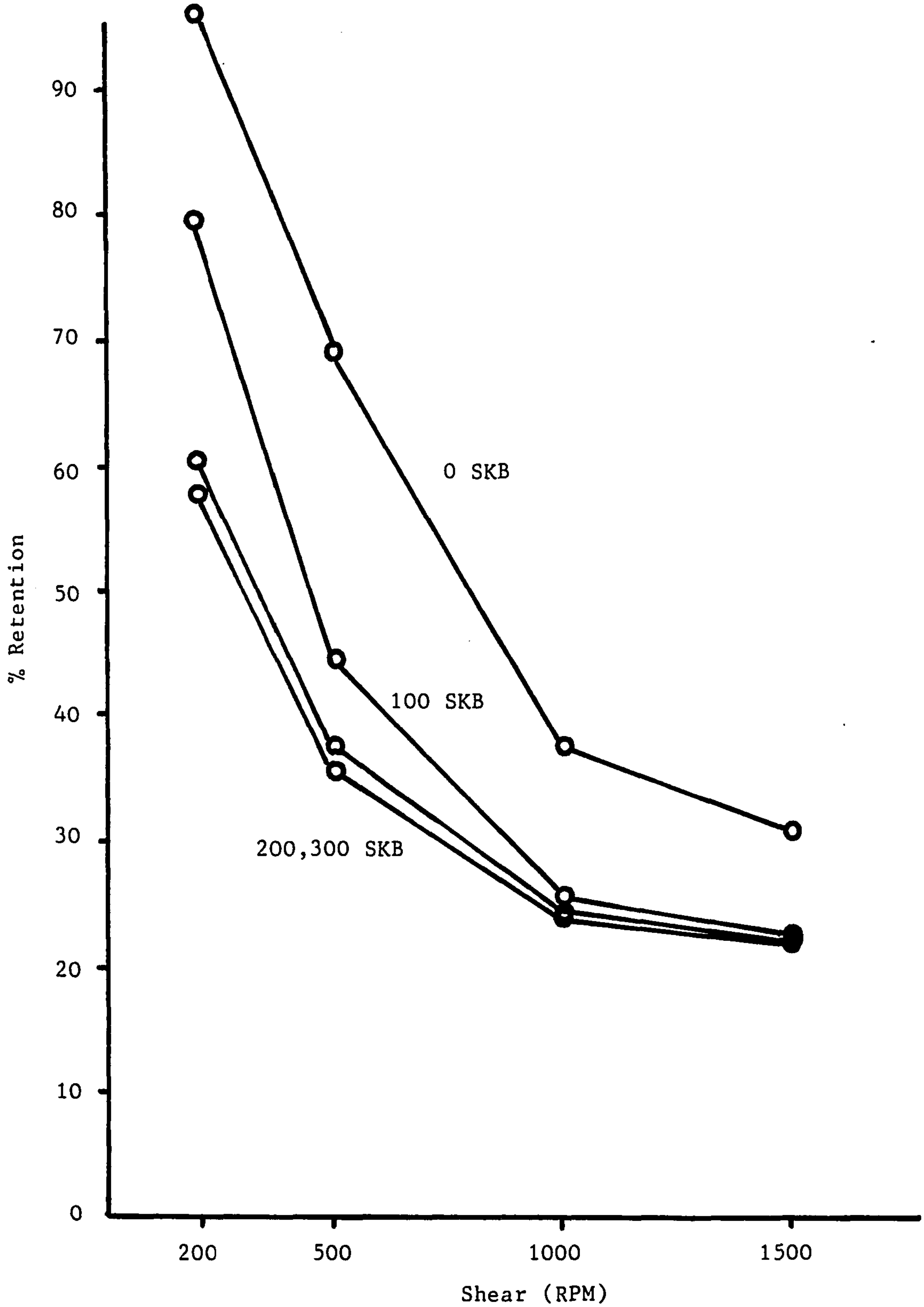


Figure 18. The Effect of Shear on Retention. pH Level: 5. Different Starch Conversion Levels are Compared.

plies that either at high pH level (pH 8) the cationic starch can resist higher shear or the aggregated particles were deflocculated by shear to a greater extent at low pH (pH 5). Figure 17 shows that the later postulate is proper. The changes in degree of influence may be caused by change in charge due to pH or by polymer degradation. Since the mechanism of retention at pH 3 and 4 has been proved to be mainly that of electrical neutralization, the effect of polymer degradation should have little influence on these two levels. A further indication can be seen from Figure 18 that at pH 5 the higher the molecular weight the steeper the slope of the curve. And in Figure 19, the molecular weights of polymer are almost unimportant at pH 4; since the parallel curves mean retention was equally sensitive to the change in molecular weight. This suggests that the degradation of polymer at high pH levels is a possible explanation. From all these phenomena we can infer that over high pH ranges the mechanism of particle aggregation favors polymer bridging. And from Figure 17 we also can conclude that while pH increases within this range the bridging effect will become less important. The reduction of polymer bridging effect may be explained by the electrokinetic nature of cationic starch at high pH ranges. Figure 6 shows that the charge of cationic starch decreases as pH changes from 5 to 8. However, Figure 14 shows the overall charge of system changes only slightly in this range.

(PH)X(SHEAR) GROUP-WISE BREAK DOWN TESTING

Based on the materials covered in the previous sections, it is

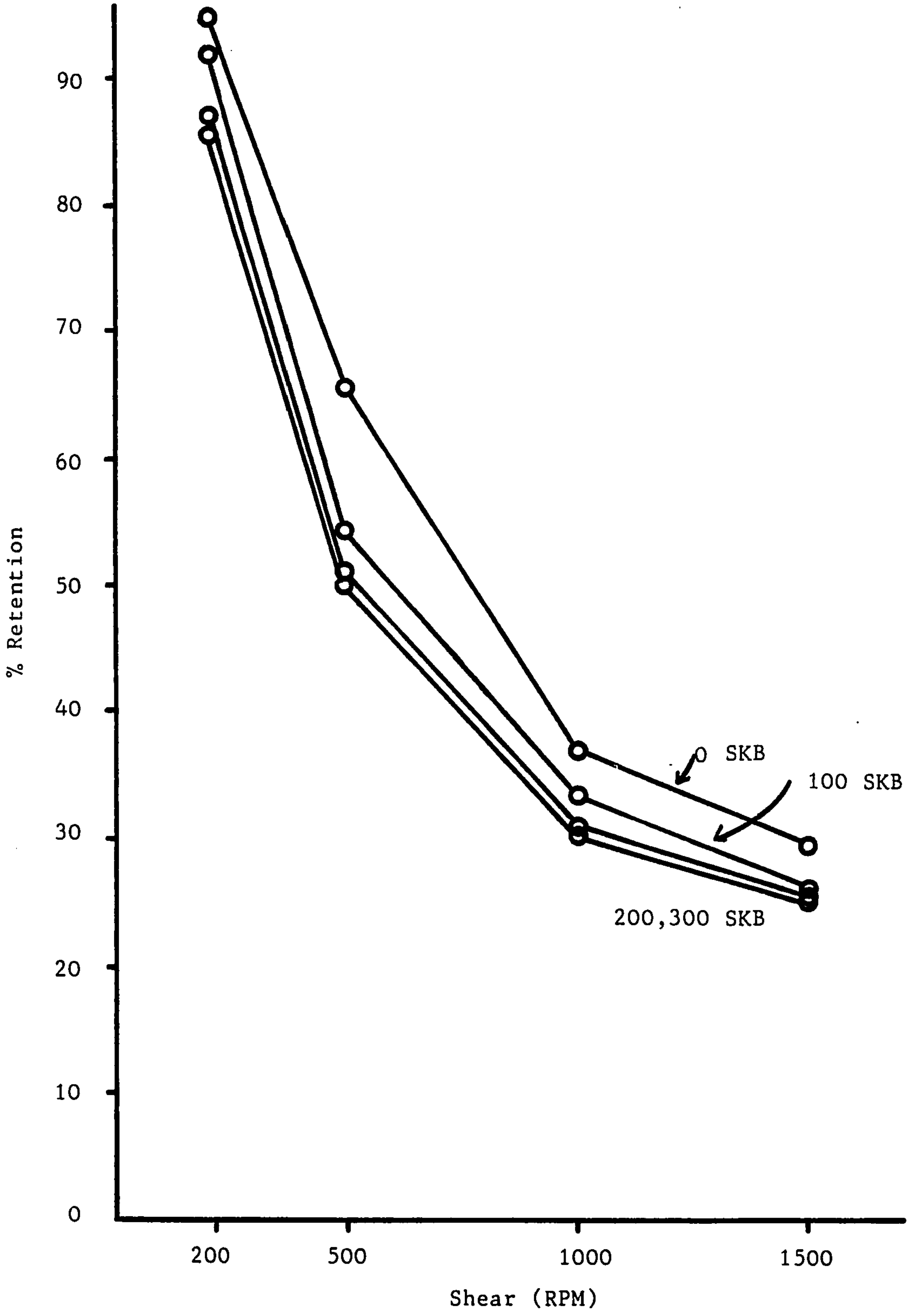


Figure 19. The Effect of Shear on Retention. pH Level: 4. Different Starch Conversion Levels are Compared.

much easier for this section to explore the possible reasons for interaction between pH and shear.

pH break down:

The non-significant interaction between pH and shear with the non-converted starch level has been explained. From Table X, we can find that while conversion increased, the response model shifted to a unified one. This implies that at low starch conversion levels the charges of cationic starch acted differently from that of high conversion levels. This difference in charge, while interacting with moleculer dimension, results in characteristics of polymer bridging at different pH levels. Thus, polymer bridging, which occured at high pH levels, should be explained by both characteristics of polymer molecule dimension and charge at the specific pH level.

Shear break down:

The trend as shown in Table XI cannot give us further information, except the model of non-converted starth level which has been explained in the primary ANOVA. And it is obvious that with different mechanism of aggregation at various pH ranges, the interaction between pH and shear is inevitable.

COMPARISON WITH CONTROL DATA

The models of retention mechanism have been explored by viewing from different angles. Most of the results could only supply the information of where and how the responses are interacted. Effi-

TABLE X

(pH)X(SHEAR) INTERACTION TESTING. pH BREAK DOWN AND FOUR CONVERSION LEVELS ARE COMPARED

	CONVERSION LEVEL			
pH	0	100	200	300
3	A	A	A	A
4	A	A	B	A
5	A	B	C	B
6	A	C	D	B
7	A	C	D	B
8	A	C	D	B

TABLE XI

(pH)X(SHEAR) INTERACTION TESTING. SHEAR BREAK DOWN AND FOUR CONVERSION LEVELS ARE COMPARED

	CONVERSION LEVEL			
SHEAR LEVEL	0	100	200	300
200	A	A	A	A
500	A	B	B	B
1000	A	C	C	C
1500	A	D	D	C

ciency of cationic starch as a retention aid is not evident by just looking at the model. Sample data thus have to be compared with control data.

Figure 20 shows the results of the comparison. At pH 3 and 4, while the addition of hydrogen ion compressed the electric double layer, further addition of cationic starch actually acted as a dispersing agent. For the other pH levels the increments in retention are almost identical. By comparing to Figure 14 it is found that the most effective electrokinetic environment for retention was not necessarily at the isoelectric point. Thus, electrokinetics do not explain the increased retention. Bridging appears as a more likely mechanism.

Further comparison of the control stock data with 100 SKB converted starch is shown in Figure 21. The peak at pH 5 indicates more specifically that most efficient effect of cationic starch as a retention aid should be acquired at this level. For a better understanding of the electrokinetic interaction between fiber and cationic starch, the comparisons are listed in Table XII.

In the table, row C represents the "Electrocontrast" between the Zeta potential of fiber and cationic starch. Providing that the charge neutralization effect is excluded from this case, the "Electrocontrast" is then a good representation for the efficiency of the bridging effect. This can be shown when the "Electrocontrast" compares with the response of Figure 21. While the "Electrocontrast" decreased, the increment in retention also decreased. And at pH 5

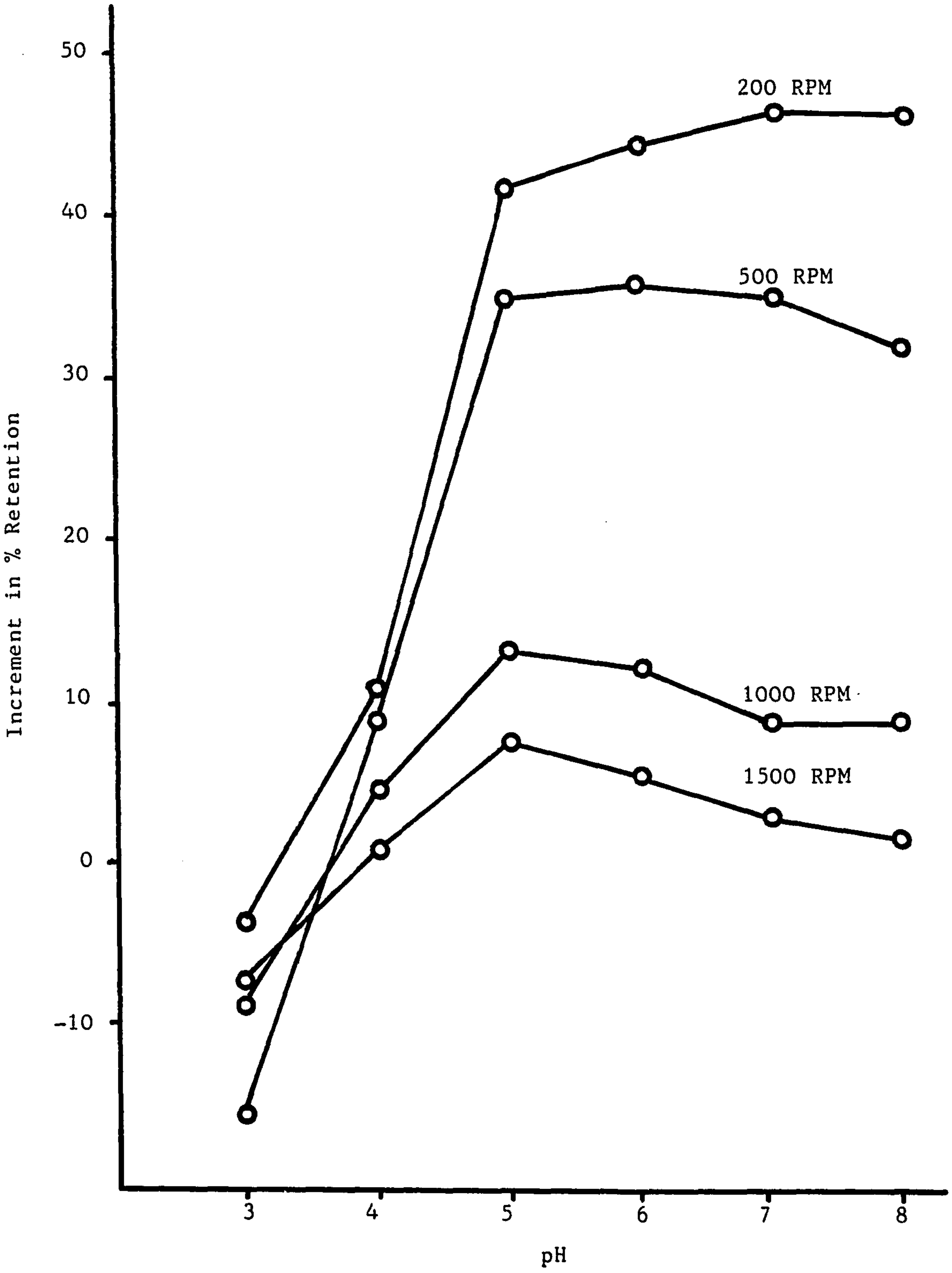


Figure 20. Increase in Retention by the Addition of Non-Converted Cationic Starch at Different pH Levels.

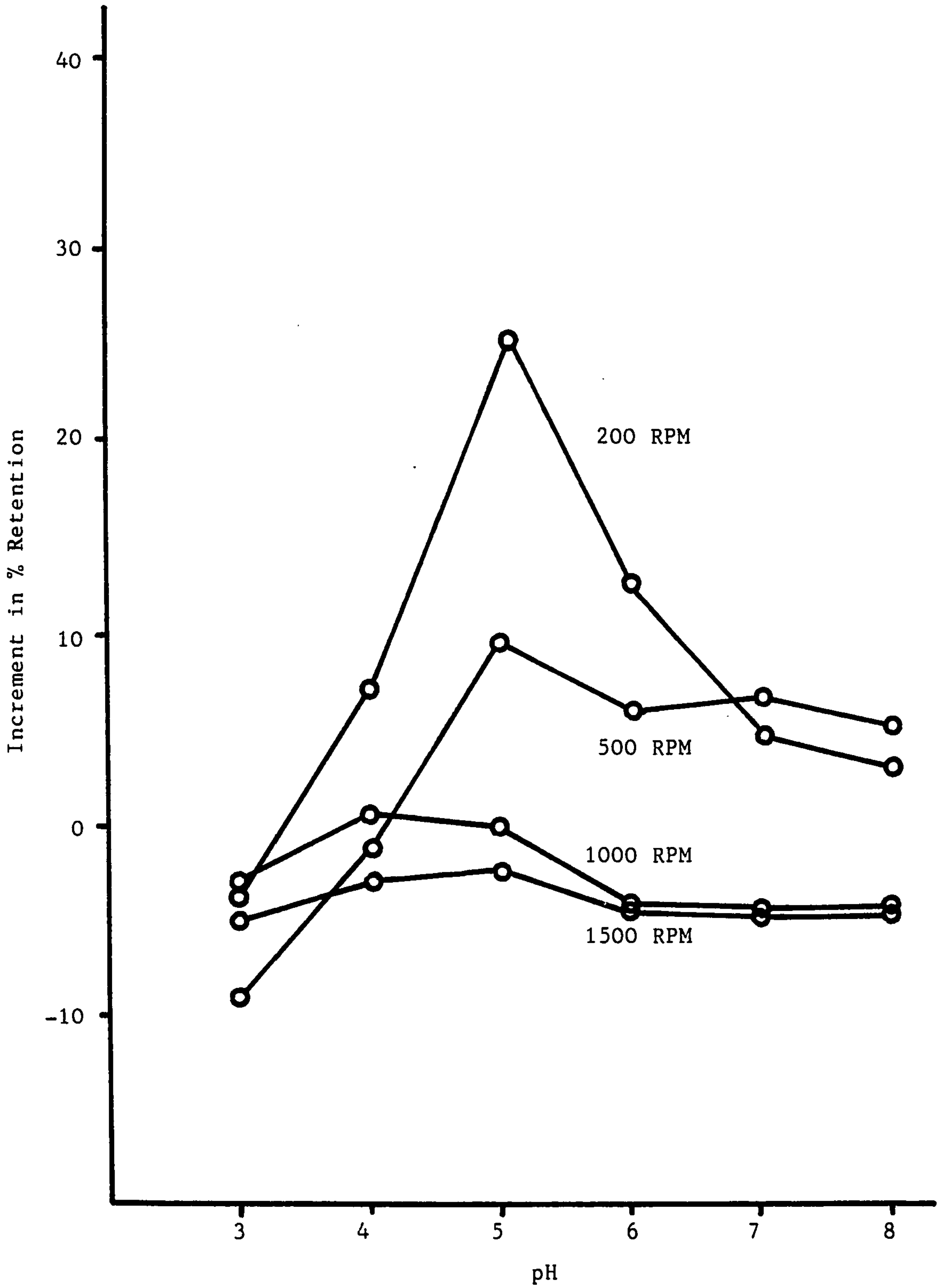


Figure 21. Increase in Retention by the Addition of 100 SKB Converted Cationic Starch at Different pH Levels.

TABLE XII

COMPARISON OF ZETA POTENTIAL

	PH 3	4	5	6	7	8
A. Zeta Potential* of Fiber	-29	-33	-33	-33	-33	-35
B. Zeta Potential of Cationic Starch	+25	+30	+34	+29	+23	+20
C. A+B	-4	-3	+1	-4	-10	-15
D. Zeta Potential	+11	+4	-5	-8	-9	-10

*The Unit of Zeta Potential is mV.

the "Electrocontrast" reaches +1. This contrast is predominately due to the charge of cationic starch. But, while this effect interacts with the natural effect of fiber, overall Zeta potential is not necessarily a representation of both effects. Thus, it can be seen that the "Electrocontrast" changes in large scale at different pH levels while Zeta potential of the whole system almost maintains on a plateau. A single measurement of Zeta potential as to determine the bridging effect is improper in this case. Also, by simply judging the system Zeta potential to control fines retention is an oversimplification, likely to be doubtful, and possibly biased.

SUMMARY AND CONCLUSIONS

The group-wise break down testing approach was developed by this researcher. Facing such massive data it is difficult to spot the high lights. The basic principle of two-way analysis of variance is to determine the model of response whether or not there is an interaction term. Whenever there is interaction, the trend of response can be found by breaking down the variable levels. This led us to find which range of levels had the highest responsibility for the interaction. Many confusions were avoided by using this method. Since with 288 sets of data there are at least 28 (=2X(6+4+4)) ways to draw graphs including two variables, no attempt was made to explain all the phenomena involved in the results. Thus the simplicity of approaching by this method avoided plotting meaningless and unnecessary graphs. Nevertheless, sophisticated programming ability and familiarity of computer systems is required to utilize this approach.

There were two possible mechanisms for aggregation of particles that were inferred by this analyses; namely, charge neutralization and polymer bridging. The charge neutralization mechanism appeared to occur at low pH levels, where retention of the fines and filler was almost independent of molecular weight (conversion level) of the cationic starch. The bridging mechanism appeared to be favored in the pH range from 5 to 8. Since the charge of cationic starch decreased as the pH increased, the increment in retention diminished the same way; although the Zeta potential of the system maintained at a -5 to -10mV plateau.

The bridging effect for high molecular weight cationic starch may have overshadowed the electrokinetic effect of the system. As the molecular weight was reduced, both effects became equally important. And eventually, at high conversion level (low molecular weight), the electrokinetic effect appeared to play the main role.

Since the shear effect in these analyses was not an absolute factor, it is difficult to make a specific conclusion. Efficiency of cationic starch as a retention aid was evident only when it was compared to control data containing no starch. Nevertheless, the postulate of polymer degradation under shear condition has been inferred in these analyses.

The efficiency of cationic starch was judged by comparing sample data with control data. Comparisons suggest that the bridging effect was most active within a pH range of 5 to 8. The change in increment was possibly due to the interaction between cationic starch molecular weight and charge of cationic starch at that specific pH level. Also, it showed that by further converting the cationic starch, the highest increment in retention was found at pH 5. From the electrokinetic point of view this bridging effect is proposed to be predominately caused by the electric charge difference between fiber and cationic starch. The Zeta potential of the system was found to be not an absolute guideline. Thus, the "Electrocontrast" effect was postulated.

The results of this research work can be concluded in the following:

1. The mechanism of particle aggregation by utilizing cationic starch was found to be the charge neutralization at pH 3 and 4. This was inferred by the statistical analyses. Here the models of fines and filler retention did not shift to different models as responding to the changes on molecular weight of cationic starch and shear gradient of bulk flow.

2. As pH changes in the range of pH 5 to 8, the mechanism was found to be polymer bridging. This was detected by the model's shifting while molecular weight and shear gradient changed.

3. For fines and filler retention purposes the improvement in fines retention could not be achieved by the mechanism of charge neutralization. The mechanism of polymer bridging significantly improved fines and filler retention by utilizing cationic starch.

4. The optimum condition for fines and filler retention could be justified by measuring the Zeta potential of fiber fines and polymer separarately. Nevertheless, the hypothesis needs further proving. This research work found that the measurement of overall Zeta potential could not specifically point out optimum conditions.

SUGGESTIONS FOR FURTHER RESEARCH

The maximum effectiveness of cationic starch as a retention aid was found at pH 5. "Electrocontrast" was postulated to explain this phenomenon. Due to limited data this postulation has not been proved. Since the electrokinetic environment of a papermaking system is usually evaluated by one single measurement, this omission of electrokinetic interaction may cause control problems. The postulation of "Electrocontrast" has not yet been proved in this research. Further work is suggested to verify this postulation. Where the charge of fiber fines in the work is recommended to be controlled by the addition of electrolytes, retention aids with different charge densities are also needed. Electrokinetic interactions could be explored by measuring the Zeta potential of fiber fines, polymer and the system. And the effectiveness of the retention aid could be justified by using the Dynamic Retention/Drainage Jar.

APPENDIX I

PULP PREPARATION

1. 50% Weyerhaeuser bleached hardwood kraft pulp and 50% Espanola bleached softwood kraft pulp was blended and beaten in a Valley beater to a CSF Freeness of 350ml.

2. 25% of titanium dioxide (anatase) was then added and mixed thoroughly in the beater. The furnish was wrapped in muslin cloth and dewatered in a centrifuge.

3. Further evaporation of moisture was accomplished by drying the wet furnish in a constant humidity room until the moisture content reached equilibrium. The final moisture content was found to be 7.3%.

4. Dried pulp was weighed, disintegrated and diluted with distilled water to form a 0.5% consistency batch of approximately 40 liters.

5. An arbitrary quantity of stock was taken from the batch and diluted to five times its volume. This 0.1% stock was weighed to 500g for the fines content test.

6. 2000ml of 0.05% Tamol 850 and 0.05 % sodium carbonate solution were used to wash away the fines. The rotating speed of Dynamic Retention Jar was set at 1500rpm and filtrate was drained while replenishing with washing solution to a constant level. Additional

500ml distilled water was added to insure maximum removal of fines content.

7. The residue was collected on a preweighed filter paper, dried, weighed and the percent content of fines calculated.

APPENDIX II

STARCH PREPARATION

1. Enzyme solutions were prepared and labeled so for each 100ml of solution there would be adequate units of enzyme to convert 5gm of cationic starch.

2. 5gm cationic starch was weighed each time. 100ml of amylose enzyme solution was then added. For the nonconverted level distilled water was used instead.

3. The mixture was heated to 160-180° F with agitation for 20 minutes, and then the temperature was raised to 208° F for additional 30 minutes to inactivate the enzyme.

4. The cooked starch was diluted with boiled water to make a 1% solution. From this a 100ml solution was further diluted to make a 0.1% working solution.

5. The working solution was stored in a hot water bath (150° F) and used within 8 hours.

6. Fluidity was determined by running the 1% solution through a capillary tube viscometer and was recorded for reference. The average values were 3.44 centistokes for non-converted cationic starch at 150° F, 0.81 for 100SKB converted cationic starch, 0.77 for 200 SKB level, and 0.76 for 300SKB level.

APPENDIX III

DETERMINATION OF PERCENT FINES RETENTION

1. Two full 250ml beakers of stock were collected from the batch. This added up to 500ml with ± 10ml deviation.

2. First, pH was adjusted with diluted HCl or NaOH to the desired level, then 17ml of working solution of cationic starch was added using mild agitation.

3. Every 5 minutes the prepared stock were agitated gently with a stirring rod for 30 seconds. Dynamic retention tests started at least 1 hour later.

4. The stock was transfered into a Dynamic Retention Jar and the speed of rotation of the stirrer was set to the desired level for 30 seconds. Then the drainage valve was opened to allow drainage for 10 seconds. Thereafter, approximately 100ml of filtrate was collected in a pre-weighed can.

5. The filtrate was dried in an oven, and the dried weight of fines determined.

6. Percent fines retention was calculated by the following equation:

$$\%\ \text{fines retention} = \left(1 - \frac{FW}{FT \times C \times FN}\right) \times 100\%$$

where

FW = gm, weight of collected fines

FT = gm, weight of filtrate

C = %, consistency of stock

FN = %, percent fines content

APPENDIX IV

PROGRAM FOR PRIMARY DATA MANAGEMENT

```
C       ( *PROGRAM:  RETEN.FOR, A PROGRAM TO ACCESS DATA OF THE RESULTS
C          OF FINES AND FILLER RETENTION TESTS.  FUNCTIONS INCLUDES:
C               1.  INPUT RAW DATA
C               2.  CALCULATE %RETENTION AND STORE
C               3.  OUTPUT ALL DATA TO A FILE
C               4.  OUTPUT ALL DATA ON TTY *)
C               5.  OUTPUT A SET OF DATA ON TTY

        OPEN(UNIT=20,DEVICE='DSK',FILE='RETEN.DAT',
        1     ACCESS='RANDOM',RECORD SIZE=144)

10      WRITE(5,100)
100     FORMAT(1X,' WHICH COMMAND ',$)
        READ(5,200, END=99)COM
200     FORMAT(A5)
        IF(COM.EQ.'INPUT')CALL INPUT
        IF(COM.EQ.'OUTPU')CALL OUTPUT(COM)
        IF(COM.EQ.'TYPE')CALL OUTPUT(COM)
        IF(COM.EQ.'SORT')CALL SORT
        GO TO 10
99      CLOSE(UNIT=20)
        STOP
        END


        SUBROUTINE INPUT
        DIMENSION DAY(2)

        CALL DATE(DAY)
        WRITE(5,400)
400     FORMAT(1X,'INPUT CONC, FINE, VISC:',$)
        READ(5,500,END=99)CONC,FINE,VISC
500     FORMAT(3F)
10      WRITE(5,600)
600     FORMAT(1X,'ID=',$)
        READ(5,700,END=99,ERR=10)I1,I2,I3,I4
700     FORMAT(4I1)
C       (*CALCULATE THE POINTER POSITION BY REFERING INDEXES *)
        IPT=(I4-1)*6*4*4+(I3-1)*6*4+(I2-1)*6+I1
        WRITE(5,800)
800     FORMAT(1X,'INPUT CUP WT, CUP+FT, CUP+FN:',$)
        READ(5,900,ERR=10)CUP,CFT,CFN
900     FORMAT(3F)
        FT=CFT-CUP
        FN=CFN-CUP
C       (* CALCULATE % RETENTION AND OUTPUT ALL DATA TO DSK *)
        RET=(1-(FN)/(FT*CONC*FINE))*100
```

APPENDIX IV cont.

```
         WRITE(20#IPT,1000)IPT,VISC,CONC,FINE,CUP,CFT,CFN,FT,FN,RET,
         1                 DAY(1),DAY(2)
1000     FORMAT(I3,9F15.7,A5,A1)
         GO TO 10
99       RETURN
         END


         SUBROUTINE OUTPUT(COM)
         OPEN(UNIT=21,FILE='RESULT.DAT')

C        (* CHOOSE THE METHODS OF OUTPUT *)
         IF(COM.EQ.'OUTPU')WRITE(21,100)
         IF(COM.EQ.'TYPE')WRITE(5,100)
100      FORMAT(1X,T8,'VISC',T13,'CONC',T19,'PULP',T25,'CUP',
         1      T30,'CUP&FT',T37,'FILTRT',T44,'CUP&',T50,'FN IN'
         1      ,/1X,T3,'ID',T8'-SEC',T14,'-%',T18,'%FINE',T24,
         1      'WT-GM',T31,'WT-GM',T38,'WT-GM',T44,'FN-GM',T50,
         1      'CUP-GM',T58,'%RETN',T66,'DATE',/)
         DO 10 I=1,6
          DO 10 J=1,4
           DO 10 K=1,4
            DO 10 L=1,4
         IPT=(L-1)*6*4*4+(K-1)*6*4+(J-1)*6+I
         READ(20#IPT,200)NUM,VISC,CONC,FINE,CUP,CFT,CFN,FT,FN,
         1               RET,DATE1,DATE2
200      FORMAT(I3,9F15.7,A5,A1)
         IF(NUM,EQ.0)GO TO 10
         CONC=CONC*100
         FINE=FINE*100
         IF(COM.EQ.'OUTPU')WRITE(21,300)I,J,K,L,VISC,CONC,FINE,
         1                 CUP,CFT,FT,CFN,FN,RET,DATE1,DATE2
         IF(COM.EQ.'TYPE')WRITE(5,300)I,J,K,L,VISC,CONC,FINE,
         1                CUP,CFT,FT,CFN,FN,RET,DATE1,DATE2
300      FORMAT(1X,4I1,T8,F4.0,T13,F4.3,T18,F5.2,T24,F5.2,
         1      T30,F6.2,T37,F6.2,T44,F5.2,T50,F6.4,T58,F5.2,
         1      T65,A5,A1)
10       CONTINUE
         RETURN
         END

         SUBROUTINE SORT
         WRITE(5,100)
100      FORMAT(1X,'LAST TWO CONST.:',$)
         READ(5,200)K,L
200      FORMAT(2I1)
C        (* ASK FOR PRIORITY IN OUTPUT SEQUENCE *)
         WRITE(5,300)
300      FORMAT(1X,' R OR L ? ',$)
         READ(5,400)S
```

APPENDIX IV cont.

```
400     FORMAT(A1)
        IF(S.EQ.'L')GO TO 20
        DO 10 I=1,6
         DO 10 J=1,4
        IPT=(L-1)*6*4*4+(K-1)*6*4+(J-1)*6+I
        READ(20#IPT,600)RET
        WRITE(5,500)I,J,K,L,RET
500     FORMAT(1X,4I1,3X,F5.2)
10      CONTINUE
        GO TO 99
20      DO 30 J=1,4
         DO 30 I=1,6
        IPT=(L-1)*6*4*4+(K-1)*6*4+(J-1)*6+I
600     FORMAT(123X,F15.7)
        WRITE(5,500)I,J,K,L,RET
30      CONTINUE
99      RETURN
        END
```

APPENDIX V

STATISTICAL ANALYSIS METHODS

There are many statistics packages available in Western Michigan University Computer Center. Two packages were selected for the analyses of results, namely, TWOAOV (58) and ADVAOV (59). In most cases each point of datum has to be coded with a specific number. From a well constructed data-base 'DO' or 'REPEAT' loops can easily sort and code the data in a desired order. Once the coded data files were created, execution could be carried by either time-sharing or batch. Detailed procedures for this thesis work are listed in the following:

1. Wrote a program that read data from the data file which was generated by the program listed in Appendix IV. This program then wrote the data with codes into another data file, e.q., 'SIMPLE. DAT', in the desired order.

2. Wrote another program which read data from 'SIMPLE.DAT', input desired ranges and messages from the terminal, generated desired data files and created a control file. A sample program is listed in Appendix VI.

3. 'SUBMIT' the control file to batch.

4. Print the analysis results in the data file created by the package.

APPENDIX VI

PROGRAM FOR GENERATING CONTROL FILE

```
         COMMON/A/NAME,UNIT(6,4,5,3,),I1,I2,J1,J2,K1,K2
         OPEN(UNIT=20,FILE='SIMPLE.DAT')
         OPEN(UNIT=22,FILE='TWOAOV.CTL')
10       READ(20,100,END=99)I1,I2,I3,I4,RET
100      FORMAT(1X,4I1,F)
         UNIT(I1,I2,I3,I4)=RET
         GO TO 10
99       WRITE(22,150)
150      FORMAT(1X,'R TWOAOV',/,'DSK:TWOAOV.DAT')
C        (*INPUT UPPER AND LOWER BOUNDS OF EACH LEVEL *)
20       WRITE(5,200)
200      FORMAT(1X,'I=?,?')
         READ(5,300,END=999)I1,I2
300      FORMAT(2I)
         WRITE(5,210)
210      FORMAT(' J=?,?')
         READ(5,300)J1,J2
         WRITE(5,220)
220      FORMAT('K=?,?')
         READ(5,300)K1,K2
         WRITE(5,230)
230      FORMAT('FILE NAME')
         READ(5,400)NAME
400      FORMAT(A5)
         CALL CONTL
         GO TO 20
999      WRITE(22,900)
900      FORMAT('FINISH')
         STOP
         END

         SUBROUTINE CONTL
         COMMON/A/NAME,UNIT(6,4,5,3),I1,I2,J1,J2,K1,K2
         DIMENSION MES(14)
         OPEN(UNIT=21,FILE=NAME)
         DO 20 I=I1,I2
         DO 20 J=J1,J2
         DO 20 K=K1,K2
         IQ=I-I1+1
         JQ=J-J1+1
         KQ=K-K1+1
         DO 20 L=1,3
         IF(I1.EQ.I2)WRITE(21,10)JQ,KQ,UNIT(I,J,K,L)
         IF(J1.EQ.J2)WRITE(21,10)IQ,KQ,UNIT(I,J,K,L)
         IF(K1.EQ.K2)WRITE(21,10)IQ,JQ,UNIT(I,J,K,L)
10       FORMAT(1X,2(I1,','),F)
```

APPENDIX VI cont.

```
20       CONTINUE
         WRITE(5,100)
100      FORMAT(1X,'ID MESSAGE')
         READ(5,200)(MES(I),I=1,14)
200      FORMAT(14A5)
         WRITE(22,300)NAME
300      FORMAT('DSK:',A5,'.DAT')
         WRITE(22,400)
400      FORMAT('STD')
         WRITE(22,500)(MES(I),I=1,14)
500      RETURN
         END
```

BIBLIOGRAPHY

1. Sennett, P. and Olivier, J. P., Interfaces Symposium, June 15 & 16, 1964, Chemistry and Physics of Interfaces, American Chemistry Society Publications, Washington, D. C., 75 p.

2. Matijevic, E., Surface and Colloid Science, Vol. 7, New York, Wiley, 1974, 356 p.

3. Rosen, M. J., Surfactants and Interfacial Phenomena, New York, Wiley, 1978, 252 p.

4. Levine, S., Mingins, J. and Bell, G. M., Can. J. Chem. 43:2834 (1965).

5. Adamson, A. W., Physical Chemistry of Surfaces, Third Ed. New York, Wiley, 1976, 323 p.

6. Jaycock, M. J. and Pearson, J. L., J. Colloid and Interface Sci. 55:181(1976).

7. Jaycock, M. J., Int. Seminar on Paper Mill Chem. Amsterdam, Holland, 1975.

8. Onabe, F., J. of Appl. Polymer Sci. 23:2909(1979).

9. Kindler, W. A., Adsorption Kinetics in the Polyethyleniminecellulose Fiber System, Doctor's Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1971.

10. Das, B. S. and Lomas, H., Pulp and Paper Magazine of Canada, 74(8):95(1973).

11. Lindstrom, T., Soremark, C., Hernegard, C. and Loof, S., Tappi 57(12):94(1974).

12. Sandell, L. S. and Luner P., J. Appl. Polymer Sci. 18:2075(1974).

13. Silberberg, A., J. Colloid and Interface Sci. 38:217(1972).

14. Hoeve, C. A., J. Polym. Sci. Part C, 34:1(1971).

15. Alince, B. and Robertson, A. A., Tappi 61(11):111(1978).

16. Lindstrom, T. and Soremark, C., J. Colloid and Interface Sci. 55:5(1976).

17. Strazdins, E., Tappi 57(12):76(1974).

18. Britt, K. W., Dellon, A. G. and Evans, L. A., Tappi 60(7):102 (1977).

19. Goossens, W. S. and Luner, P., Tappi 59(2):89(1976).

20. Britt, K. W., Tappi 56(10):46(1973).

21. Walkush, J. C. and Williams, D. G., Tappi 57(1):112(1974).

22. Strazdins, E., Tappi 53(1):80(1970).

23. Ruehrwein, R. A. and Ward, D. W., Soil Science, 73:485(1952).

24. Healy, T. W. and La Mer, V. K., J. Phys. Chem. 66:1835(1962).

25. La Mer, V. K. and Healy, T. W. Reviews of Pure and Appl. Chem. 13:112(1963).

26. Unbehend, J. E., Tappi 59(10):74(1976).

27. Williams, D. G., Tappi 56(12):144(1973).

28. La Mer, V. K. and Smellie, T. H., J. Colloid Sci. 13(6):589(1958).

29. King, C. A. and Williams, D. G., Tappi 58(9):138(1975).

30. Sandstrom, E. R., Improvement in Wet Strength Resin Efficiency Through Maximum First Pass Retention of Fines, int. Seminar on Paper Mill Chem. New York, Sept. 1978.

31. Kasper, D. R., Theoretical and Experimental Investigation of the Flocculation of Charged Particles in Aqueous Solution by Polyelectrolytes of Opposite Charge, Doctor's Dissertataion, Pasadena, California, California Institute of Technology, 1971.

32. Sikora, M. D., The Role of Polyelectrolyte Charge Density in the Mechanism of Hydrodynamic Shear-Induced Restabilization of a Flocculated Colloidal Dispersion, Doctor's Dissertation, Appleton, Wisconsin, The Institute of Paper Chemistry, 1978.

33. Beck, V., Muller, F., Goosens, J. W. S., Rohleff, E., and Treffer, H., Wochbl. Papierfabr. 105:391(1977), (Translation, IPC).

34. Penniman, J. G., Some Practical Electrokinetic Considerations, Int. Seminar on Paper Mill Chem. New York, Sept. 1978.

35. Valette, P., Revue A.T.I.P. 29(1):1(1975), (Translation IPC).

36. Britt, K. W. and Unbehend, J. E., Tappi 57(12):81(1974).

37. Strazdins, E., Tappi 55(12):1691(1972).

38. Jaycock, M. J. and Pearson, J. L., J. Appl. Chem. Biotechnol. 25:815(1975).

39. Jaycock, M. J. and Pearson, J. L., ibid, 25:827(1975).

40. Mekenzie, A. W. and Davies, G. W., Appita 25(1):32(1971).

41. Moore, E. E., Tappi 56(3):71(1973).

42. Chen, T. C., A Historical Study of Chinese Hand-Craft Paper, Taipei, Taiwan, Chong-Wai Publication Co. 1979, 67 p., (Chinese).

43. Penniman, J. G., Paper Trade Journal, Aug. 1:35(1978).

44. Should Additives Be Positvely Charged? Reader's Response to Cationic Column. ibid, Feb. 15:40(1979).

45. Marton, J., Tappi 63(2):121(1980).

46. Rogols, S. and High, R. L., Tappi 46(7):424(1963).

47. Pummer, H., Das Papier 27(10):417(1973), (Translation IPC).

48. Schiesser, R. H., Tappi 59(10):71(1976).

49. Pummer, H., Tappi 56(4):112(1973).

50 Hogg, R., Healy, T. W. and Fuerstenau, D. W., Trans. Faraday Soc. 62:1638(1966).

51. Milichovsky, M., Vyskumne Prace z Odbory Papiera a Celulozy, 19:V65-V69, V73(1974), (Translation IPC).

52. Van der Brugh, L. F., Pulp Paper Mag. Can. 71:7403(1970).

53. Marton, J. and Marton, T., Tappi 59(12):121(1976).

54. Britt, K. W. and Unbehend, J. E. Tappi 59(2):7(1976).

55. Unbehend, J. E. Tappi 60(7):110(1977).

56. Schmut, R., Interface Symposium, June 15, 16, 1964, Chemistry and Physics of Interface, American Chemistry Society Publications, Washington, D. C., 95 p.

57. Janes, R. L. and Chen, N. S., Research Work in Dept. of Paper Science and Engineering, Western Michigan University, Kalamazoo, Michigan, June 1979.

58. TWOAOV, Program Number: 1.9.2, Computer Center, Western Michigan University, Kalamazoo, Michigan.

59. ADVAOV, Program Number: 1.9.8, ibid.