Paper Engineering Senior Theses

Chemical and Paper Engineering

4-1977

Temperature Dependence of the Retention of Organic Fines Using a Cationic Retention Aid

Danny R. McRae
Western Michigan University

Follow this and additional works at: https://scholarworks.wmich.edu/engineer-senior-theses

Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

McRae, Danny R., "Temperature Dependence of the Retention of Organic Fines Using a Cationic Retention Aid" (1977). *Paper Engineering Senior Theses*. 339.
https://scholarworks.wmich.edu/engineer-senior-theses/339

TEMPERATURE DEPENDENCE OF THE

RETENTION OF ORGANIC FINES

USING A CATIONIC

RETENTION AID

by

Danny R. McRae

A Thesis submitted to the

Faculty of the Department of Paper Technology

in partial fulfillment

of the

Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

April 1977

ABSTRACT

Stock of 50:50 bleached Kraft softwood and hardwood run through the Valley beater at 350 CSF with high fines content (25-30% fines from softwood and hardwood fractions run through a Wiley mill) was prepared and tested for fines fractionation, fines retention, and system surface charge at 10, 25, 40, and $55^{o}C$ using a Dow Chemical cationic polymer of 1,000,000 molecular weight: SEPARAN CP-7. The Britt Dynamic Drainage Jar was used for fines fractionation and retention data and Halabisky's Colloid Titration Technique for surface charge data. Cationic polymer loadings were taken at 0.25, 0.50, and 0.75 pounds of polymer per ton of paper produced (pulp present). Rotor or agitation speed for retention determinations was held constant at 1000 rpm. Surface charge reagents were not diluted (5X) as suggested by Halabisky.

Fines fractionation decreased on rising temperature to show increased fines to fiber attraction. An increase in SEPARAN CP-7 loading increased fines retention though instabilities existed below room temperature. The optimum retention temperature was around $40^{o}C$ then fell off from there while there was no point of diminishing returns on retention with loading. Because of strong polymer-temperature interactions, many unexpected charge decreases and charge inversions appeared upon cationic loading increases though data error was very high. Extensive temperature range; pH; polymer molecular weight, combination, and charge nature; stock alteration; filler; and agitation effects were suggested as important parameters to research in terms of temperature effects on fine and filler retention and surface charge.

TABLE OF CONTENTS

INTRODUCTION

The development of retention and drainage aids began in the 1950's with low molecular weight cationics and soon moved to solid anionics and emulsion, high molecular weight anionics and cationics. Their use has been specified for coagulation or charge neutralization between fines, fiber, and filler particles and for flocculation or fiber mechanics in terms of polymer bridging. Some common aids are alum, sodium aluminum, and polycationics, which produce flocs of the "soft" (reformable) or "hard" (unreformable from shear) classification(32). In this project, a 1,000,000 molecular weight cationic polymer, SEPARAN CP-7, will be used on a 50:50 Kraft softwood and hardwood pulp mixture at various temperatures to see any predictable effect on fines retention using the Britt Dynamic Drainage Jar (6) and on suspended particle potential using Halabisky's Colloid Titration Technique (18).

Retention aids, in general, are able to produce some of the following benefits depending on the process and type of paper made: 1)increased production, 2)reduced sewer charge, 3)increased water reuse, 4)reduced steam, 5)increased felt-life, 6)increased sizing efficiency, 7)reduced wet-end deposits, 8)improved profile, 9)improved runnability, 10)fewer rejects, 11)better coating coverage, 12)reduced BOD, 13)reduced additive costs, 14)reduced saveall loadings, 15)allows furnish substitutions, 16)less refining, 17)saves dye, 18)reduced breaks, and 19)improved filler retention (32). One-pass retention needs good opacity and gives reduced titanium dioxide, speed, steam, downtime, additives, and fiber losses. Screening tests used are the Static Retention Drainage Test, the Britt Jar Dynamic Test, and the Charge Demand Determination.

FINES RETENTION

Han (21) found that the distribution of fines in a relatively thin mat

showed decreasing bound particle concentration through the mat, but that the bottom part of the thick mats showed nearly constant particle retention. Deviation was attributed to particle saturation at fiber surfaces due to a dynamic balance of the forces of attraction and repulsion or disruption. He defined fines as fragmentary materials incidentally produced by mechanical and chemical treatments and are difficult in dealing with because of wide ranges of sizes and shapes. There are three aspects of fines retention that are functions of the distance of separation of particles. The first is the hydrodynamic aspect concerned with the motions of the particles, their collisions with one another, and their interception by fibers. Large particles will act much like fibers that are retained by deposition at the sheet face, medium-size ones plug pores, and small ones move freely with the fluid and are trapped by fibers. the colloidal aspect is next where fines from fibers are charged to keep away from each other and fibers on collision, then the refined fibers have a fine network of fibrils which are able to trap in fines. Additives and contaminants are then adsorbed onto the surface of hydrophobic particles. The molecular aspect dictates that two particles in close proximity and in absence of repulsive forces will attract each other due to Van der Waals-London forces. Han (21) also found that the distribution of fines in a fiber mat formed by filtration is $K = A_f/V_f(1 - \epsilon)E$, where ϵ = porosity, A_f = projected fiber area, and V_f = fiber volume. From this an attenuation coefficient K was determined and used to define a collection efficiency E, which has the physical meaning of the fraction of particles collected by the fibers from the total free particles in the fluid stream approaching the cross-sectional area of the fibers (20,35). As an example, the effect of temperature on drainage of a heavy board made from a groundwood furnish on a special cylinder machine could not be reliably predicted by the change of viscosity alone. The retention of fines would increase

with increasing temperature; thus, offsetting a part of the gain in drainage due to lower viscosity (21).

With small particles in slow flow, retention in a permeation process is controlled by Brownian motion or diffusion. Retention here depends on the particle, fiber, and fluid properties, the flow pattern in the porous structure, and the ionic conditions in the suspension (20). From this Johnson (23) found with use of titanium dioxide that collection of small particles by diffusion increases with decreasing fluid velocity because the particles remain longer in the neighborhood of each fiber (and increasing porosity). He ran at 25 and 50°C and ironically the lower temperature in lower fluid velocity would cause higher retention from diffusion at various runs. In filtration processes both fibers and particles are to be retained from the suspension. The retention of fibers is accomplished by their elongated form (1,14).

Another benefit concerning fines is the addition of cationic polymeric retention and dewatering aids with cationic condensation products of urea and aliphatic amines (amounts of .002-.05% on weight of fiber) to prevent many pitch problems from even arising (5).

FILLER RETENTION

Hansen (22) saw the distribution of filler in paper made on the paper machine is characterized by a very high content close to the felt-side of the paper, decreasing more or less rapidly to a value slightly higher than the average content of filler in the paper. "Wet" stuff or low consistency and the dandy roll increase the filler content on the felt-side. In handmade papers filler content is highest within the sheet. In machine papers less filler by wire-side and more filler by felt-side with constant filler content in central sections is seen. Increased paper weight increases the average content of filler. Decreases in filler content near the wire-side is caused neither by the influ-

ence of the table rolls, nor the suction boxes nor the wet presses, but is already established immediately after the stuff has been run on the wire (22).

INITIAL RETENTION

In screening concerning initial retention, square-mesh grids are thought to be a good fiber holders, but parallel meshes might be thought to be the best geometry for maximum retention, since below $L/b < 3.5$ (L = fiber length, b' = grid distance) square-meshes pass more material while above $L/b > 3.5$ parallel-mesh retention decreases less rapidly than with square-meshes. However, the final trends will depend upon the fiber length distribution in the suspension. Kallmes and Corte (24) also have shown that for randomly deposited fibers, a nonuniform formation pattern will exist even with complete retention, while with incomplete retention, nonuniformity (a function of fiber length) increases. Modifications in these relationships will ultimately have to account for fiber flexibility, more complex screen geometries, hydrodynamic effects, and fiber interactions (14). It's obvious that by decreasing the size of the openings in the wire, the retention of fibers will be increased. However, the resistance to drainage will also be increased, making it necessary to compromise between retention and flow resistance in an optimum wire design. Higher losses on the paper machine (higher than in lab with same type of wire) must be attributed to small fibers and fines or unfavorable hydrodynamic conditions where fine particles not attached to larger fibers by surface forces will pass through (14).

FORMATIONAL RETENTION

Britt (7) defines one-pass retention as the comparison of headbox filler with paper filler and overall retention as the comparison of filler added to the furnish to that in the paper. From this premise, he conducted static and dynamic tests on wet pulp plus filler samples and determined suspended solids

by gravimetric analysis. The static test, detecting slight degrees of affinity between pigment particles and fiber (flocculation), gave nearly 100% retention by numerous additives. In the dynamic test (with agitation as in turbulent real systems) zero retention of fines and filler were essentially given at degrees of turbulence above 1000 rpm, and true filler was retained essentially at 100%. These tests showed that the flocculation of pigment filler in paper stock by usual chemical agents results in a soft floc that is easily disrupted by hydraulic shear forces characteristic of sheet formation. Normally these soft flocculations reform almost instantly when the turbulence is removed. This type of flocculation increases the one-pass retention of fines only to an intermediate degree. The tensile stress or tenacity of this flocculation can be increased by a sequence of additions of polyelectrolytes of opposite charge (7). The tenacious type of floc requires mechanical redispersal to avoid uneven formation.

MONITORING RETENTION

It is evident from Britt (10) and others that there is a marked decrease in retention with increased turbulence and that the curve of retention vs. turbulence roughly indicates the degree of flocculation of a stock sample. Also, such a stock shows a relatively low level of retention at high turbulence and thus is considered to have a low "flocculation index." This is expected from its low specific conduction (see equation for mobility U_E), as with low salt content and the absence of a flocculating additive. Any sample of paper stock containing an appreciable fines content has a characteristic curve showing relative fines retention with levels of turbulence, called the A-line or hydrodynamic index, given by hydrodynamic conditions and colloidal forces (10).

HISTORICAL BACKGROUND

MECHANISMS

Britt (8), by use of what is commonly known as the Britt Dynamic Drainage Jar, found that additions of surface-active agents produce samples showing progressive increases in fines retention under dynamic conditions. This "retention jar" is used to predict effects on paper machine performance; therefore, it will be of primary use in determinations within this present project. Under these turbulent conditions, the retention aids' effectiveness is traced to their ability to form a somewhat tenacious floc by "polymer bridging." Also, Britt (8) found through electrokinetic measurements that complete charge neutralization is not a requirement for flocculation, which in itself leads to high fines retention and a flocculated, nonuniform stock appearance.

Optimum drainage or retention of a papermaking system in which a drainage and retention aid is used, Moore (33) found, does not necessarily correlate with the point of charge neutralization of the substrate surface. In a bleached pulp suspension containing alum, drainage and retention can increase greatly with increasing amount of cationic polyacrylamide, even though the fiber surface has been charge reversed. The lack of correlation of these properties with zero zeta potential shows that mechanisms other than charge neutralization may predominate (33).

Coagulation

The retention of colloidal material (fines) and fibers as studied by Walkush and Williams (47) under controlled agitation conditions in various simple electrolyte environments was determined in terms of fines retained by a hydrophobic colloidal coagulation mechanism. Retention was found by measuring the concentration of free fines, prepared from aspen seedlings grown in a $C^{14}O_2$ atmosphere, by scintillation counting. Maximum retention was realized at

"critical coagulation concentrations" (CCC) which were in agreement with the Schulze-Hardy Rule (the sodium, calcium, and lanthanium chloride CCC were 4.50, 0.33, and 0.023 mM/liter, respectively). The electrophoretic mobility of the fines approached zero near the CCC. The equilibrium retention level was controlled by the relative shear conditions and the electrolyte environment. These results (42) indicated that cellulose fines can be retained by a coagulation process, which, because of its reversible nature, was interpreted to be of a secondary "minimum" nature.

Titanium Dioxide Particles

Johnson (23) studied the effects of fiber diameter, mat porosity, fluid velocity, and fluid temperature on the collection of titanium dioxide particles by the internal structure of a mat of nylon fiber. Particle retention increased with increasing mat porosity and fluid temperature and with decreasing fiber diameter and fluid velocity, provided the pH, ion concentration, and total volume and concentration of the suspensions were held constant. Over the range of variables studied, Brownian diffusion (of the five probable ones: (1) inertial impaction, (2) flow-line interception, (3) settling, (4) Brownian diffusion, and (5) sieving) was shown to be the controlling mechanism of collection (23). Collection of particles retained takes place mostly in the storage chests and stock preparation system. Collection during formation occurs from high fluid velocities. Unlike Johnson (23), Haslam and Steele believe the retention process is ascribed to one, two, or all three mechanisms of (1) sieving, (2) coflocculation, and (3) mechanical attachment.

General Particle Application

An empirical form of the Han equation describing pigment distribution for imcompressible pads was found for a compressible wood pulp system by Williams and Swanson (49). The resulting apparent hydrodynamic collection efficiency

appears to be closely related to a true collection efficiency. Pre-mat-formation retention, apparent retention coefficient, and percentage retention of free pigment retention properties having different hydrodynamic factors - but common colloidal factors - are correlatable. Such correlations have as controlling parameters the relative magnitude of the colloidal forces between pigment and fiber. Thus, favorable colloidal forces are necessary not only for retention prior to mat formation, but also for retention during mat formation. Pre-mat-formation retention (49) can amount to a sizable portion of the total pigment retained. For paper sheets it is probably the major source of pigment retention. The pigment distributions in handsheets, machine-made sheets, and handmade sheets, as in Groen's findings (49) are readily explained by beginning with the premise that most of the pigment was already retained by the fibers prior to sheet formation.

ZETA POTENTIAL AND ELECTROKINETICS

Zeta Potential Fundamentals

Poppel (38) used polyamine-polyamide-epichlorohydrin resin (PPE) for determining zeta potential application and the nature and formation of the electrical double layer. Zeta potential is important in influencing sorption and retention phenomena with a close connection between zeta potential and sizing. There is a large effect of zeta potential on filler retention; small amounts of PPE change the zeta potential, and large amounts drops retention. PPE speeds up filtration and dewatering rates of pulp. Zeta potential is also shown to influence the rheology of pulp dispersion and the mechanical properties of paper (38).

When electrokinetic conditions have been optimized (zero zeta potential) in the wet-end first-pass retention is high; drainage is excellent; physical properties of the sheet, including formation uniformity, burst strength, and sizing degree, are excellent; the white water is relatively clear; foam is

absent; and dyestuff use is minimized (37). When the zeta potential drifts
away from zero these process and control parameters deteriorate rapidly.
Regulating the pH, specific conductance, and furnish composition adequately
controls zeta potential (37).

Flocculation and Dispersion Effects

Lindstrom (29) varied the zeta potential and thus the tendency for floc-
culation by adding cationic polyacrylamides (PAA) to dispersions of cellulose
material (microcryst cellulose sol). The flocculating polyelectrolyte para-
meters and fiber suspension conditions were affected by: charge density and
molecular weight of the polyelectrolyte, surface area of the fiber material,
pH of the system, salt concentration and concentration of dissolved wood based
polymers (pine xylan and LSA) in the system (29). All Lindstrom's findings
showed that optimum flocculation occurred at a zeta potential of ca. zero.
Increased retention as the zeta potential and single-pass retention on the
wire used (29).

Britt (9) used electrophoretic mass transport techniques to determine the
surface charge or zeta potential in paper stock relative to the suspended solids,
which, in turn, aids in studying flocculation and dispersion behavior. This
method allows a wide range of sizes in the measurements, and shows that the
intermediate particle sizes cause a peak and plateau of the apparent electro-
phoretic mobility, while smaller particle sizes cause a drop-off. The carboxyl
content effect on zeta potential or original mobility gave a lower charge for
lower acid group contents and vice versa. High acid group content pulps will
commonly adsorb large amounts of cationic polymer. Observation shows that the
addition of a cationic agent which reduces the surface charge also increases
the flocculation tendency. Thus, some observers have concluded that flocculation
and fines retention are solely or predominantly determined by electrokinetic

factor ($\underline{3},\underline{15}$). However, zeta potential is only one factor of several that de-
termines the degree and tenacity of flocculation; others are cationics used,
dynamic variations, polymer bridging, coagulation and sedimentation of solids,
and other resistants to redispersion to hydraulic shear forces ($\underline{9}$). Pulp fines
show much better retention than filler when the retention mechanism is simple
filtration, but when flocculation polymers are added to the system, the improve-
ment in filler retention is far more dynamic than with pulp fines. Evidently,
bridging is more effective and the larger pulp fines present a greater target
for the flow of water ($\underline{9}$).

In electrophoretic mobility, the equation given by Britt ($\underline{9}$) is
$U_E = \Delta W \cdot \lambda / t \cdot i \cdot m$, where U_E = electrophoretic mobility (cm/sec/volt·cm), ΔW =
weight of migrating material (mg), λ = specific conductance (μmho), t = time
(sec), i = current (m-amps), and M = average concentration of suspended parti-
cles (g/100m).

Mathematical Representation

Temperature is found to be a definite variable in particle charge densities
and potentials as seen through Adamson's ($\underline{2}$) representation of the double-layer
potential at a point located a distance x from the surface, ψ. The electrical
potential at the surface is taken to be ψ_0, and decreases as one proceeds out
into the solution. At room temperature for singly charged ions, the potential
is seen as
$$\psi = \psi_0 \, e^{-Kx}$$
where $K^2 = (4\pi e^2 / DkT) \Sigma n_i z_i^2$, showing the functionality in T. Variables here
are e, the electronic charge; D, the dielectric constant of the medium; k,
Boltzmann's constant; n, the concentration level at altitudes from the particle
(n_0, at zero altitude); z, the valence of the ions; and T, the existing temp-
erature. Here, then, potential rises with rising temperature. The gradient
of the electrical potential at a point has been shown by ($\underline{2}$):

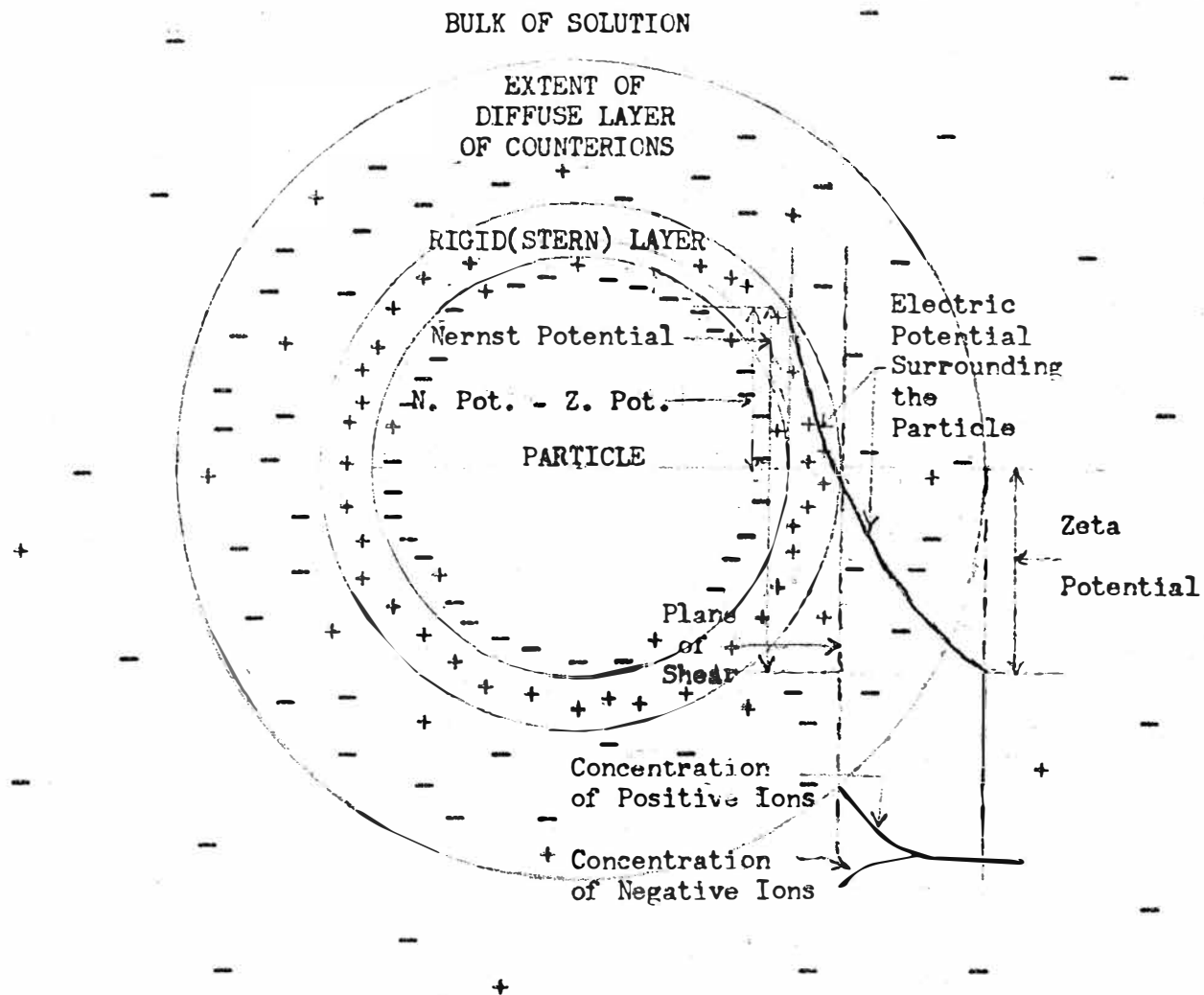FIGURE 1. The concept of the zeta potential. Most colloidal particles have a negative charge, as shown here, surrounded by stationary positive charges. These in turn are surrounded by a diffuse layer of negative charges. The zeta potential is the difference between the charge of this moveable layer and that of the bulk of the suspending liquid. For most natural substances, zeta potential is negative.

$$\Delta\psi = 8\pi n_o z^2 e^2 \psi / DkT = K^2\psi$$

This gradient also will rise with rising temperatures, but it is expected not to rise as rapidly as simple potentials since the exponential T function in the numerator is segmented by the increasing denominator T. For spherical particles (an assumption usually made in such calculations) the thickness of the double layer is given by:

$$\iota = (DkT/8\pi e^2 \Sigma n v^2)^{\frac{1}{2}}$$

where n is the concentration of ions of valency v in the bulk liquid (40). Again, double-layer expansion is expected with increasing temperatures in some-what moderate fashion because of the low exponential functionality.

The surface charge density, σ, does experience increases upon rising T but only in certain ranges since the exponential power function dominates the simple expanding ratio as seen in (40):

$$\sigma = \sqrt{DnkT/2} \left[\exp(ve\psi_o/2kT) - \exp(-ve\psi_o/2kT) \right]$$

However, it is an entire temperature dependent function. In terms of net charge density, ρ, at any point, the equation is given (40):

$$\rho = -2n_o ze \sinh(ze\psi/kT)$$

where again a temperature rise breeds a more and more negative charge density. All these functions also are consistent with the fact that increased temperatures cause increased expectations to find ions of z valence and e charge to be found more likely farther from particle surfaces than at lower T; this being seen in the expression: $x = ze\psi/kT$ (2).

Figure 1 gives an illustration of the double layer (rigid or stern layer and diffuse layer) with the potential drops indicated through the layers and the negative and positive ion concentrations indicated from the plane of shear to the bulk of the solution.

FILTRATION

General

Variables for filtration according to Wrist (51) are viscosity of the draining water, its temperature, specific surface area of the pulp, pore size distribution of the forming sheet, drainage pressure, and the kind and compressibility of the pulp sample. Cowan (12), too, did some work with mathematical and variable expressions for drainage over tube rolls, but neglected the kinetic nature of the problem involved. Sir Taylor (42) and Lewis (28) have since modified such mathematical expressions to more accurately describe the drainage around the rolls and nips and the formation into a mat on the wire. Again, they provide data that drainage becomes improved in heavier sheets on medium speed machines.

Mathematical Expression

Conditions necessary and sufficient for a fiber to be retained by a relatively open network lying in a plane perpendicular to the direction of flow of fibers as seen by Abrams (1) are much mechanical interception of the two, thus longer fibers (in general) and proper orientation in the mat. Probability of retention is expressed in terms of a functional relationship between the geometry of the fibers and that of the retaining network. The network was represented (1) by a frequency distribution of network distances in a two-dimensional model. Yet, the experimental results for continuous retention were lower than the predictions because of the suspension-network interactions. Also, the fluid drag and fiber impact forces seriously irregulated the stability of the network structure. The equations primarily used in the data manipulations were first, $R = 1 - \beta \exp(-\alpha L_f/\overline{L_3})$, where R = retention efficiency, β = a constant, $\alpha = .31$ (theoretical), L_f = fiber length, and $\overline{L_3}$ = average network distance; and second, $W_t = W + (1/\beta)\left[\ln x(1 - (1 - R_0)\exp(-\beta W))/R_0\right]$, where W_t = total approaching

mass of fibers, W = mass of fiber retained, ϕ = a constant, and R_o = initial
mass fraction retained or initial retention probability (1). The latter was
first suggested by Han (20) and developed later by Estridge (14). The reten-
tion efficiency approached one at rather low basis weights. Fiber flocculation
also aids to increase the rate of retention, but can prevent a fiber from freely
rotating into the network plane, thus possibly reducing retention (1). Moss
(34) found that a velocity gradient between the stock and wire causes fiber
alignment.

Applications - Vacuum Former Example

When Han (19) measured the drainage rate, driving force, and white water
consistency in an experimental vacuum former, the specific resistance of the
sulphite pulp used was evaluated from the drainage data and found to be in a-
greement with that determined by the constant rate filtration method. Through
assuming no fiber-wire interaction, a fixed slice opening at the inlet of the
former roof from basis weight and consistency manipulation, and a neglect of
initial drainage, a power function relationship is derived matching drainage
rate with forming distance in $(q/q_L)^n = x/L$, where q = drainage rate, q_L =
initial drainage rate, x = forming distance, and L = forming length (19). In
the rare case of complete retention throughout the entire sheet forming process,
the above equation becomes parabolic with n = 2.

TWO-SIDEDNESS FROM DRAINAGE

Its Causes

Normally, says Underhay (44), the top surface of the paper, from the pre-
sence of a greater fraction of short and fine material, has a closer and finer
structure (thus drainage benefits) than the under surface where the longer
fibers of the furnish predominate and cause the top texture to be more open.
The ash content of sheet top surfaces is more than twice that on the wire side.

Some proposed causes of composition two-sidedness are adverse drainage effects from breast box stock composition and variance from machine chest stock composition, sheet structure caused from wire assembly oscillation and high speed formation, and drainage conditions of high suction from boxes and underside washing from table rolls (44). Underhay suggests eliminating or reducing such factors by the implementation of mesh, scolled, and doctored table rolls, table rolls with water repelling surfaces, and a stripper or scraper bar instead of table rolls.

Its Elimination

Smith (41) points out that in two-sidedness not only the shade on each side is different in coloring but there is a difference in (1) texture, (2) formation, (3) smoothness, and (4) reflectance. The presence of suction boxes and high speed machines cause much two-sidedness so that the faster the machine runs, the greater the wire losses. Another big problem on the paper machine is table rolls. Everytime the unformed sheet rode over a table roll, the water in the nip was squeezed through the wire (lifting momentarily the whole sheet, flooding and loosening the smallest fibers and loading in the lower layers), and almost immediately withdrawn by the suction generated by the parting of the roll and wire surfaces (41).

This washing effect was obviously considerable when repeated at every table roll, and, after much consideration, it was realized that this phenomena could explain (a) the much higher losses sustained in the mill than in the laboratory; (b) the fact that the percentage backwater solids did not decrease uniformily as in a normal filtration; (c) the great scarcity of "fines" on the wire side of the sheet, and in particular, why the majority of the remaining long fibers were oriented in the machine direction; and (d) the reason why fast machines with their highly rotating tube rolls show such a marked two-sided effect and

have such high wire losses (41). All methods, however, so far are merely de-
terents not cures for two-sidedness according to Smith. Yet, use of a tube
roll with a carefully cut groove (to correct depth and width) actually channeled
water away from the nip. When the best depth was discovered, it not only
eliminated some two-sidedness, but also losses through the sire were greatly
reduced, and, in consequence, the freeness of the headbox stock (in a closed
system) was increased (41).

EFFECTS

Beating Effects

Kibblewhite (21) found that retention and drainage are highly influenced
by types of beating and refining since these determine the morphology and sur-
face structure of fiber. Fiber ends were found unfrayed or fibrillated, and
fibers were not preferentially shortened. Twisting and collapsing structures
were very predominant which facilitates drainage but doesn't necessarily pro-
mote fine and filler retention. The Valley beater at high stock concentration
was most effective in removing lamellae from the S_1 layer, while under normal
conditions the entire layer was removed. Thus, it opens up the fiber, and pro-
duces a tight network to trap small particles including fluids which need to be
drained. Thus, chemical additives are needed for proper charged particles to
allow for open drainage yet less breakdown in the fines and filler structure
of the sheet (25).

It is also generally accepted that when a wet paper web is dried, surface
tension forces operate which pull adjacent fiber surfaces together and allow
molecular interfiber bonds to form (11,30,45). Increased fiber flexibility
appears to be the most important visible effect of beating. Throughout the
formation and consolidation of a paper web, the effectiveness of wet pressing
and drying depends on the degrees of fiber flexibility. Many beating-caused

morphological and intrawall changes can be described in terms of their effect on fiber flexibility, fiber flattening and twisting, and intrawall dislocation (26). To the point fiber flexibility determines the degree of web consolidation, the intensity and extent of interfiber bonds probably depends on the quantity and quality of molecular fibrils developed on fiber surfaces. Fiber fibrillation and fibrillar fines appear to effect formation only as much as entangled interfiber fibrils probably increase wet web extensibility and tensile properties (26). Wet pressing minimizes any effect of fibrils on mat consolidation and the development of interfiber bonds.

Refining Effects

Richardson (39) has revealed that while refiner control reduced the uncertainty in standard deviation of freeness test on pulp, it did much to regulate the fiber length and fines in the furnish. Apart from this these fines added to the sheet strength but had an adverse effect on the drainage to more than offset any benefit. With modified procedures to induce a 5% fines content, the freeness and drainage time (under TAPPI Standard) were very predictable so that the Mullen and tensile continued to improve with the addition of these fines, where the smaller the particle size of the fines, the greater the strength improvement (39).

Agitation Effects

The effect on filler retention and sheet formation of retention aid molecular weight has been studied by Arvela, Swanson, and Stratton (4) using a laboratory web former and a series of high-charge-density cationic polyelectrolytes. Controlled amounts of addition agitation were introduced into the stock prior to the slice. Filler retention less caused by the agitation unit was rapidly and reversibly recovered when the polyelectrolyte was employed. At equal dosage an increase in molecular weight of a high-charge-density cationic polyelectrolyte produces slightly higher filler retention but poorer formation with no

enhancement of the retention shear resistance (4). Increased violence in stock agitation reduces filler retention considerably but improves sheet formation.

Goossens and Luner (17) studied the flocculation of microcrystalline cellulose suspensions with cationic ionene halides (60,000 mol. wt.) in which special attention was given to the effect of degree and time of agitation on the flocculation-redispersion behavior. They found that with increased time of agitation as well as degree of agitation, more polymer was needed to flocculate the suspension. Based on polymer adsorption and electrophoretic mobility data as well as the effect of polymer molecular weight on the flocculation, they concluded that the mechanism for the flocculation could be best explained by the "patch model" - flocculation being induced by the attraction between positive and negative sides of particles (17). The increase in stability is caused partially by the release of Ca^{++} from the surface of the particles due to polymer adsorption as well as by the diffusion of polymer into the pore of the particle.

Sheet Strength Effects

Thode (43) and others found that the precise technique of finding the surface area of beaten pulps containing fines, a variable to understand to predict retention trends in a fiber mat, is the filtration resistance method. The silvering technique and the dye adsorption methods both are too difficult to perform and inaccurate. The filtration resistance method also yields good swollen specific volume data for pulps with and without fines. Fines here had been helpful in giving higher Z-tensile, Mullen, and fold but hindered high tear. However, fines compound problems in the freeness test and also at times make retention specifics highly unpredictable (43).

Economic Effects

With the aid of a cationic retention aid (at rate of 0.7 ib/ton of paper

produced). Walsh (48) found the retention was improved greatly, and the mill could use lower amounts of pigment and fillers without loss of paper properties. Pigment costs were reduced more than $3.00/ton with an outlay of less than $0.75/ton. Cationic starches are used at the wet end to reduce BOD pollution problems. Often the use of cationic products provides the most economical solution to various difficulties, with added improvement in paper properties and increased operating efficiency (48).

The relationship between white water solids content and one-pass retention is important in terms of material losses from a production machine (economically speaking) to the point that Frankle (16) has used one-pass retention to optimize the retention aid level by minimizing costs. The optimization depends upon the kind of polymer used, the flocculation created, the amount of polymer, the pH level, the hardness of the mixture ($CaCO_3$ content), and the amount of relatively cheap alum. The cationic polymers behaved better at low pH than high while being insensitive to alum addition at low levels. On the other hand, the anionic retention aid performs better at high pH and is very sensitive to alum amounts. Polymer choice is dependent on three factors that determine good retention: the machine itself, the headbox chemistry, and the paper being produced (specifically, gentle mechanical action and drainage elements) (16). The predictions here were made by use of the Britt Dynamic Drainage Jar because of two factors (supporting its use): laboratory retention has been correlated with machine retention now, and sewer losses have been shown to be a function of retention independent of grade or basis weight (16).

Pollution Effects

To minimize chemical and fines buildup in white water, it is necessary to effect maximum retention of these components in the finished sheet. Williams (50) has also postulated that the retention of colloidal materials during the

papermaking process is dominated by the coflocculation mechanism as compared to sieving or mechanical attachment. Significant coflocculation in a furnish is achieved through effecting the collapse of the electric double layers of the surface charged bodies by providing a suitable electrolyte concentration, as described by the Derjaguin-Landau-Verwey-Overbeek theory (46) of the stability of hydrophobic colloids. The chemistry of aluminum salts in solution, the ability of its cations to effect coagulation, and the interference of complexing anions, such as sulfate, are used to optimize effective coflocculation. Additional coflocculation can be had by the appropriate addition of a polyelectrolyte through the establishment of polymer bridges as hypothesized by Laner (27). The success of the polymer retention aid depends upon achieving adsorption of polymer segments on the surfaces under conditions of low coverage and upon the ability of the created floc to withstand the shearing forces in the process (50).

FURTHER ANALYSES

Transverse Direction Analysis

This method used by Parker and Mih (36) consists of freezing the sides of the water-soaked sheet to the surfaces of two metal rolls, cooled below the freezing temperature of water and rotating with a spring-loaded nip. The wet sheet, introduced into the roll nip, is split internally into two frozen sections on the outgoing side of the nip. A major advantage of this method is that samples of large area can be uniformily sectioned, making possible the analysis of distribution of macroscopic sheets structure such as gross formation in the transverse direction (36). A test method to measure the specific filtration resistance of small samples of pulp has been used in conjunction with the sectioning device to measure the transverse distribution of specific filtration resistance in paper. Again, generally, the distribution of filtration resistance in many types of filled sheets reaches a minimum on the wire side

(lower ash) as in Inverform sheets which is consistent with previous reported measurements of filler distributions (36).

Closed System Analysis

Martin-Löf and assistants (31) believe the main cause of possible operating problems can be related to the change in the white water composition and temperature from poor retention, process temperatures, machine speeds, and so on. Problems with product quality can mainly be related to the increase in fines content of the sheet. Fines and fillers can cause drainage problems on the machine and affect paper quality. Dissolved materials can cause operating problems because of deposition on equipment or foaming. The single-pass retention on the wire of fines and filler is normally about 50% and dissolved materials about 2% (31). Thus a closed system has offered an alternative for pollution abatement in paper manufacture; however, care is needed since operating conditions and product quality may be affected. Moreover, in many cases positive influences on operating conditions have been noticed as in improved drainage and reduced slime problems because of increased white water temperature. Also, savings in fiber and heat are inherent in the closed system approach (31).

EXPERIMENTAL ANALYSIS

INTRODUCTION

Objectives

In this analysis temperature effect on retention aid activity was investigated by determining fines, one-pass retentions, and surface charge by titration at various temperatures. The Dynamic Drainage Jar or Britt Jar was used to touch the first objective of finding if temperature has a somewhat regular or predictable relationship with retention of fines. Then, the surface charge titration measurements technique developed by Halabisky (18) served to touch objective two to see if temperature has such a noted effect on various potentials around suspended particles in the presence of cationic polymer so as to depict relationships to the retentions found. The temperature interval was 15°C where a cationic polymer produced by the Dow Chemical Company (SEPARAN CP-7) (13) was applied at different loadings to a stock of 50:50 bleached Kraft softwood and hardwood at four different temperatures: 10, 25, 40, and 55°C. At least three determinations were done at each temperature and loading of polymer for each type of test and calculation; if data was erratic, then nine or ten determinations were in order to double the reliability of tests made. Fines fraction and fines retention was done in the Britt Jar application procedure.

SEPARAN CP-7 Cationic Polymer

SEPARAN flocculants are high-molecular-weight synthetic water-soluble polymers made by polymerizing acrylamide. All of the products are based on polyacrylamide, as shown by $\left(\!-CH_2 - \underset{\underset{NH_2}{\overset{\overset{\displaystyle C=O}{|}}{|}}{CH}\!\right)_n$. Because of the abundance of amide groups ($-NH_2$), unmodified polyacrylamide is essentially nonionic in solution, although a very small number (< 0.5%) of the amide groups are usually hydrolyzed to anionic carboxyl groups ($-COO\ Na^+$). The thermal stability of CP-7 is good above room temperature though it has much weight loss under 150°C, yet

this loss is primarily due to water loss without drastically changing polymer bulk. Prolonged heating, though, can lead to degradation. CP-7 has a nominal molecular weight of about 1,000,000 and a pH of 10-11 with high activity in furnishes from pH 4 to pH 8. Brookfield viscosity (23°C, #5 spindle, 20 rpm) is 6,000-13,000 cps, and freezing point is about -1°C. Density of this liquid is 8.35 lbs/gal at 5% active solids. Recommended loadings for retention are 0.2 to 0.75 pounds of active solids per ton of paper production so 0.25, 0.50, and 0.75 loadings were used in this analysis. CP-7 is noncorrosive, essentially non-irritating to eyes and skin, and has low toxicity with single oral consumption (13).

Under stable temperature conditions the use of CP-7 in retention increases retention of fines, fillers, size, wet strength resins, pigments, and dyes; improves distribution of fillers in the sheet with less two-sidedness; gives more uniform moisture profile; gives better sheet formation and more uniform sheet quality; produces cleaner white water systems and greater saveall efficiency; and provides lower suspended solids and BOD in mill water effluent (13).

PROCEDURES

Dynamic Drainage Jar Procedure

There are three particular operations for which the dynamic jar is useful (the first two being done for this project): (1) determination of the fines fraction in a stock sample, (2) retention of fines (and/or filler) by the fiber under dynamic conditions, and (3) determination of drainage rate under dynamic conditions. An important consideration is that paper formation takes place under turbulent conditions. Thus, the drainage jar has a two-fold purpose: to carry out tests under conditions similar to those on a paper machine and to minimize hydromechanical effects and keep them under close control. The two most important variables in the use of the dynamic jar are the rpm of the

stirrer (which was held constant at 100 during drainage and at 350 for retention aid mixing) and the hole size of the screen (which was 76 microns from 125P screens) (6).

(a) Fractionation - With a stock consistency (suspended solids) of 0.1% (measured exactly) at the proper temperature, place a 500 ml sample in the jar which contains a 125P screen, 76 micron hole, 14.5% open area. Agitate at 1500 rpm for complete dispersion, then down to 1000 rpm for drainage where the plug is pulled and drainage is caught in a 2000 ml beaker. A stock solution of 2.5% concentration of TAMOL 850, tri-polyphosphate, and sodium carbonate is needed, where 1 ml of this is added to 500 ml of stock sample. Dilute to 0.01% for all ingredients (250 times), and use 500 ml portions as wash water for repeated drainage on the same sample. The advantage of TAMOL 850 as a wetting agent is that it is non-foaming which seriously interferes with the fractionation test. When the 2000 ml beaker is full, the fines fraction should be complete. To make sure wash again with 500 ml of water to be drained into a clean glass beaker. This filtrate is observed for clarity and should contain no appreciable amount of suspended matter. The residue of fiber on the screen is transferred to a weighed filter paper on a Büchner funnel, dried, and weighed. Whatman No. 30 11 cm is recommended. The use of dispersing agent (TAMOL) and sodium carbonate in the wash water is to overcome any tendency of the fine to flocculate and hence remain with the fiber (6).

Calculations start with subtrating the residue of fiber filtered (mg) from the total solids (mg) to get total fines. Its percentage is then based on the total solids.

(b) Fines Retention - A 500 ml sample of 0.1-0.5% (about 0.3% used) consistency stock to be tested is put at the proper temperature and placed in the jar with the bottom outlet hole stoppered at 350 rpm. The stopper carries a

short glass tube 5/16" O.D. connected with a rubber tube with a pinch clamp
to a typical medicine dropper. The purpose of this arrangement is to restrict
the flow during the test so that the screen remains free and open during the
test. The retention aid is readied and added for 20 seconds at 350 rpm, then
moved to 1000 rpm. About 100 ml of the sample is removed and re-added into the
jar. Then the clamp is again removed to collect 50 ml of bleed before collect-
ing the sample in a weighing jar without interrupting the flow. These samples
are tested at the blank and other desired loadings at all the temperature levels
desired (6).

For the calculations divide the fines present in the aliquot by the weight
of the aliquot filtrate, then divide by the stock consistency and by the total
fines fraction found during fractionation. This ratio multiplied by 100 gives
the percentage of unretained fines. Therefore, fines retained is simply
100% - % unretained.

Surface Charge Titration Procedure

Two polymeric colloids that react almost stoichiometrically, neutralizing
one another to form an insoluble precipitate, are methyl glycol chitosan and
potassium polyvinyl sulfate which were used in this method:

$$R_1-SO_4^-K^+ + I^-(CH_3)_3NR_2 \longrightarrow R_1SO_4N-R_2 + KI \quad .$$
$$(CH_3)_3$$
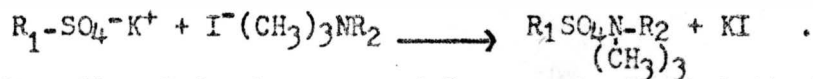
Toluidine Blue O dye has a special property in that it changes color in the
presence of anionic polymeric systems (blue to pink) but has no interaction in
cationic polymer solutions (remains blue). This dye, therefore, is a suitable
indicator for titrating a cationic polymer with an anionic polymer (18).

This method was used in place of the common Electrophoretic Mobility Tech-
nique since the Colloid Titration Technique has many advantages over it. It
measures charge on the total headbox furnish, including the long fiber fraction;
it's inexpensive since no elaborate equipment is required; operators may be

easily trained to use this technique; its very opaque and disperse systems can be measured; it yields reproductible results by different operators; it determines accurately optimum conditions for optimum drainage and retention improvement; it's fairly rapid, 10 minutes being necessary to make one measurement; systems having a high specific conductance can be measured; thick stock and tray water solids can be measured; and adsorption of wet end additives can be determined. Its only disadvantages is that highly colored systems are presently difficult or impossible to measure. Also, high levels of alum or organic acids interfere, but running a blank sample simultaneously overcomes much of this problem (18).

Of course, the stock used here was still 50:50 bleached Kraft softwood and hardwood that had been beat in a laboratory Valley beater to a freeness of 350 CSF. Also, the fractions were run through a Wiley mill to increase the amount of fines from the longer fibers present (mostly from softwood fraction).

(a) Reagent Preparation - Toluidine Blue 0 dye is prepared at a 0.1% solution in distilled water. The cationic polymer solution is made by dissolving approximately 760 mg of methyl glycol chitosan in 400 ml of distilled water. The anionic polymer solution is made by slowly adding 265 mg of potassium polyvinyl sulfate to 400 ml of hot distilled water. The two polymer solutions have to be standardized so that one volume of the cationic reagent is neutralized exactly by one equivalent volume of the anionic reagent. To accomplish this, 5 ml of the cationic reagent is pipetted into 25 ml of distilled water and 1 or 2 drops of indicator dye is added. This sample is titrated with the anionic polymer reagent until the color changes from blue to pink. The volume of either the anionic or cationic polymer solution is adjusted so that 5 ml of the cationic polymer solution is neutralized by 5 ml of anionic polymer solution (18).

(b) Procedure - Measure out two 25 ml samples of headbox stock into two

centrifuge tubes (a recalibrated 25 ml graduated pipette that has been cut off at the tip to avoid fiber plugging was not needed since the fibers were so finely grounded). To one sample, add 4 ml of the standardized cationic polymer solution. To the other sample, add 4 ml of the standardized anionic polymer solution. Agitate both slightly. After about one minute, centrifuge both samples until the liquid phase is clear. Transfer 10 ml of clear supernatant liquid from each sample into two separate 50 ml beakers and add one drop of indicator solution (for titration purposes, diluted standard reagents (5X) can be used). Titrate each 10 ml sample with the polymer solution of opposite charge. In the event that the endpoint is missed, the sample can be back titrated. For this precise analysis, a blank determination on a 25 ml clear supernatant sample was run (18).

(c) Calculations - The colloid titration ratio is calculated using:

$\frac{A - 2.9(a)}{C - 2.9(c)}$, where A is the ml of titrant necessary to neutralize 4 ml of the standard anionic polymer solution which has been added to 25 ml of distilled water (or centrifuged base stock slurry), a is the ml of titrant to neutralize 10 ml of the clear supernatant from the centrifuged sample containing the anionic polymer solution, C is the ml of titrant necessary to neutralize 4 ml of the standard cationic polymer solution which has been added to 25 ml of distilled water, and c is the ml of titrant necessary to neutralize 10 ml of the clear supernatant from the centrifuged sample containing the cationic polymer solution. The factor 2.9 comes from using only 10 ml of the original 29 ml sample that was centrifuged. The logarithm of this ratio is recorded.

Equipment and Chemicals

Equipment included the Britt Jar, a centrifuge, a temperature bath, an evaporation oven, and other miscellaneous equipment for solution handling and titration. Chemicals included SEPARAN CP-7, TAMOL 850, tri-polyphosphate, sodium carbonate, potassium polyvinyl sulfate, methyl glycol chitosan, and Toluidine Blue.

RESULTS AND DISCUSSION

INTRODUCTION

The final values for fines fractionation, fines retention, and surface charge are cited in the following table under the three loading conditions (0.25, 0.50, 0.75 lbs. polymer/ton paper produced) at the four temperatures (10, 25, 40, 55°C).

TABLE I

TESTING RESULTS

Temp. & Loading	Fines Fract.	Fines Blank	Fines Retent.	FR – FB	Charge CTR	Blank log	CTR	log CTR	Δlog CTR
10°C;0.25#	27.5%	44.6%	44.6%	0.0	.798	–.098	4.20	+.623	+.721
0.50#	"	"	61.5	16.9	"	"	1.13	+.053	+.151
0.75#	"	"	48.5	3.9	"	"	0.46	–.341	–.243
25°C;0.25#	27.3%	46.4%	49.0	2.6	.958	–.019	0.58	–.234	–.215
0.50#	"	"	53.5	7.1	"	"	2.84	+.453	+.472
0.75#	"	"	57.6	11.2	"	"	1.03	+.013	+.032
40°C;0.25#	26.5%	57.4%	71.8	14.4	.875	–.058	.835	–.078	–.020
0.50#	"	"	74.8	17.4	"	"	4.50	+.653	+.711
0.75#	"	"	85.9	28.5	"	"	1.60	+.204	+.262
55°C;0.25#	24.1%	55.2%	68.5	13.3	.800	–.097	.273	–.564	–.467
0.50#	"	"	73.2	18.0	"	"	.241	–.618	–.521
0.75#	"	"	80.4	25.2	"	"	.060	–1.22	–1.12

Specific fines fractionation and retention values are listed in Appendix I: Table II, while the other tables in the appendix show experimental and propagated errors in the values shown in Table I. Table III gives the sample standard deviation, the universal standard deviation, the best estimate of the standard deviation of the means, and the sample 90% confidence interval for

fines fractionation and retention values. Table IV lists the sample propagated errors of the colloid titration ratio (CTR) and the logarithmic form. Note that the percentages in the retention procedures are in terms of weight. The surface charge values $\underline{A}$, $\underline{C}$, $\underline{a}$, and $\underline{c}$ are in milliliters but yield a unitless value when put into the proper ratio.

Fines fraction decreased with rising temperature in Figure 2. In Figure 3 and 5 fines retention and the logarithm of the colloid titration ratio (log CTR) were plotted against cationic polymer loading. Rises in retention with loading except for the 0.75 lb. loading at 10°C were seen for all four temperatures, while surface charge values went down for all temperatures between 0.50 and 0.75 pounds/ton loading but varied in charge at loadings between 0.25 and 0.50 pounds polymer per ton. Figures 4 and 6 show retention and log CTR plotted against temperature to see the effect of temperature at specific loading levels. In general, retention rose then dropped off with rising temperature, and surface charge values also rose then dropped off with the exception of the 0.25 pound/ton loading. Temperature obviously introduces complex interactions between loadings and values seen in retention and charge. Figure 7 in Appendix I was provided to see the relationship between the CTR and loading and/or temperature, and to recognize the corresponding values measured with those given in Figure 5. Figures 2, 3, and 4 have been plotted showing 90% confidence limits for each level tested.

EXPERIMENTAL AND PROPAGATED ERROR

The various polymer loadings were well controlled by use of a syringe; however, temperature varied through each determination by roughly $\pm$ 3-4°C. Yet having temperature intervals of 15°C gave the data validity and reliability through the temperature range it represented. The temperature variation, though, was not the source of inducing the most error, but the actual propagated error

through calculations and the relatively small number of trials per level tested produced large sample standard deviations. Unfortunately, the calculated error in each surface charge determination was much too large due to sources discussed later, such as, the calculation itself, the omission of a dilution factor to the reagents, and so on.

FINES FRACTION

The fines fraction that was extractable through drainage was seen to decrease with rising temperature in Figure 2. The 90% confidence boundaries crossed over other boundaries and in most cases included average values at other temperatures, which suggests that only moderate or little difference existed between them. However, the uncertainty was cut to one-third when replications were increased from the three trials at 10°C to the seven at 25°C. If time had permitted, the uncertainties could have been cut in half for nearly all the determinations by increasing replications from three to nine or from two to five. This decrease in fines fraction, though temperature induces a higher probability for particles to be farther apart, could be predicted by the fact that potential and other electrostatic interactions were increased with temperature so that though particles were spread out, they could not be as easily removed from the system as at lower temperatures. In other words, though only 24% fines were determined at 55°C, the total fines of the system were much greater than 24% so only 24% was removable fines that could be analyzed and used as a standard.

FINES RETENTION

Consistent with behavior of effective retention aids, increased loading at each temperature caused more fines to be retained from larger charge densities introduced in the solutions except at 10°C. The SEPARAN CP-7 loading range of 0.2 to 0.75 pounds of polymer per ton of paper produced showed great

FIGURE 2. DEPENDENCE OF FINES FRACTION ON TEMPERATURE

WITH 90% CONFIDENCE LIMITS
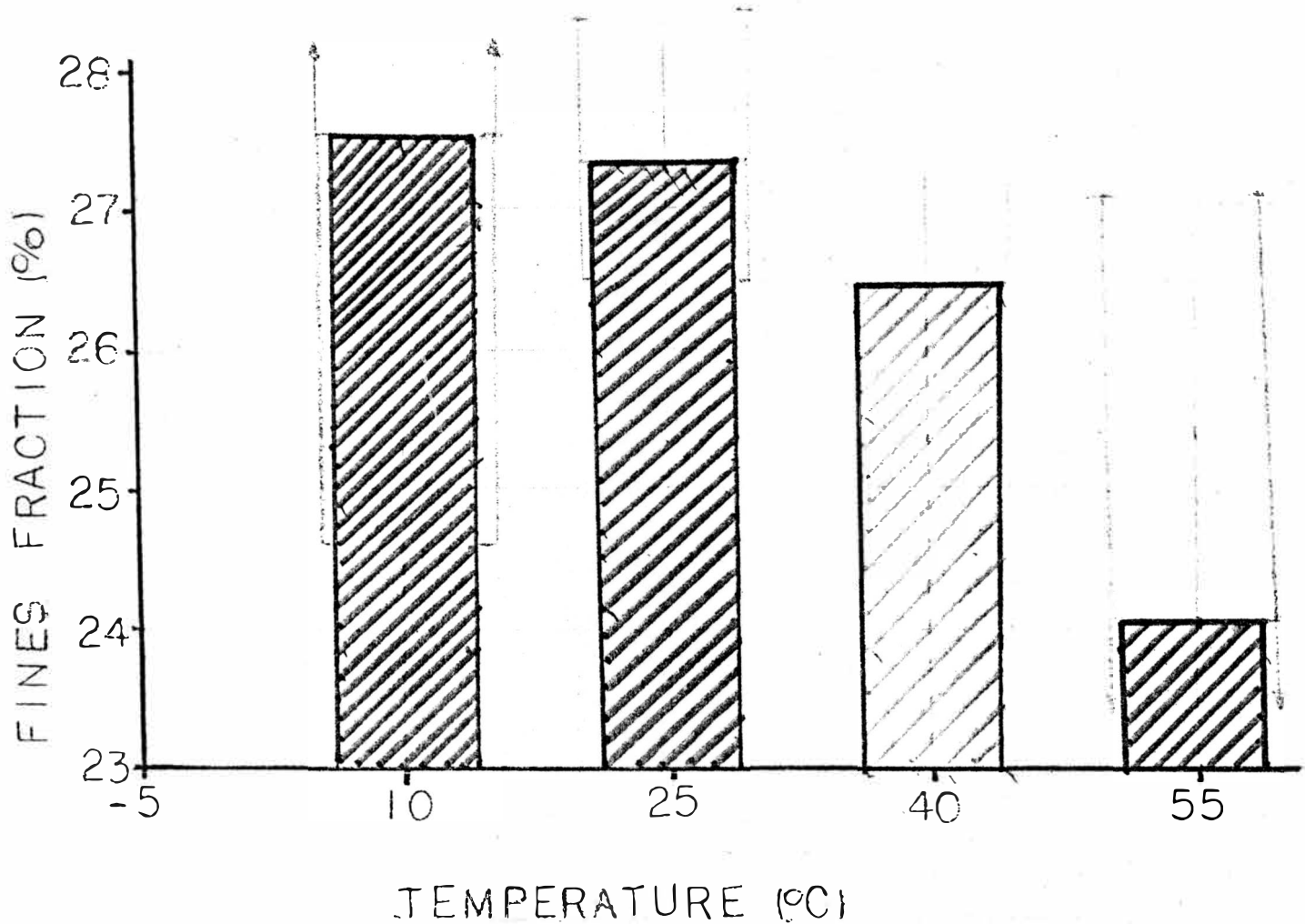
instability at 10°C (though CP-7 has good thermal stability at higher tempera-

tures) since no effect was seen from the blank at the 0.25 level, since retention

rose very drastically when approaching the 0.50 level probably due to sudden

flocculation held back previously when loading was overshadowed by the low

temperature, and since retention dropped off at the 0.75 level where for 10°C

the loading had past the point of diminishing returns for flocculation. There

also was a distinct level difference between the two lower and two higher tem-

peratures. The values with their confidence limits appeared to be significant;

FIGURE 3. DEPENDENCE OF FINES RETENTION ON LOADING WITH 90% CONFIDENCE LIMITS
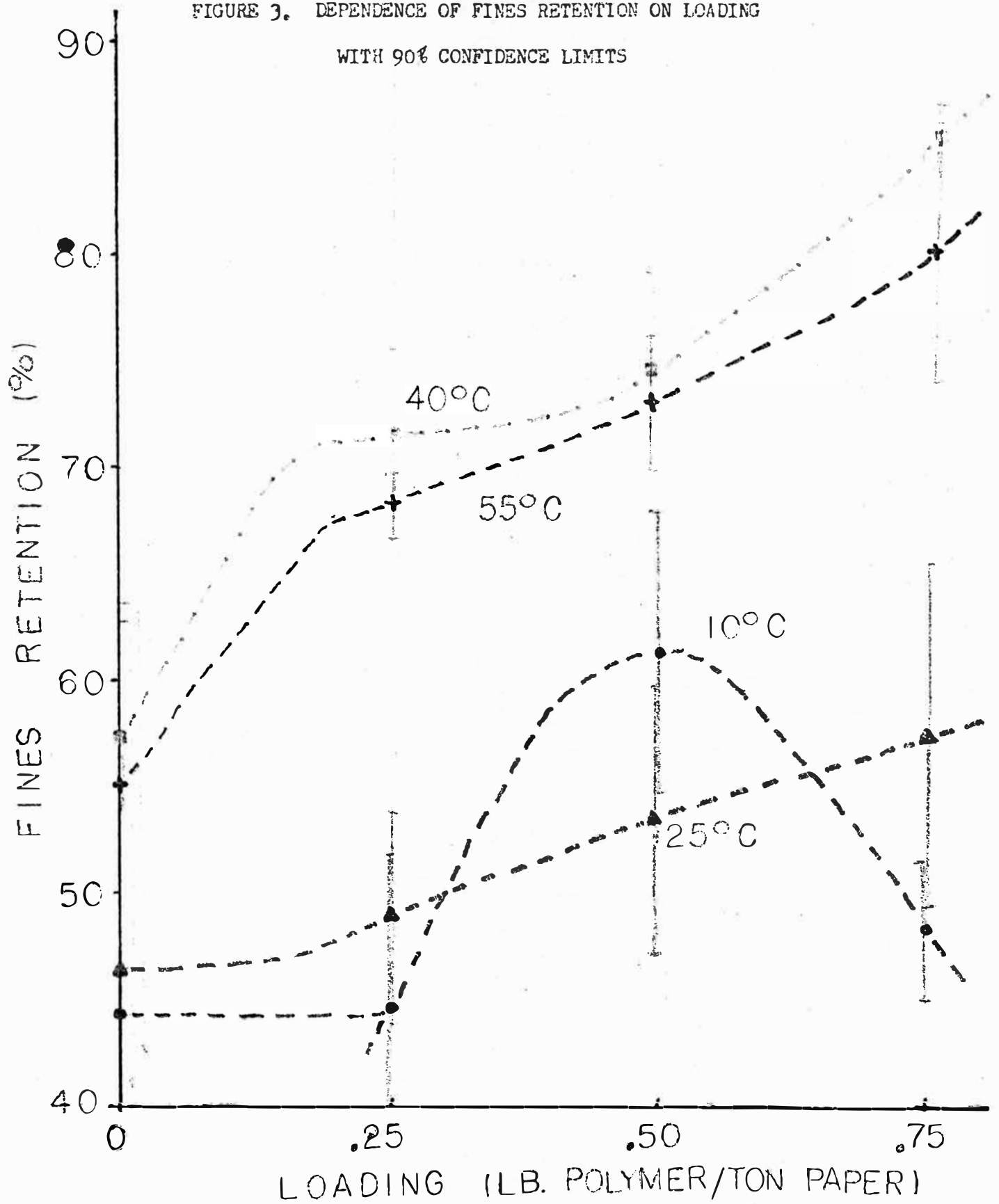
therefore, Figure 3 indicates that somewhere between 25 and 40°C there was a significant increase in flocculation to keep particles suspended. However, it also indicates that somewhere between 40 and 55°C flocculation had reached a limit where so much like-charge had been induced in the system that repulsion forces were overshadowing flocculation tendencies thus producing a retention decrease. Notice also that the actual amount retained per ton produced for 40°C over 55°C was even greater than the graph shows since the fines fraction that actually passed through the apparatus was much greater for 40°C than 55°C.

Figure 4 shows a high dependency of retention in terms of loading on temperature from the giant sweeps in retention between 40 and 90% for such a small temperature range. The line for the blank or zero loading again clearly illustrates a definite flocculation increase between 25 and 40°C and a curtailing of retention through excessive charge stimulation after 40°C. Also, the points at 10°C illustrate again the limited flocculating tendencies at high and low loading limits and that significant flocs formed at 0.50 loading which were not easily added to or easily dispersed upon slight changes in charge density (loading). At higher temperatures the initial introduction of charge induced a large increase in flocculation and retention unlike at lower temperatures. Then additional loading to moderate conditions only slightly raised retention relative to initial charge at high temperature. At the upper loading limit with high temperatures, flocculation again was greatly increased and never reached a point of diminishing returns for the chosen loading ranges.

SURFACE CHARGE

If the net surface charge of a particle suspended in water is made up of the summation of the individual positive and negative sites on the surface, then each surface would be expected to adsorb a certain amount of both an anionic (negatively charged) and a cationic (positively charged) polymer. Also, the

FIGURE 4.   DEPENDENCE OF FINES RETENTION ON TEMPERATURE
WITH 90% CONFIDENCE LIMITS
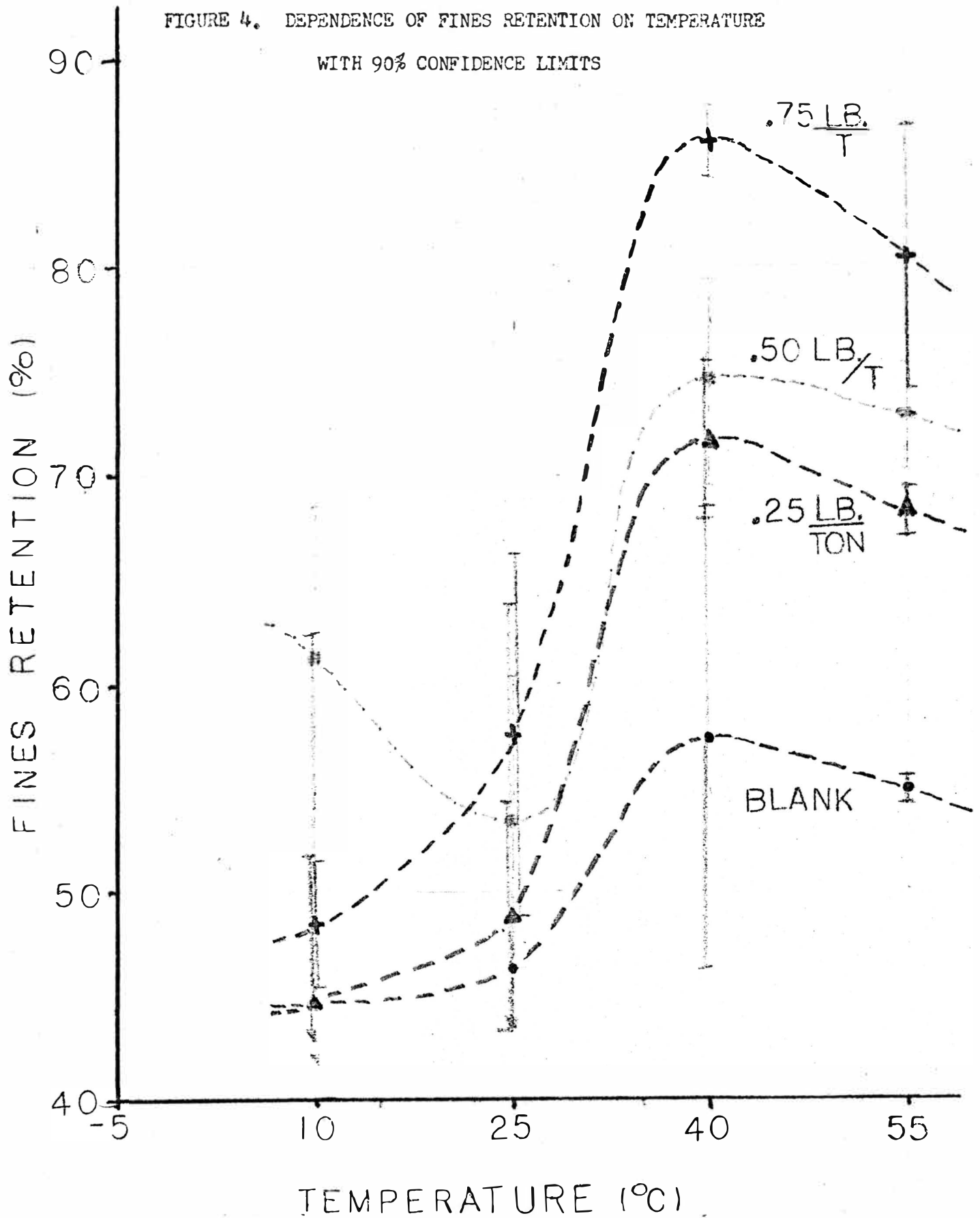
charge on that particle surface will be reflected by the summation of the amount of each polymer of opposite charge adsorbed. If the particle surface in question has a net negative charge, then more of the positively charged polymer will adsorb and the colloid titration ratio (CTR) will be less than one. On the other hand, if the particle surface contains more cationic sites than anionic sites, the net surface charge will be positive, and more of the anionic polymer will adsorb. Therefore, the ratio will be greater than one. The logarithm of this ratio (log CTR) gives values less than zero for negatively charged systems and values greater than zero for positively charged systems. Systems close to neutral will adsorb equal amounts of anionic and cationic polymer, and the logarithm of the ratio will be close to zero.

Therefore, with an understanding of the meaning of the log CTR, Figures 5 and 6 clearly illustrate some major discrepancies with retention data results. First, it is not conceivable to believe that addition of cationic polymer would create more negative sites in the systems as the negative sloping curves suggest in Figure 5. Also, it suggests that a negatively charged system as for $55^{o}C$ would be more effective in retention (from retention data) of fines than positive or slightly negative systems at temperature below about $30^{o}C$. In fact, the jump of charge sites from strongly positive at $40^{o}C$ to strongly negative at $55^{o}C$ is unlikely under cationic retention aid conditions unless there was a large charge inversion due to temperature increases from 40 to $55^{o}C$. However, this seems unlikely and inconsistent with cited behavior of fines, fibers, and polymers in solution by Halabisky (18) as opposed to Britt's conclusions (9) on the relationship between retention and surface charge.

Halabisky (18) found that the papermaking system had optimum drainage and retention when this ratio (amount of anionic polymer adsorbed/amount of cationic polymer adsorbed) was close to or slightly greater than unity; therefore,

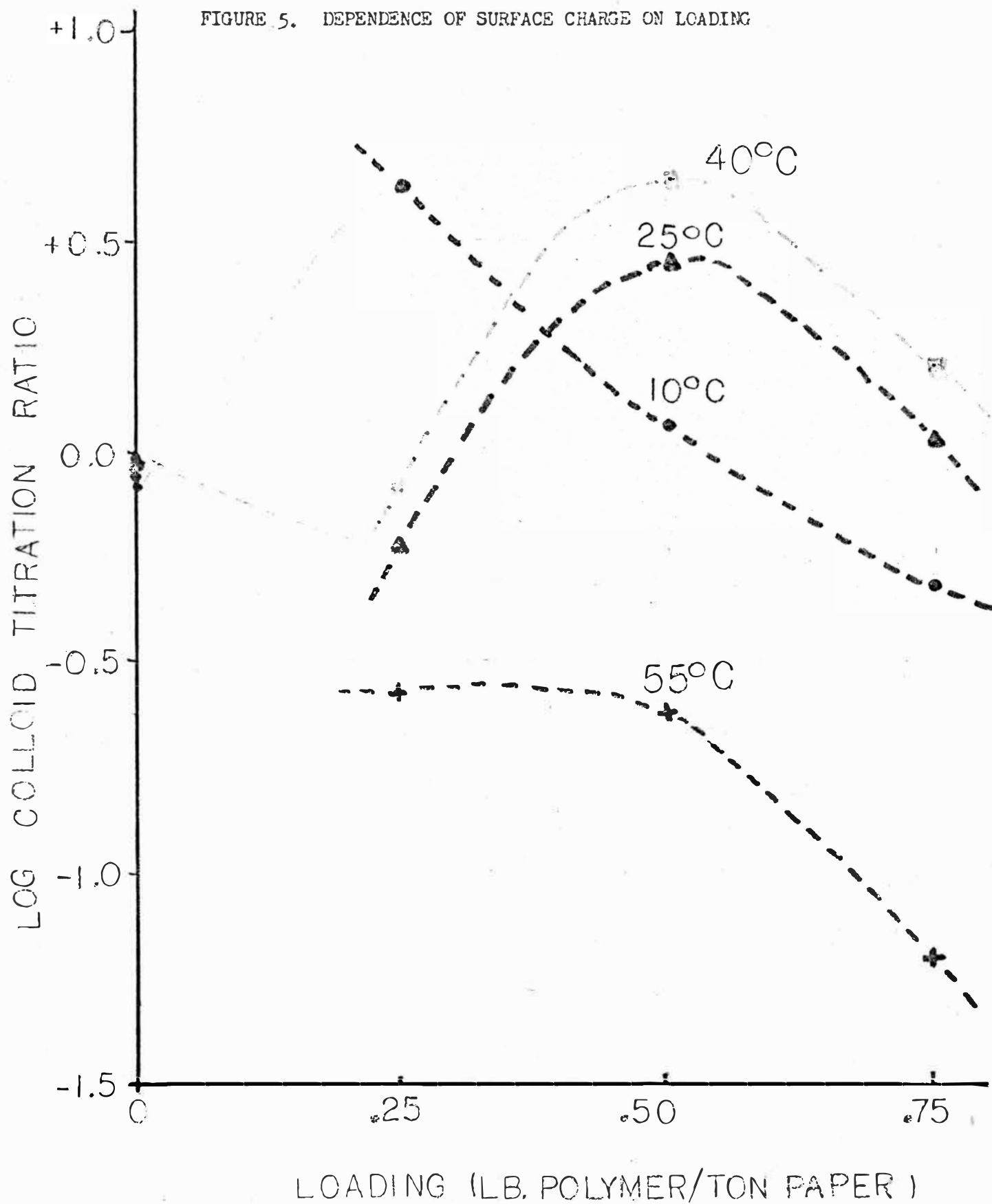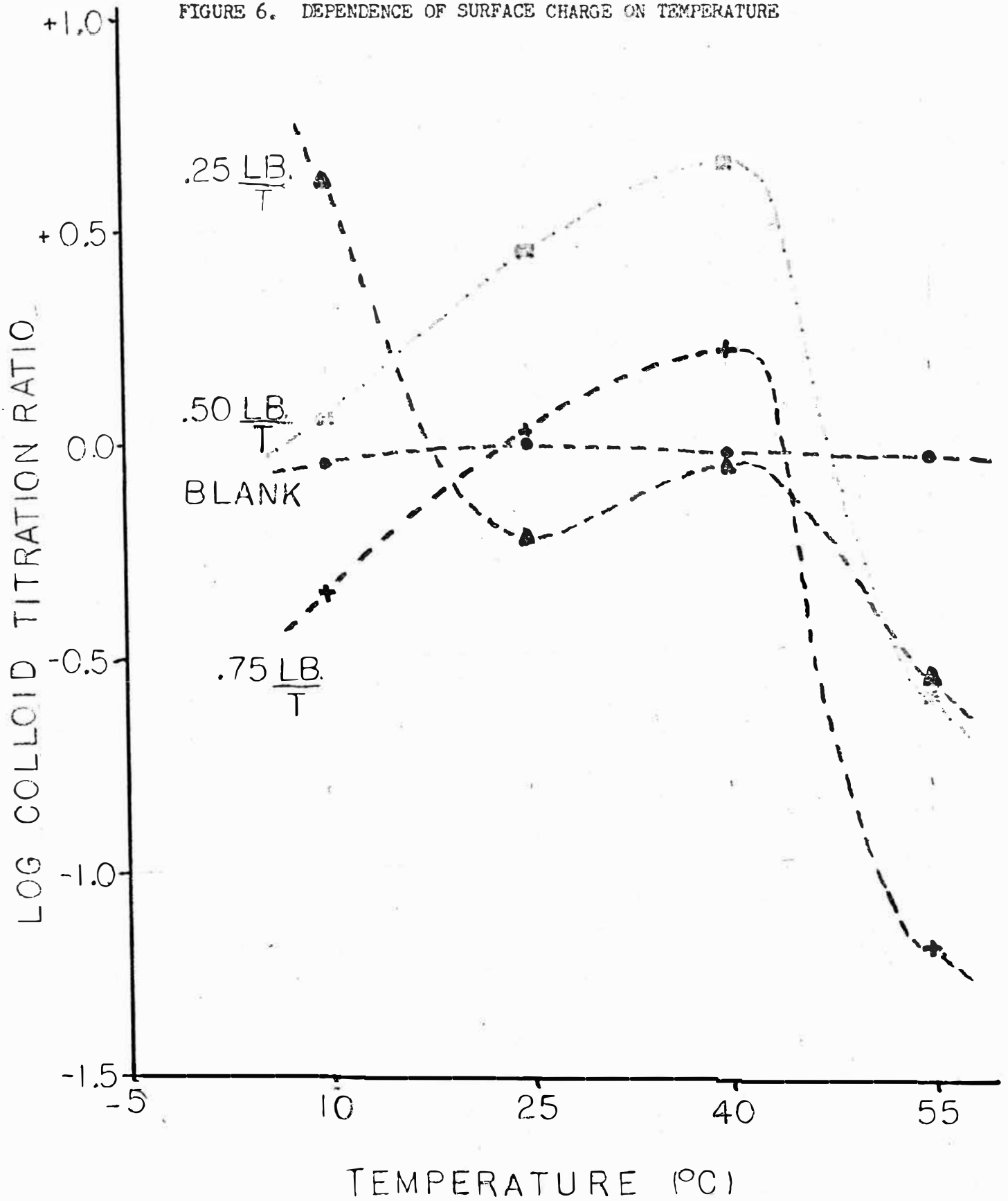FIGURE 5. DEPENDENCE OF SURFACE CHARGE ON LOADING

FIGURE 6. DEPENDENCE OF SURFACE CHARGE ON TEMPERATURE

log CTR and zeta potential would be expected to be close to zero. However, data showed highly negative 55°C systems drawing further from zero with increasing retention in Figure 5. Conversely, retention increases were seen when the log CTR approached zero from positive systems at 10, 25, and 40°C (again inconsistent with the fact that cationic polymer was being added). the high positive value at 10°C and 0.25 pounds/ton loading and medium negative values at 25 and 40°C were consistent with the retention results, yet again 55°C values are highly negative though producing moderately high retention. The transition from 0.50 to 0.75 pounds/ton positive charge loading was highly speculative since registered system charge went down to more numerous negative sites present; nevertheless, retentions were predictable according to Halabisky's findings of high retention at or near zero zeta potential except for the highly negative 55°C system. Agreement with Britt's findings that zero zeta potential does not necessarily produce optimum drainage and retention exists.

In Figure 6 there were apparent charge inversions between 25 and 55°C for all loadings and at 25 and 40°C (charge sites went negative, positive, then more negative). Unexpected charge decreases occurred at 10 and 55°C leading to the conclusion that either temperature had a very complex interaction with cationic polymer loading or large uncertainties in calculated values made it impossible to know if the averages were reliable. Since positive loading levels showed such drastic changes compared to the blank, polymer-temperature interaction was much greater than base stock-temperature interaction in terms of retention change induced by charge modification. The log CTR values again were highly speculative and should be investigated by additional trials on 350 CSF stock of 50:50 bleached Kraft softwood and hardwood.

CONCLUSIONS

The actual attraction of fines to fibers increases over the 10 to 55°C range as the fines fraction removable from the base stock decreases upon temperature increases. In general, increased cationic polymer loading produces increased fines retention except below room temperature and, depending on its interaction with temperature, does not necessarily create more positively charged systems. SEPARAN CP-7 has unstable flocculating tendencies below room temperature where loadings at high and low limits give very low relative retention and at a medium level (about 0.50 pounds polymer/ton production) give more optimum fines retention than at room temperature. For 50:50 bleached Kraft softwood and hardwood stock at 350 CSF, there is a significant increase in retention and thus flocculation between 25 and 40°C for all polymer loadings, and the temperature for optimum fines retention in the 10 to 55°C range is around 40°C. However, there is no point of diminishing returns in the loading range. Above room temperature the initial additions and additions close to the upper limit (0.75#/ton) of cationic polymer yield the most relative flocculation for any loading below the upper limit.

In terms of surface charge, the strongly negative system at 55°C induces greater fines retention than slightly negative and/or strongly positive systems below 30°C. Because of high polymer-temperature interaction (as opposed to stock-temperature interaction), increased loading gives more negative sites available on particles within the 10 to 55°C range at all loadings for 10 and 55°C and at loadings above 0.50#/ton for 25 and 40°C (inconsistent with classical understanding). Highly relative charged positive or negative systems do not necessarily provide poor retention while near zero zeta potential systems do not necessarily give high retention with cationic polymer additions (consistent with Britt (2) and inconsistent with Halabisky (18)). Charge inversions occur

through 40 and 55°C for all cationic polymer loadings (within each loading) and at 25 and 40°C taking all loadings collectively where charge sites move negative, positive, than more negative from blank conditions (whose charge is so stable through temperature changes suggesting little stock-temperature influence). Statements on these surface charge results are made assuming the data to be reliable though calculated errors are very high.

RECOMMENDATIONS

1. Employ a wide temperature range study to especially include very low ($-10-0^{\circ}$C) and very high ($65-100^{\circ}$C) temperatures, being sure to use the dilution factor (5X) for reagents in the Colloid Titration Technique.

2. Use the Britt Dynamic Drainage Jar and the Colloid Titration Technique at various temperatures to study fines retention and surface charge from classical retention aids, cationic polymers, and anionic polymers of varying molecular weight.

3. Examine the influence system pH has on retention and surface charge at each temperature tested for specified loadings of specified retention polymers.

4. Study fines and filler retention and filler influence on surface charge for a specified retention polymer using common industrial paper fillers.

5. Find variations due to base stock softwood-hardwood ratio changes on retention and surface charge.

6. Research the effect agitation at various temperature levels has on retention, surface charge, and ultimate two-sidedness on the paper machine. Also use various rpm levels with the Britt Jar.

7. Combine common retention aids (cationic vs. anionic, etc.) at various relative loading levels to each other and determine their retention and surface charge influence at each temperature to be studied.

REFERENCES

1. Abrams, R.W., Tappi 47(12): 273 (1964).

2. Adamson, A.W., "Physical Chemistry of Surfaces" 1st ed., New York, Interscience, 1960, pp. 179-84.

3. Anderson, R. G. and Penniman, J. G., Paper Trade J. 158(2): 56 (1974).

4. Arvela, P., Swanson, J. W., and Stratton, R. A., Tappi 58(11): 86 (1975).

5. Bauer, E., Poschmann, F., and Auhorn, W., Ger. pat. 1,546,237 (April 18, 1974) (Engl. abstr. in ABIPC).

6. Britt, K. W., The CF Dynamic Drainage Jar, State University of New York, College of Environment Science and Forestry, 1973.

7. Britt, K. W., Tappi 56(3): 83 (1973).

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

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

10. Britt, K. W. and Unbehend, J. E., Tappi 59(2): 68 (1976).

11. Broughton, G. and Wang, J. P., Tappi 38: 412 (1955).

12. Cowan, E., Pulp Pap. Mag. Can. 38: 85 (1937).

13. Dow Chemical Company, SEPARAN CP-7 Polymer Drainage and Retention Aid for Paper, Designed Products Department, Midland, Michigan, 1975.

14. Estridge, R., Tappi 45(4): 285 (1962).

15. Frankle, W. E. and Penniman, J. G., Paper Trade J. 157(32): 30 (1973).

16. Frankle, W. E. and Sheridan, J. L., Tappi 59(2): 84 (1976).

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

18. Halabisky, D. D., Surface Charge Measurement of the Headbox Furnish by Titration, 1975.

19. Han, S. T., Tappi 45(4): 292 (1962).

20. Han, S. T., Tappi 47(12): 782 (1964).

21. Han, S. T. and Chang, Nai L., Tappi 52(4): 688 (1969).

22. Hansen, E., Tappi 34(4): 180 (1951).

23. Johnson, R. C., Tappi 46(5): 304 (1963).

24. Kallmes, O. and Corte, H., Tappi 43(9): 737 (1960).

25. Kibblewhite, R. P., Appita 26(3): 196 (1972).

26. Kibblewhite, R. P., Appita 26(5): 341 (1973).

27. Lamer, V. K. and Healy, T. W., Pure Appl. Chem. 13: 112 (1963).

28. Lewis, D. J., Proc. Roy. Soc. A202: 81 (1950) (Wrist, p. 117).

29. Lindstrom, T., Soremark, C., and Heinegard, C., Tappi Conf. (Boston): 77(1974).

30. Lyne, L. M. and Gallay, W., Tappi 37: 581, 694, 698 (1954).

31. Martin-Löf, S., Framzen, T., and Heinegard, C., Tappi 56(12): 121 (1973).

32. Miller, R. C., Lecture at Western Michigan University, Nalco Chemical Co., Product Manager (September 29, 1976).

33. Moore, E. E., Tappi 58(1): 99 (1975).

34. Moss, L. A., Doctoral Dissertation, Appleton, Wis., The Institute of Paper Chemistry: 159 pp (1936) (Abrams, p. 778).

35. Nelson, R. W., Tappi 47(12): 752 (1964).

36. Parker, J. and Mih, W. C., Tappi 47(5): 254 (1964).

37. Penniman, J. G., Pulp Paper 49(2): 134 (1975).

38. Poppel, E., Zellstoff Papier 23(2): 55; (3): 79; (4): 111 (1974).

39. Richardson, C. B., Paper Industry, pp. 54-6 (July, 1965).

40. Sennett, P. and Olivier, J. P., in "Chemistry and Physics of Interfaces," Washington, D.C., American Chemical Society, 1965, pp. 75-94.

41. Smith, J. F., Paper Trade J., Ind. Dev. Sect. p. 468-70: 29 (1949).

42. Taylor, Sir Geoffrey, Proc. Roy. Soc. A201: 192 (1950) (Wrist, p. 117).

43. Thode, E. F. and Ingmanson, W. L., Tappi 42(1): 74 (1959).

44. Underhay, G. F., Tappi 37(11): 547 (1954).

45. VanDenAkker, J. A., Tappi 35: 13 (1952).

46. Verwey, E. J. W. and Overbeek, J. Th. G., Amsterdam, Elsevier, 1948 (Williams, (12): 147).

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

48. Walsh, T., _Am. Paper Ind._ 56(4): 31 (1974).

49. Williams, D. G. and Swanson, J. W., _Tappi_ 49(4): 147 (1966).

50. Williams, D. G., _Tappi_ 56(12): 144 (1973).

51. Wrist, P. E., _Pulp Pap. Mag. Can._ 55(5): 115 (1954).

APPENDIX I

TABLE II

FINES FRACTIONATION AND RETENTION DATA

Temp. & Loading	Replications (%)							Averages
FRACTIONATION								
10°C	29.46	26.62	26.55					27.5
25°C	26.42	28.68	29.18	27.08	26.82	27.01	26.11	27.3
40°C	25.57	28.43	25.37					26.5
55°C	25.95	22.54	23.70					24.1
RETENTION								
10°C; Blank	46.84	42.43						44.6
0.25#	47.3	40.3	46.3					44.6
0.50#	59.4	66.8	58.2					61.5
0.75#	48.7	51.3	45.4					48.5
25°C; Blank	52.68	40.10*						46.4
0.25#	47.87	50.02						49.0
0.50#	50.98	51.33	58.10					53.5
0.75#	52.28	58.21	62.46					57.6
40°C; Blank	58.33	56.51						57.4
0.25#	70.51	74.34	70.53					71.8
0.50#	72.56	78.22	73.46					74.8
0.75#	86.73	85.50	85.36					85.9
55°C; Blank	55.22	55.48						55.2
0.25#	67.59	68.93	68.98					68.5
0.50#	73.07	74.26	72.22					73.2
0.75#	80.43	76.33	84.37					80.4

* Spread and few number of trials contribute to large errors.

TABLE III

CALCULATED ERROR IN FINES FRACTIONATION AND RETENTION DATA

Temp. & Loading	Sample Standard Deviation	Universal Standard Deviation	Best Estimate of Deviation of the Means	Sample 90% Confidence Limits
FRACTIONATION				
10°C	1.42	1.74	1.00	± 2.94
25°C	1.03	1.11	0.421	± 0.818
40°C	1.33	1.63	0.943	± 2.75
55°C	1.47	1.80	1.04	± 3.04
RETENTION				
10°C; Blank	2.82	4.00	2.82	± 17.8
0.25#	3.54	4.34	2.50	± 7.31
0.50#	3.22	3.94	2.28	± 6.65
0.75#	1.61	1.97	1.14	± 3.33
25°C; Blank	2.76	3.90	2.76	± 17.4
0.25#	0.816	1.15	0.816	± 5.15
0.50#	3.28	4.01	2.32	± 6.77
0.75#	4.17	5.11	2.95	± 8.62
40°C; Blank	1.77	2.50	1.77	± 11.2
0.25#	1.93	2.36	1.36	± 3.98
0.50#	2.38	2.92	1.68	± 4.92
0.75#	0.975	1.19	0.690	± 2.01
55°C; Blank	0.020	0.0283	0.020	± 0.126
0.25#	0.644	0.788	0.455	± 1.33
0.50#	1.09	1.33	0.771	± 2.25
0.75#	3.20	3.92	2.26	± 6.61

TABLE IV

CALCULATED ERROR IN SURFACE CHARGE DATA

Temperature and Loading	Sample Standard Deviation for Colloid Titration Ratio	Sample Standard Deviation for Log Colloid Titration Ratio
10°C; Blank	0.093	± 0.051
0.25#	7.14	± 0.74
0.50#	0.773	± 0.30
0.75#	0.418	± 0.40
25°C; Blank	0.713	± 0.32
0.25#	0.243	± 0.18
0.50#	8.10	± 1.24
0.75#	3.86	± 1.62
40°C; Blank	1.02	± 0.51
0.25#	1.23	± 0.64
0.50#	99.1	± 9.56
0.75#	6.49	± 1.76
55°C; Blank	4.40	± 2.39
0.25#	2.70	± 4.30
0.50#	1.06	± 1.92
0.75#	0.578	± 4.16

FIGURE 7. DEPENDENCE OF ANTILOG OF SURFACE CHARGE ON LOADING