

**A STUDY OF PARTICLE RETENTION**  
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A STUDY OF PARTICLE RETENTION

SUMMARY

This report covers the work of the past year on particle retention. It also serves to summarize the present status of the theory of the retention process. The original objective of the particle retention phase of Project 2570 was to extend the retention theory developed in Project 2348 to predict retention behavior under continuous sheet-forming conditions. After completion of the work on particle retention at high velocities in thin fiber mats, Progress Report Two, Project 2570 (3), it was felt that it was premature to attempt to describe retention in continuous forming. Accordingly, a more fundamental outlook was adopted for the remainder of the work.

A new technique has been developed which permits local values of free and bound particle concentrations and of the retention rate to be determined from constant-rate-filtration particle-distribution curves. Application of this technique to experimental pads formed at 1 cm./sec. gave unexpected results. The rate of particle attachment was found to be dependent on bound particle concentration as well as being first order in free particle concentration. Removal of particles was found to increase rapidly after a shear-dependent critical bound particle concentration was exceeded. The implications of these observations are discussed in the report which follows.

The effects of fines and particle size distribution on retention behavior were explicitly studied. To some extent, the effect of fines was found to be dependent on the method of fines addition to the particle-fiber system. The size-distribution experiment showed clearly that smaller particles were preferentially retained.

The present understanding of the retention process is still inadequate to allow prediction or proper interpretation of particle distributions for sheets made on actual paper machines. The new technique, described above, promises to be a powerful tool in obtaining the information required to meet this ultimate objective.

## INTRODUCTION

## MEANING OF RETENTION

The concept of particle retention must begin with a differentiation between particulate matter and fibers. There must be present a particulate system and a retention medium. In the case of a beaten pulp, for example, such a differentiation is not necessarily straightforward. The boundary between a large fine and a short fiber can be very hazy. Nevertheless, such a separation is necessary, at least in a conceptual sense.

Particle retention can be defined as the process by which particulates are collected in a retention medium. To the papermaker, this medium is always a fibrous sheet. It is important to note that retention is defined to be a process, and not a measure of the amount of material retained. In this report, the word "retention" will not be used in a quantitative sense.

Once the process of retention is defined, it then becomes necessary to have some criterion for determining if a particle is retained, and the amount retained. With regard to the paper machine, several criteria are available. One of the simplest, and of great economic significance, is the amount of particulate retained at the reel. The ratio of the amount of particulate matter which arrives at the reel to that introduced at all of the various points in the process is a direct measure of the retention efficiency of the whole papermaking system. Another retention criterion often used in the industry is the wet-end, one-pass retention efficiency, often called one-pass retention. This is a measurement of the amount retained at the wet end based on the particle content of the headbox and the sheet. During steady operation, wet-end, one-pass retention efficiency will be lower than system retention efficiency due to recycling of the particles in the white water. Each of these retention criteria

can be quite significant, depending on how it is used. They are both valid criteria.

With regard to the process of retention itself, the most fundamental criterion for what is or is not retained is a local criterion. Particles are considered to be in one of two states - free or bound. A free particle exists in suspension and is not associated with the retention medium. A bound particle is associated with the fiber and is unable to move freely in suspension. At any particular instant of time those particles which are bound are considered to be retained. Then retention can be defined as the process by which free particles are converted to bound particles. This concept will be used in this report.

#### MEASUREMENT OF RETENTION

Although retention was defined as a process, and hence as nonquantitative, the aspects of this process are quantitative, and hence subject to measurement. The basic measurement of retention phenomena is the determination of the amount retained. This is normally done by measuring the weight of particles retained, either by direct weighing or by chemical means. The weight of particles can then be divided by the weight of the sheet to express the measurement on a unit basis. If the particle weight is divided by sheet weight minus particle weight, the result is the ratio of particles to pure fibers. This can be directly interpreted as a bound-particle concentration.

Indirect means for measuring the amount retained are available. These are used where it is inconvenient or impossible to measure the amount retained directly. One of these is a difference technique, where the amount of free particles is measured before and after the retention process, and the amount of material retained determined by difference. This method is sometimes used in laboratory

experiments. Fines are especially troublesome. They are hard to define and even harder to measure quantitatively. Radioactive tagging and dye absorption have been used to measure fines.

A much greater amount of information about the retention process can be obtained by measuring the distribution of particles through the thickness of the sheet. Such a measurement involves splitting the sheet and determining the amount retained in each layer. There are many methods which have been used to split sheets into layers, some of which are used on wet mats and some on dry mats. Among these are the Beloit sheet splitter, adhesive tape method, microtome method, and the dissecting needle method. Needless to say, a measurement of the bound-particle distribution is no more accurate than the splitting method used.

Other means for measuring particle retention are various usage measurements. These are measurements of sheet properties which are related to the presence of particles in the sheet. Examples of such measurements are opacity, bulk, and printing characteristics. These measurements can be very important to the papermaker, who may add the particles to enhance certain properties. However, they do not give much information about the retention process itself.

#### REQUIREMENTS OF A RETENTION THEORY

Increased understanding of retention phenomena must eventually culminate in a theory of the retention process. The development of a comprehensive retention theory incorporating the many facets of the retention process is the goal of this and future studies. The requirements of such a theory are rather stringent, and are at present far from being realized. The retention of particles in a papermaking system is still almost entirely in the art stage.

The first requirement of a retention theory is that it must put the retention process on a quantitative basis. Fundamental parameters must be defined and interrelated. This quantitative description of the retention process must be based on sound physical and chemical principles. The sequence of events which occur during retention must be sufficiently defined so that rate-controlling steps can be determined. The theory must be broad enough that it encompasses all major variables which affect retention. This includes hydrodynamic factors involved in forming a sheet as well as colloidal phenomena governing the behavior of particle suspensions.

The second requirement of a theory of particle retention is that it must be adaptable to the conditions which prevail on a paper machine. The paper machine sets the range over which the effects of major variables must be known. The theory must account for retention occurring simultaneously with sheet formation. In addition, it should be able to handle such peculiarities of the paper machine as intermittent drainage at table rolls and foils.

The third requirement of the theory is that it must be useful. There are four major uses of a theory - prediction, control, optimization, and insight. The ability to predict would take retention out of the art category. It is necessary for both control and optimization. The economic benefits which could be obtained through control and optimization are obvious. Among them are more efficient utilization of raw material and reduced time for grade changes. Perhaps the greatest benefit would be obtained through the insight that a comprehensive retention theory would provide. This could ultimately lead to new and better methods for accomplishing the objectives of particle retention.

## FUNDAMENTAL ASPECTS OF PARTICLE RETENTION

## NATURE OF THE RETENTION PROCESS

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The quantitative description of the retention process begins with the distinction between free and bound particles. This allows the introduction of the concept of particle concentrations.

Free particles are associated with the suspending fluid. They are free to move in the fluid and can be transported by the bulk motion of the fluid. Because free particles are associated with the fluid, the free particle concentration,  $\underline{P}$ , is defined as the mass of free particles per unit mass of suspending fluid.

Bound particles are associated with the retention medium (the fibers). They are not free to move in suspension, and may be considered to have no independent motion at all. Transport of bound particles is due solely to the bulk motion of the fibers. Accordingly, the bound particle concentration,  $\underline{P}'$ , is defined as the mass of bound particles per unit mass of fiber.

Bound particles are of course particles which have been retained, and so the retention process can be considered the process by which free particles are converted to bound particles. The magnitudes of the free and bound particle concentrations measure the extent of retention. The rate at which retention proceeds can be measured by the time derivatives of the particle concentrations. Particle retention is inherently a kinetic phenomenon, and a quantitative treatment of the retention rate is the starting point for any comprehensive theory of the process.

### Retention Mechanism

The retention mechanism is of critical importance in understanding retention phenomena. It is the means by which a particle becomes constrained by the retention medium and loses its freedom of motion. It is the means by which a bound particle is captured. The retention mechanism is basic because without it there would be no retention phenomena. In fiber mats, there are two general mechanisms which could occur — sieving and coflocculation. There is one very important difference between these two mechanisms: With sieving, the retention medium is the fiber network, while with coflocculation the retention medium is the fibers themselves. The present consensus is that coflocculation is the dominant mechanism of retention on the paper machine.

### Coflocculation

In coflocculation, the particles are attached to the fiber surface by physicochemical bonds. An attractive force exists between the retained particles and the fiber. This force of attraction between a particle and a fiber is the result of Van der Waals-London forces. These are proportional to an inverse power of separation and essentially independent of the particle environment. With certain types of polymer additives, the attractive force can be aided by polymer adsorption and molecular bridging. These attractive forces are always present and will operate if the particle can be brought sufficiently close to the fiber surface.

Normally, the particles will have to overcome a repulsive barrier before they can get sufficiently close to the fiber surface to be held by the attractive force. These repulsive forces are electrostatic in nature and are proportional to an exponential power of distance and dependent on the particle ionic environment. The repulsive force is due to the formation of electric double layers on the particle and fiber surfaces. The presence of a repulsive barrier, dependent on the ionic

environment, is mainly responsible for the very strong effect of ionic conditions on retention behavior.

The retention of particles on fibers by this mechanism is very similar to the mechanism responsible for flocculation of particle systems. The same types of attractive and repulsive forces operate. This is the reason the mechanism is called coflocculation. The retention process is closely analogous to a flocculation of the particles onto the fiber surface.

### Sieving

In sieving, the particles are trapped mechanically in the fiber network. It is a mechanical entrapment of particles in the three-dimensional mesh formed by the fibrous sheet. The sieving action depends almost entirely on the particle size and the internal pore structure of the sheet. Sieving occurs when the particles are too large to pass through the pores in the fiber mat.

It is difficult to define in a specific manner the region where sieving is important and where it is not. The size of the particles is the most important factor. If the particles are big enough, sieving will occur, and if the particles are small enough, sieving will be inconsequential. The dividing line between sieving and coflocculation is very nebulous. However, a particle size of about 30  $\mu\text{m}$ . may be taken as indicative of the region where sieving starts becoming important in retention in fiber mats.

### Controlling Mechanism

The controlling mechanism is determined mainly by the particle size. However, there is ample evidence to support the position that coflocculation is the dominant retention mechanism in most papermaking systems. The strong influence of colloidal variables on retention is evidence for coflocculation. This affords

at least a qualitative explanation of ionic effects. Another factor arguing against sieving for many particle systems is the relatively large pore sizes (30 to 50  $\mu\text{m}$ .) which occur in a wet, unconsolidated fiber mat. In addition, electron micrographs of retained particles show them tending to coat the fiber. This is in agreement with coflocculation.

In this report, the retention theory being considered is based on a coflocculation mechanism. This is because it is felt that coflocculation is the major mechanism. A separate theory would have to be developed for sieving because the action is entirely different. In coflocculation the mat is just a collection of fibers, but in sieving the mat structure is responsible for retention.

#### Retention Kinetics

Fundamentally, the process of particle retention is a kinetic process. Retention consists of the conversion of free particles to bound particles. This cannot take place instantaneously, and hence occurs at a finite rate. Thus, kinetics is inherent in retention.

The process of a particle becoming bound is not irreversible. The attractive forces retaining the particle can be overcome by fluid stresses or other stresses that may be present. Thus, particles can be removed as well as retained. Overall retention is, then, a net effect, and the retention rate is a net rate. In order to avoid confusion at this point, it is necessary to make some critical definitions: The absolute process by which free particles become bound will be called attachment, and the rate at which it occurs will be called the attachment rate. The absolute process by which bound particles become free will be called removal, and the rate at which it occurs will be called the removal rate. The word retention will be used to describe the net results of the competing processes, and the net rate will be called the retention rate. It should be noted

that it is the retention rate (the net rate) which can be measured by the time derivatives of the free and bound particle concentrations.

### Attachment Rate

The attachment rate can be controlled by either of two factors: particle transport from the bulk of the fluid to the fiber surface, and/or a rate process occurring at the fiber surface.

The rate nature of particle transport is easily visualized. Particles must move over to the fiber surface in order to be retained. Such movement must involve a time factor — hence, a rate. Normally, three possible methods of particle transport are considered — diffusion, interception, and impaction. Diffusion of particles is due to their Brownian motion, and becomes more intense with smaller particles. Interception is a means by which particles contact a fiber surface just by virtue of the particle size as it flows through the mat. Impaction occurs when the inertia of the particle causes it to strike the fiber rather than follow the fluid around the fiber. Impaction is favored by bigger particles. There is ample evidence that for relatively small particles (e.g.,  $\text{TiO}_2$ ) Brownian diffusion is the main mode of particle transport. Thus, if particle transport controls the attachment rate, the process will be diffusion controlled.

It is conceivable that the rate of attachment could be controlled at the fiber surface. The process could be similar to a heterogeneous chemical reaction, with the electrostatic repulsive energy barrier analogous to an activation energy. In any event, the phenomena occurring right near the fiber surface are very important. The strong effect of ionic environment on retention indicates the fiber-particle interface is controlling. It seems ridiculous to speak of attachment as being diffusion controlled when an adjustment of ionic concentration can change the

retention rate by an order of magnitude. Particle transport should control attachment when the repulsive barrier is collapsed, but not when significant repulsion exists. The only attempt to date to handle this problem assumed that the rate was diffusion controlled and that colloidal conditions determined the fraction of particles reaching the fiber surface which became attached. This method is not completely satisfactory. The concepts concerned in the action at the fiber surface are in need of further clarification.

#### Removal Rate

The kinetic nature of particle removal is more obscure than that of attachment. Bound particles are held by attractive forces and will be removed only if an external force exceeds the attractive force. The main forces tending to remove bound particles are the stresses due to the fluid motion past the fiber. Removal could also be caused by surface tension forces if an air-water interface is pulled through the sheet. It is conceivable that stresses due to relative fiber motion could remove particles.

The kinetic nature of removal probably derives from the unsteady flow inherent in flow through a porous medium. Because of the flow fluctuations, the particle is not subject to a constant stress, but rather to a time-varying local stress. There would then be a probability that the stress would exceed the attractive force leading to the removal of the particle. If this concept is applied to the large number of bound particles present in the mat, each with a certain probability of removal, the result will be a removal rate which is dependent on the amount of bound particles. The rate of removal would depend on the susceptibility of the particle to stress and on the intimacy of the fiber-particle contact. On this basis, it might be expected that large particles may be more easily removed.

The effect of ionic environment (and colloidal variables in general) on the particle removal rate is completely unknown at this time.

There is no a priori reason why there should be any relationship between the attachment rate and the removal rate. The only necessary conditions are that bound particles must be present for removal to occur, and free particles must be present for attachment to occur. Each of these rates could be affected by completely different types of variables. For example, it is conceivable that removal may be essentially independent of ionic environment.

#### COMPLEXITY OF RETENTION PROCESS

The study of the retention process is complicated by the large number of variables which affect retention. The process is simply not amenable to the vary-one-variable-at-a-time approach. This is one reason why a theory is required: to systematize all of the many variables. Among these complex factors, particle size distribution, particle self-flocculation, presence of fines, and colloidal variables will be briefly discussed. The objective is to indicate the enormity of developing a completely comprehensive retention theory and to place the present work in its proper context.

#### Particle Size Distribution

No real particle system is truly monosized. A distribution of particle sizes always exists. This can have a strong effect on retention behavior if the retention rate is dependent on particle size. There is reason to believe that particle size does influence the retention rate. Particle transport is strongly dependent on particle size. The diffusion coefficient increases as the particle size decreases. The action at the fiber surface could also be size dependent. Hence, the attachment rate could easily be size dependent. Although little is

known about the mechanics of particle removal, it is conceivable that particle size is the most important parameter affecting the removal rate.

If the retention rate is size dependent, the particle size distribution will change continuously as retention proceeds. The change would be due to the fact that particles of one size would be retained preferentially over other sizes. Since the retention rate is size dependent, the change in the particle size distribution will cause the retention rate to change. Normally, retention measurements are concerned only with the total mass of free and bound particles ( $\underline{P}$  and  $\underline{P}'$  are defined in this way) and not with the size of each particle. The effect of particle size distribution on the retention rate can then be easily confused with other variables. The problem is basically one of measurement, and the extent of the problem is dependent on the size dependence of the retention rate and the broadness of the particle size distribution. If it proves necessary to incorporate the particle size distribution into a practical retention theory, it will greatly complicate the treatment.

#### Particle Flocculation

The complicating effects of particle flocculation are dependent on the extent that particle size influences the retention rate. If the retention rate is not a strong function of particle size, flocculation will have little effect. If, however, particle size is an important parameter, flocculation can be quite significant, since it will change the size of the particles.

Flocculation of particles is inherent in the retention process. Just as the collision of a particle with the fiber can lead to retention, the collision of a particle with another particle can lead to flocculation. Because of the similar nature of the retention and flocculation processes, colloidal variables which favor retention also tend to favor flocculation. In a system where the colloidal

variables have been adjusted to obtain significant retention, flocculation will also tend to occur. The effect of flocculation will be to decrease the total number of particles and to increase the size of the individual particles. This could profoundly affect retention behavior if particle size is a significant variable.

#### Presence of Fines

The presence of fines (fiber fragments) in a retention system greatly complicates the picture. Additional degrees of freedom are introduced by the fines. The number of possibly controlling rate processes is increased. Fines can be retained by the fibers in the same manner as particles. In addition, particles can be retained on the fines. The presence of fines could lead to either an increase or a decrease in the total amount of particulate matter retained. If the particles tend to be retained by the fines, then the amount of particles eventually retained by the fibers will depend on the extent to which the fines are retained. It is also possible that particles and fines compete for the available fiber surface area. Because of the additional processes which can occur when fines are present, the distribution of particles in the sheet can be greatly affected. The effect of fines is a major component of the effect of beating on retention. This effect must be taken into account in any practical retention theory since fines are always present on the paper machine to a greater or lesser extent.

#### Colloidal Variables

Colloidal variables are of enormous practical importance in retention. They can affect the rate of retention by at least an order of magnitude. Among the important colloidal variables are: ionic concentration, ion valence, pH, and the use of polymeric retention aids. Because of the very strong effect these variables can have on the retention rate, extreme care must be used to fix the colloidal variables when studying the influence of other variables. The influence

of colloidal variables has so far been approached mainly through the theories of lyophobic and lyophilic colloidal systems. However, a need exists to integrate these variables into the retention process through their influence on the retention rate.

#### CONTINUITY CONSIDERATIONS

Although the retention rate is the fundamental quantity in retention theory, it is the principle of continuity which permits the quantitative description of macroscopic retention phenomena. Continuity equations arise from the application of conservation of mass to the fiber-water-particle system. Separate, differential mass balances are made on the water, the fiber, the free particles, and the bound particles. Combining these four balances yields a pair of retention equations. These retention equations are partial differential equations relating free and bound particle concentrations through the retention rate. They thus provide a quantitative relationship between observable phenomena and the fundamental retention rate.

There are very few restrictions on the validity of the retention equations in their general form. The most serious assumption involved is the treatment of a mat of discrete fibers as a continuum with distinct boundaries. This is a time-honored assumption in the treatment of porous media. It is a valid approach if the area of the mat under consideration is large enough that a great many fibers are involved. The distinction of free and bound particles as the only allowable particle states and the treatment of retention as a kinetic process are very reasonable assumptions.

Retention Equations

A derivation of the retention equations is given in Appendix I. The four differential material balances are carried out in a fixed coordinate system. The fluid and fiber equations are then incorporated into the free and bound particle equations. The resulting equations are then transformed into a coordinate system based on the mat. This yields the following retention equations for free and bound particles, respectively.

$$-\rho_w A \left[ U_o - \frac{U_f}{(1 - \epsilon)} + \frac{\epsilon}{(1 - \epsilon)} \frac{s \rho_w U_o}{(\rho_f + s \rho_w)} \right] \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f (1 - \epsilon)} \frac{\partial P}{\partial t} + \varphi \quad (1)$$

and

$$\frac{s \rho_w \rho_f A U_o}{(\rho_f + s \rho_w)} \frac{\partial P'}{\partial m} + \frac{\partial P'}{\partial t} = \varphi \quad (2)$$

where:

- $\underline{P}$  = free particle concentration, mass free particles per unit mass of fluid,
- $\underline{P}'$  = bound particle concentration, mass bound particles per unit mass of fiber,
- $\underline{\rho}_w$  = fluid density,
- $\underline{\rho}_f$  = fiber density,
- $\underline{s}$  = consistency, mass of fibers per unit mass of fluid,
- $\underline{A}$  = area of mat,
- $\underline{m}$  = fiber mass-mat coordinate,
- $\underline{t}$  = time,
- $\underline{U}_o$  = forming velocity,
- $\underline{U}_f$  = fiber flux, superficial fiber velocity, and
- $\varphi$  = retention rate,  $\text{time}^{-1}$ .

The retention rate,  $\varphi$ , is defined as the net mass rate of free particles becoming bound per unit mass of fibers. The dimensions of  $\varphi$  are mass of particles per unit time per unit mass of fibers. This retention rate is the fundamental quantity in retention theory.

The fiber mass coordinate,  $\underline{m}$ , appears to be the most useful coordinate for describing retention behavior. It is defined by

$$m = \rho_f A \int_z^L (1 - \epsilon) dz = \rho_f A \int_0^L (1 - \epsilon) dz - \rho_f A \int_0^z (1 - \epsilon) dz' \quad (3)$$

where  $\underline{z}$  is a position coordinate measured up from the septum and  $\underline{L}$  defines the position of the mat surface. It is clear from Equation (3) that  $\underline{m}$  represents a cumulative fiber mass measured from the mat surface. The zero value of  $\underline{m}$  is at the mat surface.

There are several reasons why this coordinate is useful. First of all, it is an easily measured quantity. The fiber mat can be delaminated and the mass of fibers in each individual layer can be determined. Sequential addition of the mass of each layer, starting with the side opposite the forming wire, will generate a series of increasing values of  $\underline{m}$ . A second reason is that the boundary conditions on the retention process occur at the mat surface,  $\underline{m} = 0$ . This is due to the fact that the conditions at the mat surface are the same as the conditions in the suspension from which the sheet is formed. Another important reason for using the fiber mass coordinate system is that it eliminates most compressibility effects. Fiber mats are in general compressible, leading to a great difficulty in relating a given quantity of fibers to a fixed reference frame. The fiber mass coordinate eliminates this problem by describing retention in terms of discrete fiber layers. There remains only a relatively weak dependence on  $\epsilon$  and  $\underline{U}_f$  in the free particle equation

and the possible dependence of the retention rate on porosity as compressibility effects. Another reason for choosing the  $\underline{m}$  coordinate is the very simple form taken by the bound particle equation. The entire coefficient of  $\partial \underline{P}' / \partial \underline{m}$  is constant except for the possible time dependence of  $\underline{U}_0$ .

The retention equations [(1) and (2)] are coupled partial differential equations, first order in each of two independent variables. Boundary conditions on these equations (and on the retention process) would normally be set at  $\underline{m} = 0$  (the mat surface) and at  $\underline{t} = 0$  (start of the process). The coupling between the two equations occurs through the retention rate. In order to get a solution, the dependence of  $\varphi$  on  $\underline{P}$  and  $\underline{P}'$  must be known. The equations are quite complex, and simplifications must be made to obtain analytical solutions. Equations of the type of these retention equations have the property of allowing so-called continuity waves. These are such that disturbances at  $\underline{m} = 0$  will tend to propagate through the mat at a rate given by the ratio of the time derivative coefficient to the  $\underline{m}$  derivative coefficient. If the conditions at  $\underline{m} = 0$  are steady, the time derivatives can often be neglected.

#### Significance of Retention Equations

The retention equations provide a quantitative relationship between the free and bound particle distributions in the mat and the retention rate. Both the time dependence and the spatial ( $\underline{m}$ ) dependence are accounted for. If the retention rate is known, the distribution of particles in the mat can be predicted. This procedure can also be reversed. The retention rate can be calculated from measurements of the particle distribution.

By using the quantitative retention equations, it becomes feasible to analyze the final particle distribution in a mat so as to extract information about the retention rate. Thus, the rate equations provide a means whereby the final

amount and distribution of particles retained in a mat can be reduced to the more fundamental parameter, the retention rate. This can be very useful in studying retention. A detailed discussion of this method of analyzing retention data and the results of applying it to experimental data are presented later in this report.

The insight into the retention process gained from the retention equations and from their derivation is quite significant. It is an obvious fact that particles which are not caught in a given layer must pass on into succeeding layers (higher values of  $m$ ). The consequences of this fact (quantitatively treated in the retention equations) are often not appreciated by workers in the retention field. For example, Groën (1), discussing the retention process in the system water/fiber/filler, gives the following qualitative explanation for the distribution of particles:

"The self-filtration of this three-phase system, containing two solid phases of entirely different size and shape, will at any rate result in an uneven final distribution. In the first stage of drainage, the filter mat is formed only by the wire, with coarse openings compared with the particle size of the solid phases and especially with that of the loading material. Consequently, the first hypothetical layer will be relatively poor in filler particles. The next layer contains somewhat more filler, because now an open layer of fibers takes the place of the wire as the filter medium. During continued drainage, subsequent layers will be built up, steadily increasing in filler content. The loading material acts as a filter aid in plugging the pores, as do small particles when filtering on filter paper. The top layer will contain less loading, however, because the filler particles are retained not by this layer, but by the next one. The resulting theoretical filler distribution will show a maximum, with a decrease toward the top side and a somewhat larger decrease toward the wire side."

This must be taken as a qualitative description of retention by a sieving process. However, the statement shows a disregard for the effects of continuity, particularly as to what must happen to the particles which are not retained by a given layer. Groën's description considers the action at some particular layer being formed, essentially independent of what must take place in the layers between that just being formed and the wire. These other layers must be continuously permeated by the particles not retained by the layer above them. Thus, retention can go on continuously throughout the mat during the whole sheet-forming process. Retention by coflocculation could occur even before the mat is formed. When it is considered that the drainage forces will lead to a decrease in porosity toward the wire side, a qualitative argument using a modification of Groën's argument could easily lead to the conclusion that "theoretically" the particle distribution should increase continuously toward the wire side. Groën's description can be valid only if the middle layers of the sheet retain essentially all of the particles available to them.

The point of this discussion is that qualitative arguments are unsatisfactory and unnecessary. The retention equations make it possible to test hypotheses about retention quantitatively. Any theory concerning retention mechanism or phenomenon should be expressed quantitatively, and the particle distributions predicted by the retention equations checked with experimental measurements.

#### SPECIAL SOLUTIONS TO EQUATIONS

Exact solutions to the retention equations can be obtained in certain special cases. These special cases involve two factors: the specification of a prescribed manner for carrying out the process, and an assumption about the retention rate. Three special cases will be considered here.

1. A constant-rate permeation with the retention rate first order in free particle concentration.
2. A constant-rate filtration with the retention rate first order in free particle concentration.
3. A constant-rate filtration with the attachment rate first order in free particle concentration and the removal rate first order in bound particle concentration.

Details of the solutions are given in Appendix II.

### Permeation

The first case is for a constant-rate permeation with the retention rate taken to be first order in free particle concentration. In a permeation, the mat is formed in the absence of particles, and a particle suspension is then passed through the mat. In a permeation, the retention process is divorced from the sheet-forming process. In a constant-rate permeation, the particle suspension passes through the pad at a constant velocity. The retention rate is assumed to be given by

$$\varphi = K_R SP \quad (4)$$

where:

$\frac{K_R}{\rho_w}$  = retention-rate constant, and  
 $\underline{S}$  = specific surface of the fiber.

The solution to this case is

$$P = P_o e^{-K_R Sm / \rho_w AU_o} \quad (5)$$

and

$$P' = K_R SP_o t e^{-K_R Sm / \rho_w AU_o} \quad (6)$$

where  $P_0$  is the concentration of particles in suspension. The distribution of both free and bound particles is exponential in this case. Both free and bound particles have their maximum value at the mat surface and decrease away from the surface according to the same exponential function. At any given  $m$  (a fixed fiber layer), the bound particle concentration increases linearly with time. The distribution of bound particles is due entirely to (and is identical with) the free particle concentration. The free particle distribution is the consequence of the first-order retention rate and particle conservation.

Equation (6) can be rewritten as

$$\ln P' = \ln K_R SP_0 t - \frac{K_R Sm}{\rho_w AU_0} \quad (7).$$

Thus, a plot of  $\ln P'$  vs.  $m$  should give a straight line. The value of the retention-rate constant,  $K_R$ , can be computed both from the slope and from the intercept. These two values must agree if the special solution is applicable.

### Collection Efficiency

In earlier work (2, 3), the concept of collection efficiency was often used in describing retention behavior. This concept was borrowed from the field of aerosol filtration and related the collection of particles to the motion of the particle. It was primarily a means of handling particle transport. The collection efficiency was initially defined as the fraction of particles approaching a fiber through a cross section equal to the fiber projected area which were caught by the fiber. This concept was then generalized to fiber mats. The concept of collision efficiency is most useful if retention is controlled by particle transport and if the retention rate is simple first order with respect to free particles. In this case, the relationship between the collection efficiency,  $e$ , and the retention rate constant,  $K_R$ , is given by

$$E = \frac{K_R}{\rho_w U_o} \quad (8).$$

This equation can be used to calculate the collection efficiency from rate constants and vice versa. It can be useful in comparing the results of this study with earlier work. The collection efficiency concept is severely restricting when the retention rate is not simple first order in free particles. This assumption is basic to the collection efficiency. Because of this fact, the collection efficiency is not used in interpreting data in this study. The general retention rate,  $\varphi$ , is taken as fundamental and then reduced to components. If the rate is simple first order in free particles, the rate constant,  $\underline{K_R}$ , is used to correlate data in preference to  $\underline{E}$ . It is felt that this procedure brings out more clearly the rate nature of the process.

#### Filtration

In a filtration, the mat is formed from a suspension of particles and fibers. The retention process occurs simultaneously with the sheet-forming process. Thus, retention and sheet forming are coupled. In a constant-rate filtration, the mat is formed at a constant rate, that is, the suspension flows toward the forming wire at a constant velocity. When the retention rate is given by Equation (4), the solution of the retention equations is

$$P = P_o e^{-K_R S m / \rho_w A U_o} \quad (9),$$

$$P' = P'_o + \frac{P_o}{s} \left( 1 - e^{-K_R S m / \rho_w A U_o} \right) \quad (10),$$

and

$$sP' + P = P_o + sP' = sP_{oo} \quad (11),$$

where

$\underline{P}'_o$  = bound particle concentration in the suspension, and

$\underline{P}_{oo}$  = total particle concentration in the suspension, mass particles per mass fiber.

It is immediately evident that the free particle distribution is the same in a filtration as it is in the permeation. Thus, the free particles cannot differentiate between a filtration and a permeation. This is not surprising. The retention rate was assumed to depend only on the free particle concentration, and the concentration of free particles at the mat surface is fixed at  $P_0$ . The same factors govern the free particle distribution in a filtration as in a permeation.

The bound particle distribution is very different for a constant-rate filtration than it is for a permeation. In the filtration, the bound particle concentration increases toward the wire side, while the opposite is true of the permeation. This is a direct consequence of the simultaneous retention and mat-forming processes. The layers of the mat which are formed first (highest  $m$ ) have the greatest amount of particles passing through them since all unretained particles must pass through the mat. This process tends to cause the bound particle concentration to increase toward the wire side. As the mat becomes thicker and more of the particles are retained in the upper portions of the mat, the decrease in free particle concentration tends to level off the bound particle concentration. For the case considered here ( $\phi = \frac{K_R SP}{P_0}$ ), the bound particle concentration rises toward the wire and asymptotically approaches the concentration where all particles are retained,  $P_{\infty}$ .

In the filtration, a bound particle concentration boundary condition,  $P'_0$ , must be introduced. This is due to the fact that in the filtration, particles and fibers can contact each other in the suspension leading to retention before the mat is formed. This is normally called prepad retention.

In the special case considered here, time does not appear directly in the solutions of the retention equations. This is because the coordinate  $m$  implicitly

accounts for the fact that one fiber layer is laid down before other layers. A fixed value of  $\underline{m}$  is always so far away from the mat surface. If the conditions in the suspension remain constant during the filtration process and the retention rate (at a given  $\underline{m}$ ) remains constant, the solutions are time independent. This is true only for constant-rate filtrations. If the forming velocity varies, time becomes a direct factor in the equations.

Equation (11) has a good deal of significance. It states that at any given layer in the mat the sum of the free and bound particle concentrations, when put on a common basis, is equal to the total concentration of particles in the suspension. It thus provides a simple relationship between the free and bound particles. It will tend to hold true in the time-dependent case if the time changes occur slowly compared to the time of transit through mat and if the retention rate is a continuous function of  $\underline{P}$  and  $\underline{P}'$ .

If removal is allowed in addition to attachment, the simplest possible function for the retention rate is

$$\varphi = K_A S P - K_D P' \quad (12).$$

With this retention rate function applying to a constant-rate filtration, the solution for the bound particle concentration is

$$P' = P'_o + \frac{(K_A S P_o - K_D P'_o)}{(sK_A S + K_D)} \left[ 1 - e^{-\frac{(sK_A S + K_D)m}{s\rho_w AU_o}} \right] \quad (13)$$

or

$$P' = P'_o + (P'_{eq.} - P'_o) \left[ 1 - e^{-\frac{(sK_A S' + K_D)m}{s\rho_w AU_o}} \right] \quad (14)$$

with

$$P'_{eq.} = \frac{K_A S (P_o + sP'_o)}{sK_A S + K_D} = \frac{sK_A S P_{oo}}{sK_A S + K_D} \quad (15).$$

The form of the bound particle distribution is identical to that for the filtration case discussed previously. The bound particle concentration is lowest at the mat surface and rises toward the wire. The concentration asymptotically approaches an equilibrium bound particle concentration where the rate of attachment just equals the rate of removal. It is important to note that the addition or removal does not lead to a maximum bound particle concentration internally in the mat. It could be shown that any removal rate which is simply power law dependent on  $P'$  will not yield an internal maximum. If the bound particle concentration shows a maximum other than right at the wire for a constant-rate filtration, it implies a complex type of removal function.

#### Use of Exact Solutions

The cases for which exact solutions are known are quite different from the action on the paper machine, and the results are not directly useful. In particular, large differences can be expected between a variable-rate filtration and a constant-rate filtration. The main function of the exact solutions is the insight they provide. The particle distributions predicted by these simple cases provide a basis for interpreting deviations found in experiments. For example, when particle distributions for constant-rate filtrations show internal maxima, it is known that the removal rate is not a simple function. A secondary use of the exact solutions is a means of correlating experimental data on parameters affecting retention, for example, correlating  $\frac{K}{R}$  as a function of forming velocity.

## PARTICLE DISTRIBUTION

### MEASUREMENT

The distribution of particles in a sheet is given by  $\underline{P}'(\underline{m})$ , the dependency of the bound particle concentration on position in the pad. A particle distribution curve is a plot of  $\underline{P}'$  vs.  $\underline{m}$ . In order to experimentally determine a particle distribution curve, it is necessary to measure  $\underline{P}'$  at various values of  $\underline{m}$ . The measurement of the bound particle concentration is based on the mathematical treatment of the bound particle concentration as a continuous function.

Thus,

$$\underline{P}' = \lim_{\Delta m \rightarrow 0} \Delta T / \Delta m \quad (16)$$

where  $\Delta T$  is the mass of particles in an incremental layer and  $\Delta m$  is the mass of fibers in the layer. Measurement of  $\underline{P}'$  and  $\underline{m}$  by this definition is completely compatible with the use of  $\underline{P}'$  and  $\underline{m}$  in the retention equations discussed previously. The coordinate,  $\underline{m}$ , is identical to that used in the retention equation and is measured from the mat surface.

The actual measurement of a particle distribution curve begins with the delamination of a fiber mat. The sheet is split into layers, and the content of particles and fiber in each layer determined. Ordering of the layers is necessary for the determination of  $\underline{m}$ . Many techniques have been used to delaminate fiber sheets. Razor blades, abrasive paper, adhesive tape, and microtomes have been used on dry paper. Groën (1) used an adhesive tape technique. In this project, where wet mats were used, the Beloit sheet splitter and a hand technique assisted by dissecting needles was used to delaminate the pads. In the earlier work on this project (3), the Beloit sheet splitter was used. In the most recent studies,

relatively thick pads ( $\approx 1000 \text{ g./m.}^2$ ) were made and split by hand. This was done so as to get a larger number of points per pad in order to more closely determine the distribution curve.

In this study,  $\text{TiO}_2$  was used as the particle, and a bleached softwood sulfite pulp was used as the fiber. Characterization of pulp and particle as well as the analytical methods for determining fiber and particle content of the layers are described in detail in the previous report (3). An approximation technique was used to convert the incremental pad data into a particle distribution curve.

The ratio of particle mass to fiber mass in a layer represent an average bound particle concentration over that interval.

$$\frac{\Delta T}{\Delta m} = \frac{1}{m_2 - m_1} \int_{m_1}^{m_2} P' dm = \overline{P'} \quad (17).$$

By the law of the mean,  $\overline{P'}$  must take on the value  $\overline{P'}$  somewhere in the interval between  $m_1$  and  $m_2$ , since  $\overline{P'}$  is a continuous function of  $m$ . If  $\overline{P'}$  is a linear function of  $m$ , then  $\overline{P'} = \overline{P'}$  halfway in the interval or  $\overline{P'} = \overline{P'}$  at  $m = m_1 + (m_2 - m_1)/2$ . If  $\overline{P'}$  is not linear, the critical  $m$  will be shifted from the midpoint. The raw experimental data can be easily converted into a layer average bound particle concentration by taking the particle-to-fiber ratio. The two values  $m_1$  and  $m_2$  are, respectively, computed as the cumulative mass of fibers up to the layer, and the cumulative mass of fibers including the layer, starting from the top surface of the mat.

The basic data provide  $\overline{P'}$  and limits on  $m$  ( $m_1$  and  $m_2$ ) between which  $\overline{P'} = \overline{P'}$  at some point. The determination of the particle distribution,  $\overline{P'}$  vs.  $m$ , from these data involves selecting the value of  $m$  for which  $\overline{P'} = \overline{P'}$ . The value

of the critical  $\underline{m}$  depends on the functional dependence of  $\underline{P}'$  on  $\underline{m}$ , which is, of course, unknown. The procedure which was adopted is as follows. As a first approximation, the critical  $\underline{m}$  was taken halfway in each increment, and a set of points of  $\underline{P}' - \underline{m}$  were computed. As a next step, a quadratic was fitted to each point through its two neighboring points, and the critical  $\underline{m}$  adjusted accordingly. This procedure was continued until there was no further significant change in the value of  $\underline{m}$ . Details of this procedure are given in Appendix III.

#### DISTRIBUTION ON A PAPER MACHINE

The most extensive study of the distribution of particles in sheets formed by various methods was made by Groën (1). He was primarily interested in paper made on fourdrinier machines, but also examined handsheets and papers made on cylinder machines. Papers chosen were made from bleached and unbleached pulp with groundwood content varying from 0 to 70%. Total filler content of the sheets ranged from 8 to 30%. Different grades of china clay, talc, and anhydrous gypsum were used as fillers. The particle size varied from about 1  $\mu\text{m}$ . to 25  $\mu\text{m}$ .

Groën found that on fourdrinier-made paper the top side of the sheet was richer in particles than the wire side. This confirmed the results of most earlier investigators. The general form of the distribution was as follows: The bound particle concentration was lowest in the extreme wire side layer. Proceeding toward the top side, the bound particle concentration increased rapidly at first and then more slowly. A relatively horizontal distribution could exist through much of the mat. A slight increase sometimes occurred on the top side. The inflection point (the location in the mat where the sharp decrease in concentration toward the wire side commenced) was found to be a function of machine speed. Use of a dandy roll could lead to a slight enrichment of the top section of the sheet.

The general forms of the distribution curves found by Groën are shown in Fig. 1. The effect of the dandy roll and machine speed are presented in this figure. A discussion of these distribution curves in the light of our present understanding of the retention process will be made later in this report. It is of interest that on a cylinder machine paper and in handsheets the distributions were reversed from those of the fourdrinier and the wire side was richer in particles.

#### INTERPRETATION OF DISTRIBUTION CURVES

The final distribution of particles in the sheet represents the net result of competing rate processes (attachment and removal) during the retention and sheet-forming processes. This follows directly from the retention equations which relate time and space changes in  $\underline{P}$  and  $\underline{P}'$  to the retention rate,  $\varphi$ . In general,  $\varphi$  is a function of  $\underline{m}$  and  $\underline{t}$  ( $\underline{P}$  and  $\underline{P}'$  are functions of  $\underline{m}$  and  $\underline{t}$ ), and the final resultant distribution of particles is integrally related to the rate. The final partial distribution is obtained from integrals of the rate function.

The final bound particle distribution gives  $\underline{P}'$  as a function of  $\underline{m}$  at a particular time,  $\underline{t}$ , the total time over which the retention process was carried out. The objective is to use the final distribution to obtain information about  $\varphi$ . The exact form of the relationship between the final particle distribution and  $\varphi$  is dependent on the process during which retention occurred. Among these processes are permeations, constant-rate filtrations, falling-rate filtrations, sheet formation on a fourdrinier, and many others. With each process, the relation between  $\varphi$  and the final distribution will be different. This is due to the interaction between retention and sheet forming caused by continuity and the relative importance of different terms in the retention equations.

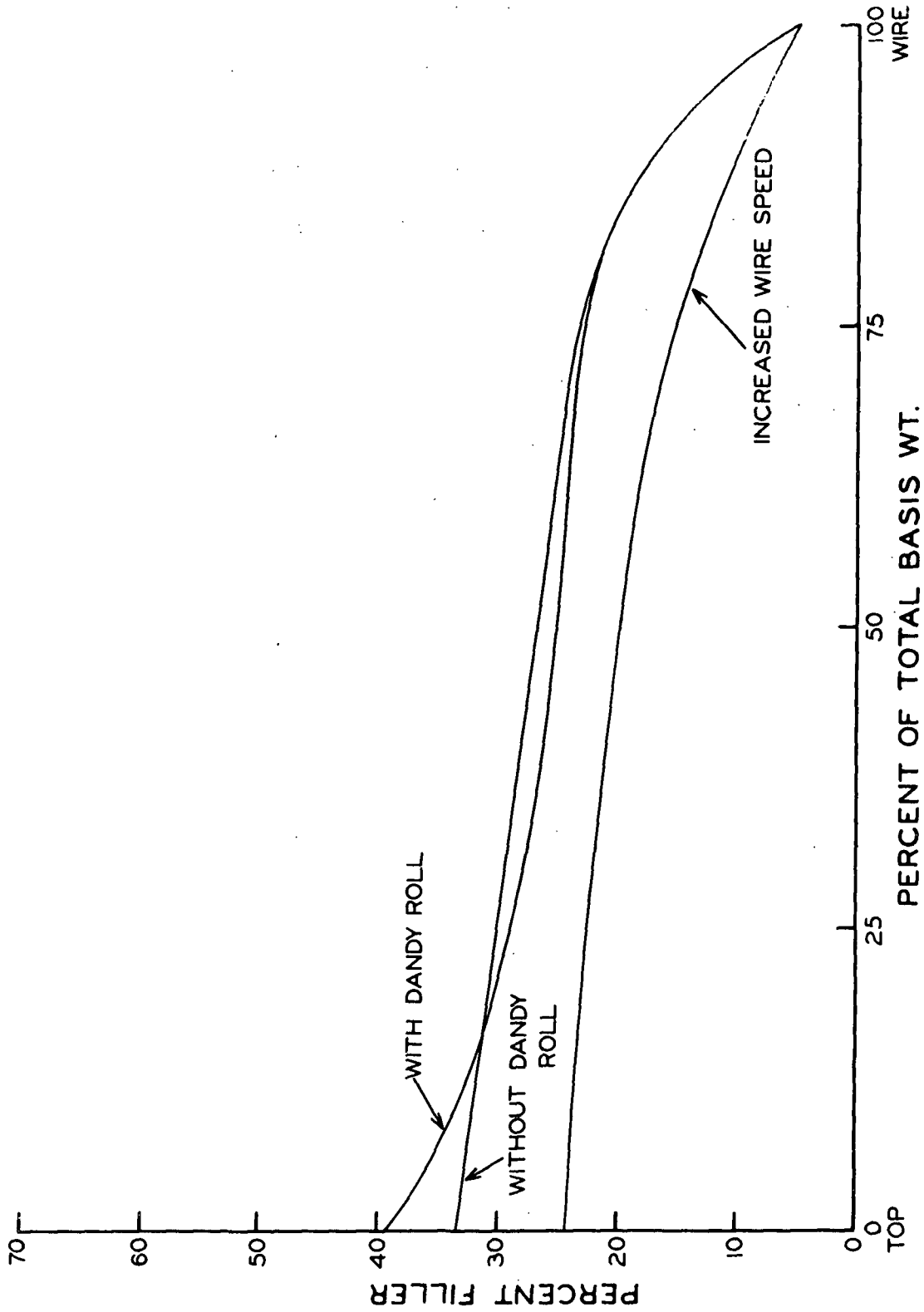


Figure 1. Typical Distribution Curves According to Groën

The relationship between the final distribution and  $\varphi$  is simplest for constant-rate permeation and filtrations. It is especially straightforward for constant-rate filtrations. Thus, these types of experiments provide a means of getting at the fundamentals of particle retention. They are highly suitable for studying the effects of certain parameters on the retention rate. In the next section, a technique for determining  $\varphi$  from bound particle distribution data is developed, and the results of the application of this technique to some experimental data are presented.

## RETENTION RATE ANALYSIS

### CONSTANT-RATE FILTRATIONS

In a constant-rate filtration, the pad is formed at a constant rate from a suspension of fibers and particles. Retention occurs simultaneously with pad formation. There is no control over the porosity in a filtration. The porosity distribution in the pad is determined by the fluid drag forces and by the compressibility of the pulp. The filtration is carried out for a length of time sufficient to form a pad of desired thickness. The pad is then removed and the particle distribution determined.

Four pads, designated 1-4, were formed and their particle distributions analyzed to determine the retention rate. Pads 1 and 2 were formed from a suspension containing classified fibers and  $\text{TiO}_2$  particles, while Pads 3 and 4 were formed from a suspension containing classified fibers, fines prepared from the same fiber, and  $\text{TiO}_2$  particles. The method of fines preparation will be discussed later, when the effect of fines on retention is discussed.

For Pads 1 and 2, the suspension was made up as follows. One hundred liters of distilled water were deaerated by bringing to a boil and then cooling. Then 4.85 g. of reagent-grade NaCl ( $8.3 \times 10^{-4} \text{M}$ ) were added and the pH adjusted to 5.0 with HCl. Ten grams o.d. of classified fiber were deaerated under vacuum, dispersed, and added to the tank. The consistency of the suspension was 0.01%. When the suspension was ready, 0.50 g. of dispersed  $\text{TiO}_2$  from a concentrated suspension was added. Fifteen minutes after the  $\text{TiO}_2$  was added, the filtration was initiated. The tank was stirred continuously during the process of making up the suspension as well as during the filtration.

For Pads 3 and 4, the suspension was made up in the same way as for 1 and 2 except that 0.25 g. o.d. of fines was added just before the  $\text{TiO}_2$  was introduced. The filtration was initiated 15 minutes after the  $\text{TiO}_2$  was put in.

The pads were formed at a constant velocity of 1 cm./sec. Since the pads were 3 inches in diameter (inside diameter of forming tube), a volume flow rate of 45.6 cc./sec. was maintained. The flow rate was measured with a rotameter downstream of the septum. The pressure drop across the pad was measured with a variable reluctance transducer and was continuously recorded on a strip chart. The filtrations were carried out long enough to allow build-up of a pad containing about 5 g. o.d. of fiber. After this time, flow was stopped and the slurry remaining above the pad was siphoned off without disturbing the mat. The residual slurry was then drained very carefully through the mat, and the mat was then removed from the tube. The pad was then split by hand (dissecting needles were used to start the delamination and then the layer was simply peeled off by hand) and the content of  $\text{TiO}_2$  and fiber in each layer was measured. Bound particle distribution curves were determined by the method discussed previously.

#### Filtration-Rate-Analysis Equations

For a constant-rate filtration, the retention equations become

$$-\rho_w AU_o \frac{dP}{dm} = \varphi \quad (18)$$

$$\rho_w sAU_o \frac{dP'}{dm} = \varphi \quad (19).$$

The time independence of these equations is unique to the constant-rate filtration. The reasons for this time independence are discussed in Appendix II. Essentially, it is due to the choice of coordinate  $\underline{m}$ . In a filtration,  $\underline{m}$  does not correspond to a distinct fiber layer, but floats from layer to layer as time proceeds. At a

fixed  $m$ , one is always at a certain position with respect to the surface, and thus, at a fixed state in the forming and retention processes. As long as the conditions in the suspension are constant and the rate is time independent, the equations are time independent.

Equation (19) gives a direct, measurable relationship between  $\varphi$  and the final bound particle distribution. The retention rate,  $\varphi$ , is directly proportional to the slope of the distribution curve. The relationship between free and bound particle concentrations is obtained by combining Equations (18) and (19):

$$\frac{\partial}{\partial m} (P + sP') = 0 \quad (20).$$

Thus,

$$P + sP' = P_{\infty} + sP'_{\infty} = sP'_{\infty} \quad (21).$$

Equation (21) provides a means for determining the free particle distribution from the bound particle distribution. Thus, all of the necessary quantities -  $P'$ ,  $P$ , and  $\varphi$  - are readily determined from the final bound particle distribution in a constant-rate filtration.

From physical arguments, it is reasonable to suppose that the rate is first order with respect to free particle concentration. This is the basic assumption in the collection efficiency approach, which has been used in earlier studies of retention. If the retention rate is simply first order in  $P$ , then the ratio  $\varphi/P$  should be constant. Hence,  $\varphi/P$  is an excellent test of the collection efficiency concept and is also useful for a more penetrating look at retention. Combining Equations (18) and (21),

$$\frac{\varphi}{P} = \frac{\rho_w AU_{\infty} (dP'/dm)}{P_{\infty} - P'} \quad (22).$$

A program for computing  $\phi/\underline{P}$  from the bound particle distribution using Equation (22) was developed and is described in Appendix IV.

### Results of Filtration Rate Analysis

The bound particle distribution data for Pads 1-4 are presented in Table I. Values of  $\phi/\underline{P}$  computed from Equation (22) are presented in Table II along with  $\underline{m}$  and  $\underline{P}'$  for each pad. Figures 2 and 3 show  $\phi/\underline{P}$  plotted vs.  $\underline{m}$  for Pads 1-2 and 3-4, respectively. Figures 4 and 5 show  $\phi/\underline{P}$  plotted vs.  $\underline{P}'$  for Pads 1-2 and 3-4, respectively.

In comparing these curves, it is obvious that  $\phi/\underline{P}$  for Pads 3 and 4 is greater than the values for Pads 1 and 2. This is undoubtedly due to the presence of fines in Pads 3 and 4. The fines tended to increase the rate of retention in this case. The specific effect of fines will be looked at in more detail later.

Even with the presence of fines in two pads, the shapes of the curves are very similar for all four pads, both plotted against  $\underline{m}$  and against  $\underline{P}'$ . It is very obvious that  $\phi/\underline{P}$  is not constant and that the retention process is not simple first order in  $\underline{P}$  with all other factors constant. All four pads have the same basic  $\phi/\underline{P}$  curves.  $\phi/\underline{P}$  initially starts to decrease and goes through a minimum, then rises and goes through a maximum (higher than the initial value), and then drops very sharply on the wire side. The rise is significant; in Pad 4 the maximum rate is twice the localized minimum. The large drop in rate is very likely due to removal. The drop is very steep when  $\phi/\underline{P}$  is plotted vs.  $\underline{P}'$ . Interestingly, all four pads showed the drop at about the same value of  $\underline{P}'$ .

There are three main features to the  $\phi/\underline{P}'$  vs.  $\underline{P}'$  plots, which will be discussed in the order of their significance. The most important feature is the very sharp drop in the retention rate at the highest values of bound particle

TABLE I

BOUND PARTICLE DISTRIBUTION DATA FOR PADS 1-4

Pad 1		Pad 2		Pad 3		Pad 4	
$P' \times 10^3$	$\underline{m}$ , mg.	$P' \times 10^3$	$\underline{m}$ , mg.	$P' \times 10^3$	$\underline{m}$ , mg.	$P' \times 10^3$	$\underline{m}$ , mg.
3.27	132.5	3.02	199.2	3.39	194.4	2.90	155.5
5.53	375.3	5.30	514.8	7.48	561.6	7.84	551.0
8.39	660.3	8.29	861.9	12.59	989.6	11.88	921.6
10.62	913.1	11.95	1308.0	16.57	1397.1	15.43	1223.6
12.86	1136.3	14.80	1680.1	19.02	1655.2	17.52	1454.2
18.18	1650.6	16.75	1933.8	21.85	1904.3	18.70	1597.7
21.28	2158.6	19.07	2247.3	23.73	2146.8	21.87	1848.2
23.93	2635.5	21.71	2586.6	26.08	2357.6	24.33	2115.4
29.77	3083.1	24.26	2884.2	29.26	2680.4	27.03	2367.5
31.33	3304.9	26.28	3172.8	32.10	3038.6	30.22	2672.5
33.25	3567.9	28.09	3429.2	32.88	3250.4	33.35	2980.4
33.63	3837.4	30.15	3726.2	35.04	3438.2	34.52	3208.8
32.80	4107.2	31.00	3992.2	36.54	3700.1	36.63	3429.8
36.54	4394.2	32.68	4237.1	35.37	3924.2	38.13	3667.3
32.49	4667.1	32.66	4619.3			37.17	3855.8



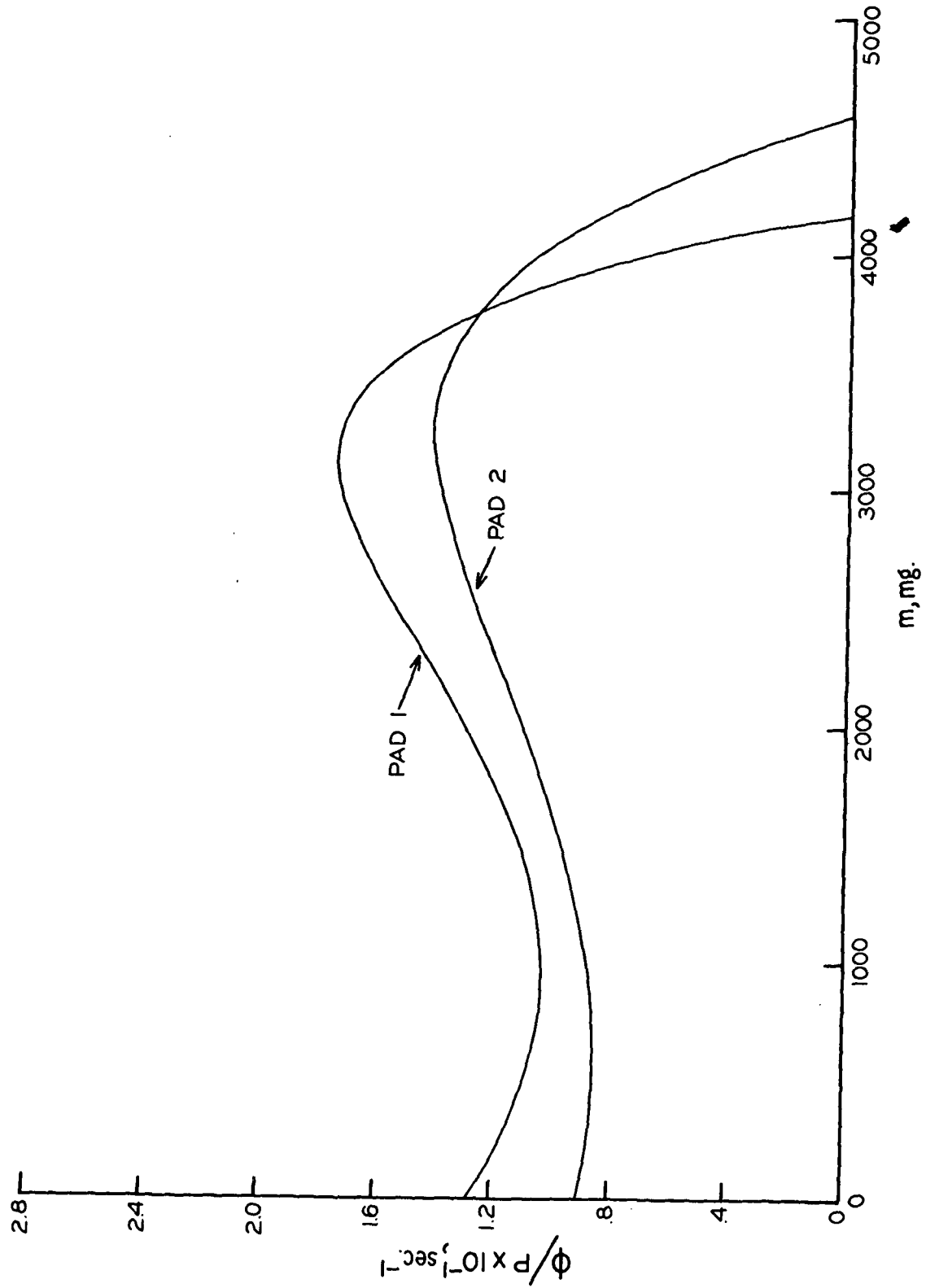


Figure 2.  $\phi/P$  vs.  $m$  for Pads 1 and 2

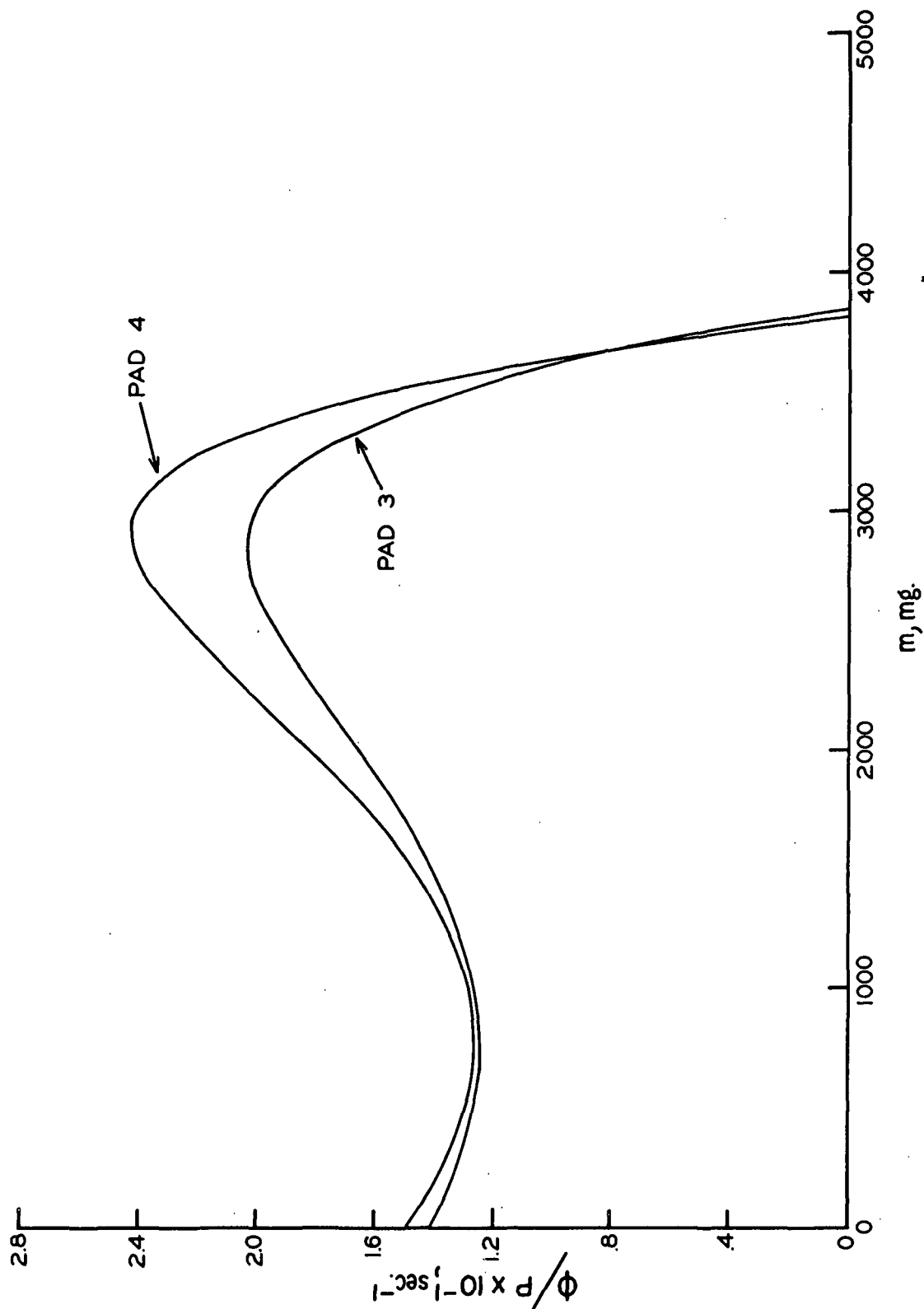


Figure 3.  $\phi/P$  vs.  $m$  for Pads 3 and 4

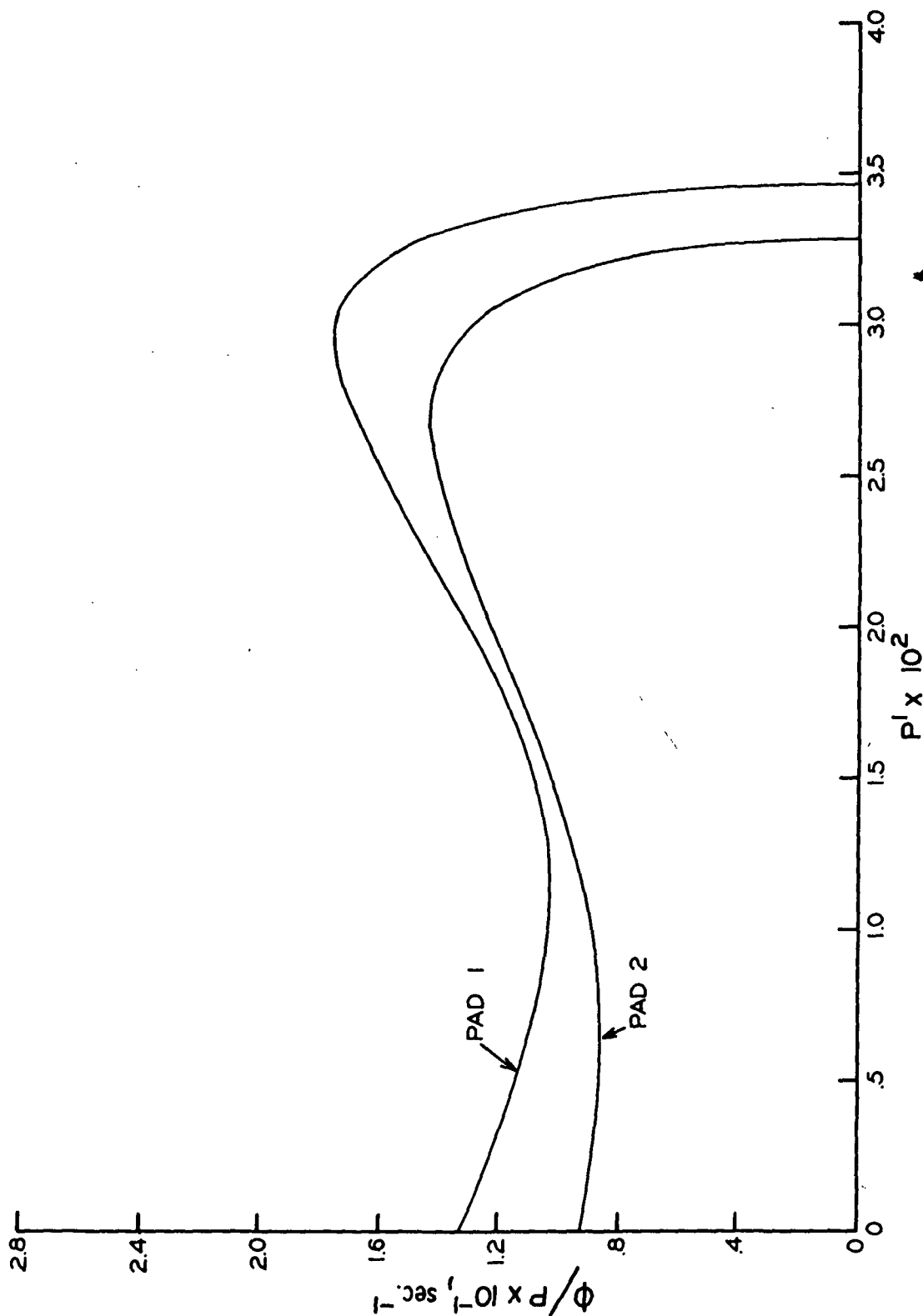


Figure 4.  $\phi/P$  vs.  $P'$  for Pads 1 and 2

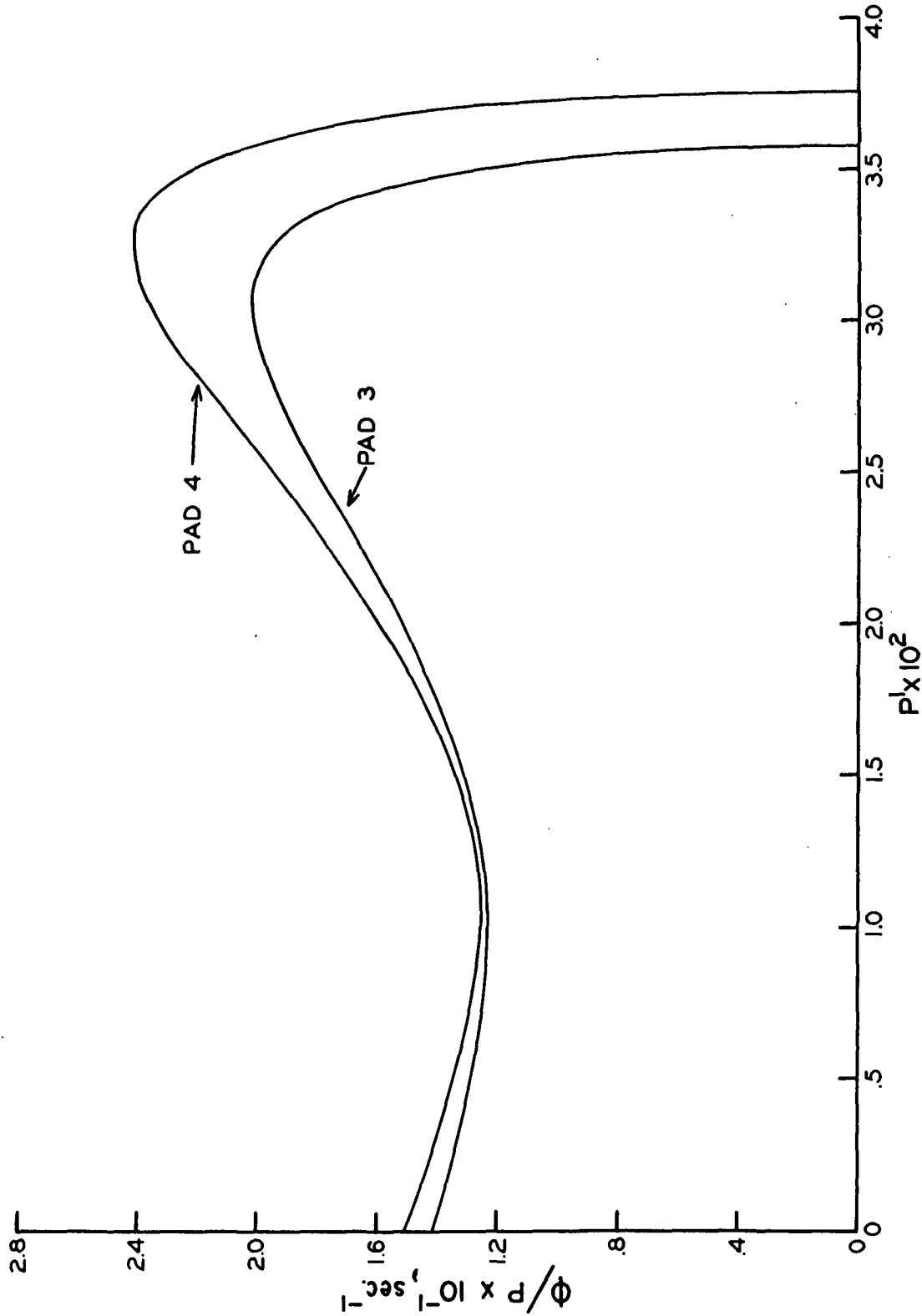


Figure 5.  $\phi/P$  vs.  $P$  for Pads 3 and 4

concentration. This is undoubtedly due to particle removal in this part of the mat. Removal apparently becomes important only when a certain bound particle concentration is reached. It is significant that this "critical" concentration is about the same for all four pads. This would indicate that the factors which govern removal were held constant in all four pads. This sudden onset of particle removal is directly related to the so-called saturation phenomenon which was observed in earlier studies (2). In order to illustrate the effect of this sudden onset of removal on the bound particle concentration, the bound particle distribution for Pad 1 is shown in Fig. 6. This saturation effect is dynamic because in permeation experiments to be discussed later bound particle concentrations much higher than these saturation levels were obtained from identical suspensions and at the same level of shear stresses.

The second major feature shown by the  $\phi/P$  vs.  $P'$  plots is the fact that  $\phi/P$  increases with  $P'$  over a fairly large portion of the mats. This means that the apparent first-order rate constant (this is what  $\phi/P$  amounts to) is a function of the bound particle concentration. The increase in  $\phi/P$  with  $P'$  is definite and significant. It indicates that the presence of bound particles on the fibers acts to increase the rate at which retention can occur. Since removal appears to be significant only after a critical bound particle concentration is reached, this would mean that particles already can act to increase the rate of attachment. This would appear to mean that for the system used in this study, free particles prefer to attach onto particles already bound rather than to the fiber surface. In any event, the bound particles tend to increase the attachment rate.

The third feature is the drop in  $\phi/P$  at low bound particle concentrations near the surface of the mat. This is the least reliable feature of the curves. The magnitude of the drop is relatively small, and the analysis is based on a polynomial fitting of the original data (see Appendix IV). Inaccuracies in the polynomial

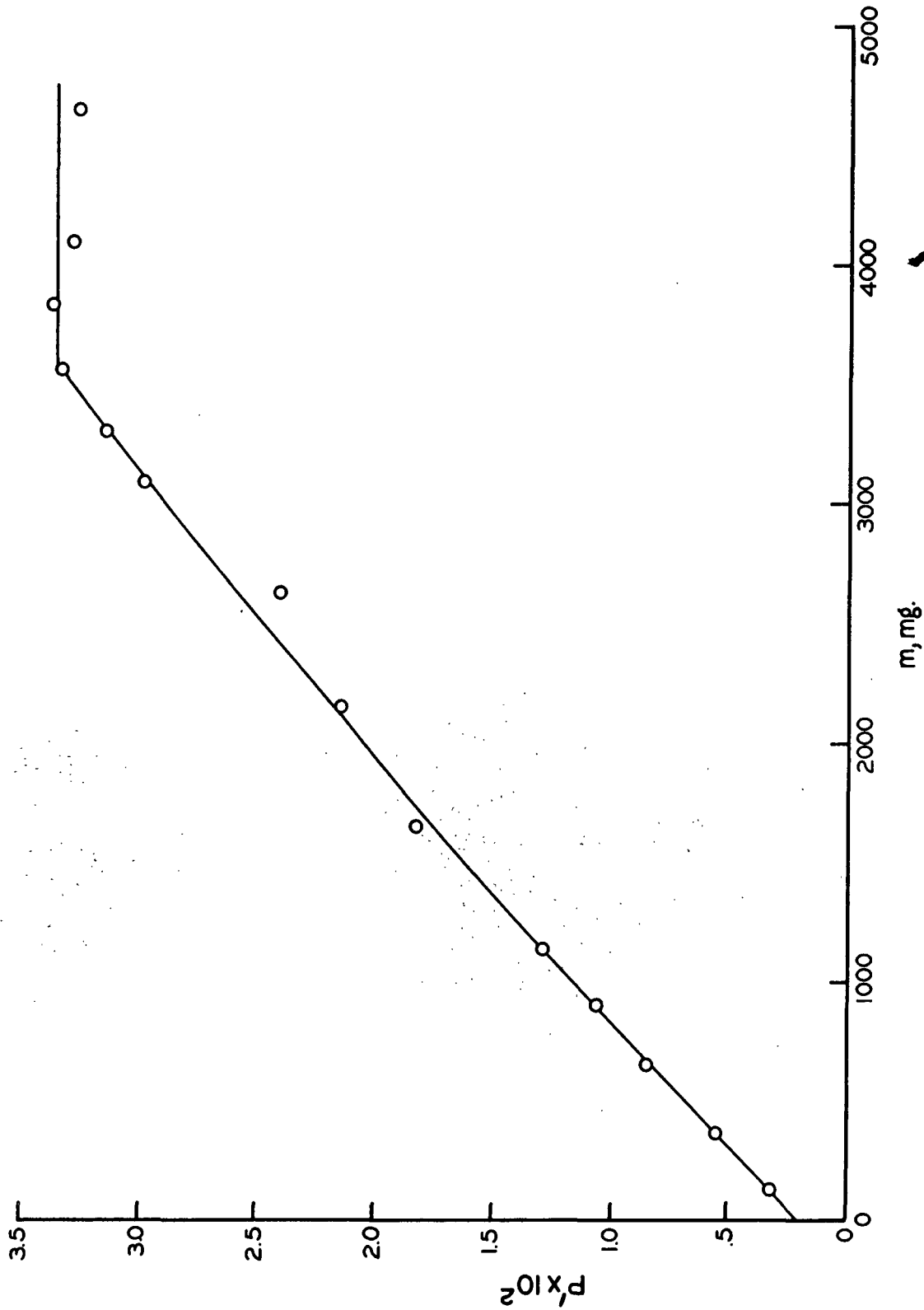


Figure 6. Bound Particle Distribution for Pad 1

fits at the mat surface end could conceivably account for the initial drop. It is, however, felt that the dip in  $\varphi/\underline{P}$  at low  $\underline{P}'$  values is real. It showed up in all four pads and extends over a large enough area of the pad that more than one or two data points are involved.

### Interpretation of Results

The retention rate is not simply first order in free particle concentration. Removal is important in addition to attachment, and even attachment is dependent on the amount of bound particles present. Various attempts were made to fit the  $\varphi/\underline{P}$  curves with assumed forms of the retention rate. None of these were very successful. No satisfactory method for handling the removal rate was developed. Attempts to describe removal by a first order in bound particle rate function were completely unsuccessful. Up to the present time no satisfactory quantitative method of accounting for particle removal has been obtained. It has been possible to fit the portion of the  $\varphi/\underline{P}$  vs.  $\underline{P}'$  curves to the left of the maximum to a reasonably simple form by assuming it represents attachment only. The form of the retention equation chosen was

$$\varphi = K_A S (1 - \gamma \underline{P}') \underline{P}' + K_A \beta \underline{P}'^2 \underline{P} \quad (23).$$

Values of  $\underline{K}_A \underline{S}$ ,  $\gamma$ , and  $\beta/\underline{S}$  obtained from a least-squares fit centered about the minimum of the curve are given in Table III. The interpretation of this form for the attachment rate will be delayed until after the permeation data have been discussed.

TABLE III  
LEAST-SQUARES-FIT VALUES OF  $\frac{K_A S}{A}$ ,  $\gamma$ , AND  $\beta/S$   
FROM EQUATION (23)

Pad	$\frac{K_A S}{A}$ , sec. <sup>-1</sup>	$\gamma$	$\beta/S$
1	13.0	42.3	1952
2	8.0	4.6	1392
3	13.6	26.9	1514
4	14.4	31.9	1722
Average	12.2	26.4	1648

#### Comparison with Conventional Theory

Before leaving these retention data which were obtained in constant-rate filtration experiments, it is useful to analyze them in terms of the previously used retention theories. In the conventional theory, the retention rate was essentially assumed to be of the form  $\phi = \frac{K_R S P}{R}$ , where  $\frac{K_R S}{R}$  is constant. Details of the solution to this case were given earlier in this report. The solution is

$$\ln (P_{OO} - P') = \ln (P_{OO} - P'_O) - \frac{K_R S m}{\rho_w A U_O} \quad (24).$$

In terms of the collection efficiency,  $\underline{E}$ , this becomes

$$\ln (P_{OO} - P') = \ln (P_{OO} - P'_O) - \frac{SEm}{A} \quad (25).$$

Thus, a plot of  $\ln (P_{OO} - P')$  vs.  $\underline{m}$  would yield a straight line. The prepad retention could be determined from the intercept, and the retention rate constant from the slope. A linear regression on  $\ln (P_{OO} - P')$  vs.  $\underline{m}$  was made for each of the four pads. Table IV summarizes the results of this analysis. A comparison is made between the value of  $\underline{P}'_O$  determined from the intercept and that found from the

polynomial fit of the original bound particle distribution data. A plot of  $\ln (\underline{P}_{\infty} - \underline{P}')$  vs.  $\underline{m}$ , and the regression line are shown in Fig. 7 for Pad 4. This is to illustrate the type of fit obtained and is typical of the behavior of all four pads.

TABLE IV

RESULTS OF ANALYSIS OF CONSTANT-RATE FILTRATION RETENTION DATA ACCORDING TO THE PREVIOUS DATA

Pad	Slope, $\text{mg.}^{-1}$	Intercept	$\underline{K}_R \underline{S}$ , $\text{sec.}^{-1}$	$\underline{P}'$ , int.	$\underline{P}'$ ; poly.
1	$-2.698 \times 10^{-4}$	-3.010	12.3	$6.97 \times 10^{-4}$	$1.24 \times 10^{-3}$
2	$-2.461 \times 10^{-4}$	-2.961	11.2	$-1.76 \times 10^{-3}$	$1.00 \times 10^{-3}$
3	$-3.469 \times 10^{-4}$	-2.942	15.8	$-2.75 \times 10^{-3}$	$4.53 \times 10^{-4}$
4	$-3.904 \times 10^{-4}$	-2.902	17.8	$-4.91 \times 10^{-3}$	$4.56 \times 10^{-4}$

The values of  $\underline{K}_R \underline{S}$  in Table IV are of the same order as the values of  $\underline{K}_A \underline{S}$  in Table III. This is to be expected. The higher values of  $\underline{K}_R \underline{S}$  for Pads 3 and 4 are higher than for the other two pads. This is in agreement with the finding that the fines caused an increase in the retention rate. Thus, the slope of this simple plot is adequate and useful for ranking of effects. The value of  $\underline{P}'$  determined from the intercept was negative in three of the four cases. This is because  $\underline{P}'$  is small compared to  $\underline{P}_{\infty}$ , and the intercept in all cases was close to  $\ln (\underline{P}_{\infty}) = \ln (0.05) = -2.996$ . If the prepad retention is a significant portion of  $\underline{P}_{\infty}$ , then this method of estimating  $\underline{P}'$  will be more reliable.

Figure 7 provides a good illustration of the limitations of the conventional theory. Although the general behavior of the data is predicted and a reasonable straight line through the data can be drawn, there is a systematic trend in the data that does not follow the predicted straight line. The points start out below the regression line, cross and remain above the line for a while, and then cross again

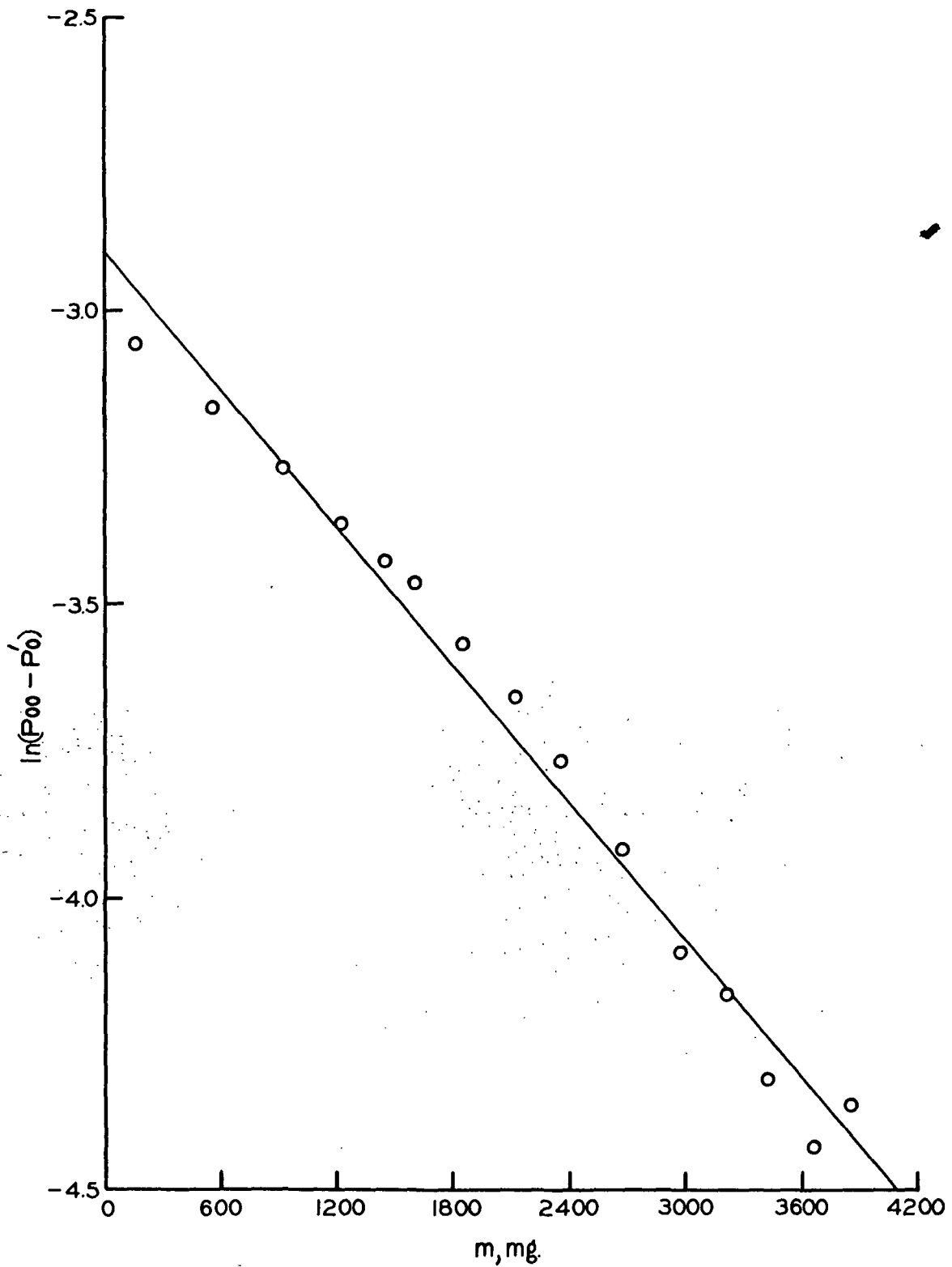


Figure 7. Conventional Retention Plot for Pad 4

and tend to finish below. This snaking around the regression line is due to the nonconstancy of the retention rate constant, and, at the wire end, on particle removal. The fact that the linear relation holds as well as it does is due to the predominance of the free particle inventory and the sequential layering of the forming process on the particle distribution in a constant-rate filtration. The effect of these two factors is so strong that it tends to obscure the details of the retention process. These details are shown much more clearly by the rate analysis procedure described previously.

#### CONSTANT-RATE PERMEATIONS

In a permeation experiment, the process of retention is separated from the process of pad formation. The pad is formed in the absence of particles, and the suspension used for the retention phase does not contain fibers. The pad is formed first and is then normally loaded mechanically to attempt to maintain a constant porosity in the pad. This pad is then permeated by a particle suspension at a constant rate for a fixed period of time. Although a permeation experiment would appear to be the simplest for studying retention since retention occurs independently of sheet formation, the analysis of a permeation experiment is not as straightforward as a constant-rate filtration. The reasons for this will be made clear in the section on analysis of results.

#### Description of Permeation Experiments

A total of twelve permeation experiments were run. These were carried out using different combinations of fines addition and also with beaten pulps. Pads 7 and 8 were run with a different batch of fines than all of the other experiments (including the filtrations). These two experiments were repeated with the common batch of fines. The particle suspensions were made up according to the

same conditions as were used for the constant-rate filtration experiments, with the obvious exception that no fiber was added. A summary of the various experimental conditions is given in Table V.

TABLE V

## SUMMARY OF EXPERIMENTAL CONDITIONS FOR PERMEATIONS

$\text{TiO}_2$  concentration =  $5.0 \times 10^{-3}$  g./liter

NaCl concentration =  $8.3 \times 10^{-4}$  M

pH = 5.0

- Pad 5: No fines added, permeated at 1.0 cm./sec. for 1100 sec.
- Pad 6: Duplicate of Pad 5.
- Pad 7: 0.25 g. of fines added to suspension just before  $\text{TiO}_2$  added. This was a different batch of fines than was used in the other experiments (except Pad 8). Permeated at 1.0 cm./sec. for 1100 sec.
- Pad 8: Duplicate of Pad 7.
- Pad 7 Rpt.: Repeat of conditions of Pad 7 with the general batch of fines.
- Pad 8 Rpt.: Duplicate of Pad 7 Rpt.
- Pad 9: Fines added to fiber suspension prior to mat formation. Same proportion of fines to fibers as in the other experiments (0.20 g. to 8 g. fiber in 80 liters of water). Particle suspension made up in usual manner. No fines in the particle suspension. Permeated at 1.0 cm./sec. for 1100 sec.
- Pad 10: Duplicate of Pad 9.
- Pad 11: A portion of the classified pulp was beaten for 15 minutes. A pad was formed from the beaten pulp and permeated with the usual  $\text{TiO}_2$  suspension. Because of the high drainage resistance of the beaten pulp, the total pad weight was only about 2 g., and the pad was not mechanically loaded. Permeated at 1 cm./sec. for 1100 sec.
- Pad 12: Duplicate of Pad 11.
- Pad 13: The pad was formed from the beaten pulp after classification to remove the fines generated during beating. No fines were added either to the pad or to the particle suspension. Permeated at 1.0 cm./sec. for 1100 sec.
- Pad 14: Duplicate of Pad 13.

The procedure for carrying out the experiments was essentially the same as that used for the constant-rate filtrations. Variations were due to the basic differences between the two processes. The fiber mat was formed first. Distilled, deionized water was boiled and cooled for deaeration purposes. The fibers were de-aerated under vacuum, dispersed, and added to the distilled water. The fiber mat was formed at 1 cm./sec. from a stock consistency of 0.01%. Thus, the mats were formed under essentially the same conditions as in the filtration experiments. After the mat was formed, it was normally loaded by a weight on a permeable piston to attempt to hold the porosity to around 0.80. A fresh batch of distilled, deionized water was used to prepare the particle suspension. The procedure for making up the particle suspensions has been described previously.

After the permeation had proceeded for the desired length of time, the flow was stopped. The suspension remaining above the permeable piston was siphoned off and the residual drained slowly through the pad. The permeable piston was then removed and the pad taken from the flow system. Pads were delaminated by hand and analyzed by the standard procedure.

#### Rate Analysis for Permeations

In the case of a permeation, all terms involving consistency drop out because there are no fibers in the suspension. The retention equations for a constant-rate permeation ( $\underline{U}_o = \text{constant}$  and  $\underline{U}_f$  negligible) are

$$-\rho_w A U_o \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f (1 - \epsilon)} \frac{\partial P}{\partial t} + \varphi \quad (26)$$

$$\frac{\partial P'}{\partial t} = \varphi \quad (27).$$

If changes in certain variables with time are slow compared to the time of transit of a fluid element through the pad and the initial conditions remain constant, the

time derivative term in Equation (26) can be neglected. Then Equation (26) can be written as

$$-\rho_w AU_o \frac{\partial P}{\partial m} = \varphi \quad (28).$$

Equations (27) and (28) form the basis for the rate analysis of the permeation data.

It is immediately evident that the system of equations describing the permeation is not as simple as the system describing the constant-rate filtration. Both time and position in the mat show up directly in the equations. Only under certain circumstances where  $\varphi =$  function of  $m$  alone [or  $\varphi = \varphi(t)$  only, a very unlikely case] are the equations separable. In general, it is necessary to be content with average properties.

Equations (27) and (28) can be combined to give

$$\frac{\partial P'}{\partial t} = -\rho_w AU_o \frac{\partial P}{\partial m} \quad (29).$$

Integrating Equation (29) from 0 to  $t$ , with  $P' = 0$  at  $t = 0$  gives

$$P'(m,t) = -\rho_w AU_o \frac{\partial}{\partial m} \int_0^t P(m,x) dx = -\rho_w AU_o t \frac{\partial \bar{P}}{\partial m} \quad (30)$$

where  $\bar{P} =$  time average free particle concentration defined by

$$\bar{P}(m) = \frac{1}{t} \int_0^t P(m,x) dx \quad (31).$$

Equation (30) can then be integrated from 0 to  $m$  with  $\bar{P} = P_o$  at  $m = 0$ :

$$\frac{-1}{\rho_w AU_o t} \int_0^m P'(x,t) dx = \bar{P} - P_o$$

or

$$\bar{P} = P_o - \frac{1}{\rho_w AU_o t} \int_0^m P' dx \quad (32).$$

Equation (32) relates the time average free particle concentration to an integral of the final bound particle distribution, the permeation time, and the suspension value.

The time average retention rate,  $\bar{\varphi}$ , is defined by

$$\bar{\varphi}(m) = \frac{1}{t} \int_0^t \varphi(m,x) dx \quad (33).$$

This can be directly related to the bound particle concentration by integrating Equation (27) from 0 to  $t$ :

$$\bar{\varphi}(m) = P'(m)/t \quad (34).$$

It is seen that in the permeation case,  $P'$  must be a function of time as well as position. If the rate,  $\varphi$ , is also time dependent (for example, if  $\varphi$  is dependent on  $P'$  as suggested by filtration results), then  $P$  will depend on time as well as position. Quantities obtainable from the particle distribution measured after the run are  $P'(m,t)$  where  $t$  = total permeation time,  $\bar{\varphi}(m)$ , and  $\bar{P}(m)$ . The average bound particle concentration is not determinable without knowledge of the time dependence of  $\varphi$ .

The analysis of the permeation data is based on determining  $\bar{\varphi}/\bar{P}$ .

$$\frac{\bar{\varphi}}{\bar{P}} = \frac{\rho_w AU_o P'}{\rho_w P_o tAU_o - \int_0^m P' dx} \quad (35).$$

It is recognized that  $\bar{\varphi}/\bar{P} \neq \overline{\varphi/P}$ , and that this could cause some difficulty. However,  $\bar{\varphi}/\bar{P}$  is the only quantity resembling the rate function determined for the filtrations which can be obtained from final distribution data. The analysis of the permeation data was carried out using Equation (35). The procedure for doing this is described in detail in Appendix V.

Results of Analysis on Permeations

The quantity  $\bar{\varphi}/\bar{P}$  was determined as a function of  $\underline{m}$  and  $\underline{P}'$  for all of the permeation experiments listed in Table V except for Pads 11 and 12. The bound particle distribution for these two pads was extremely weird and was due to beating the pulp. The distributions for Pads 11 and 12 will be discussed in detail in a later section.

The results of the rate analysis on the permeations confirmed the results obtained on the filtrations. In all cases, the presence of bound particles increased the rate of retention. Curves of  $\bar{\varphi}/\bar{P}$  vs.  $\underline{P}'$  are given in Fig. 8 for Pads 5, 7-rpt., 9, and 13. These cover all four of the cases, where fines addition was a parameter, remaining after Pads 11 and 12 were eliminated.

Examination of the curves shows that in all cases  $\bar{\varphi}/\bar{P}$  increased with increasing  $\underline{P}'$ . In some cases, the rate doubled. The gathering together and sharp drop in the curves at the low-particle-concentration end may not be real. At the low-particle end, the denominator in Equation (35) becomes the difference between two large numbers. Slight inaccuracies due to polynomial fitting could cause the behavior at the very low end. No attempt was made to fit these data to functional forms because  $\bar{\varphi}/\bar{P}$  is based on average quantities.

Comparison with Conventional Theory

The solution to the retention equations for a permeation with the retention rate  $\varphi = \frac{K_R SP}{R}$  was presented earlier in this report. The solution can be written as

$$\ln P' = \ln (K_R SP_o t) - \frac{K_R Sm}{\rho_w AU_o} \quad (36).$$

Accordingly, a plot of  $\ln \underline{P}'$  vs.  $\underline{m}$  should yield a straight line. Linear regressions were run on  $\ln \underline{P}'$  vs.  $\underline{m}$  for all of the permeation data sets, and the slope and

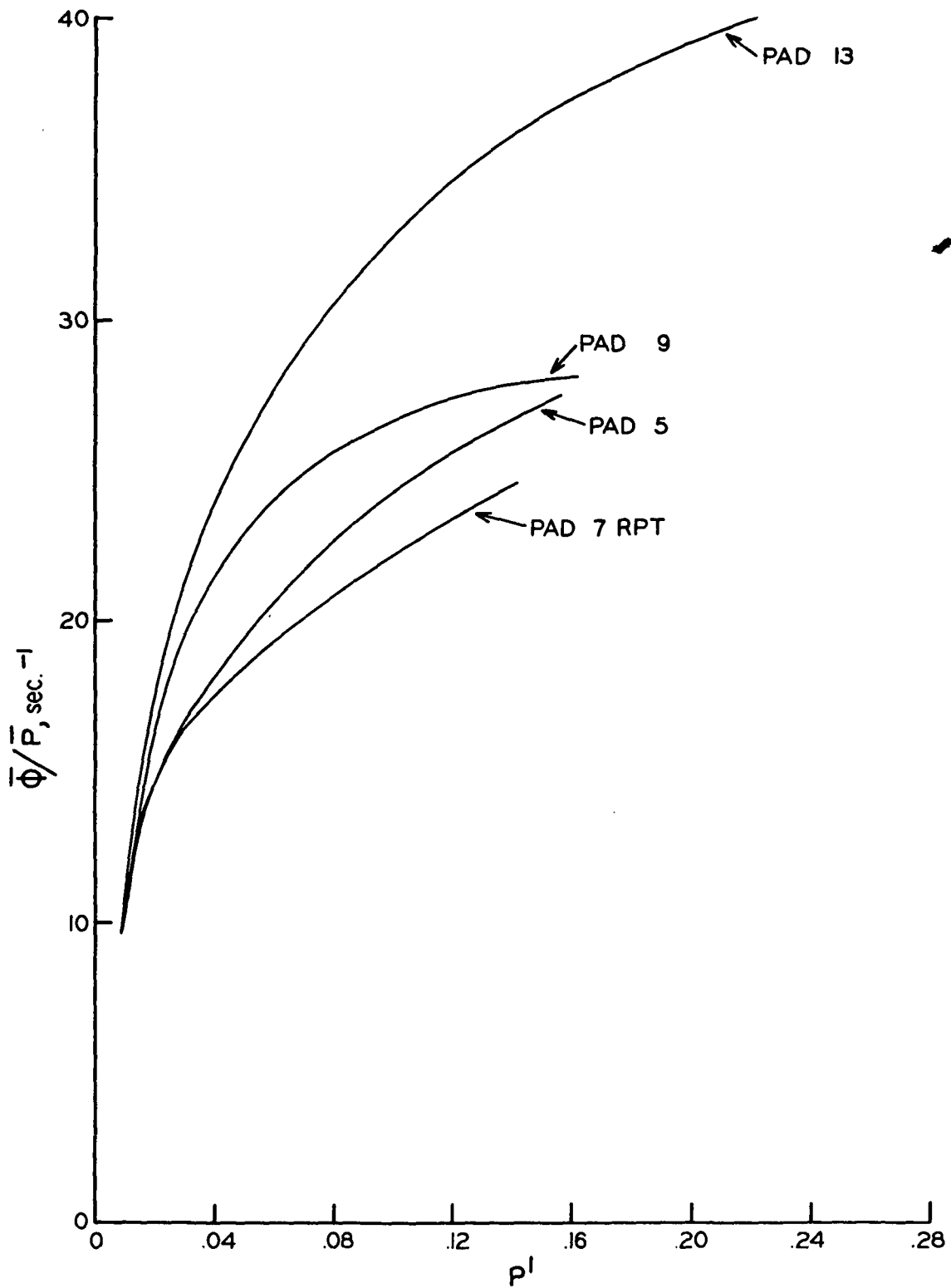


Figure 8.  $\bar{\Phi}/\bar{P}$  vs.  $P'$  from Selected Permeation Experiments

intercept of the regression line determined. Superficially, the agreement with the simple theory is excellent. Straight lines fit the data quite well. The data and the regression lines for Pads 5 and 13 are shown in Fig. 9 for illustrative purposes. These were typical of the behavior in all of the runs except Pads 11 and 12, which, as mentioned before, were unique.

Although plots of  $\ln P'$  vs.  $m$  gave reasonably good straight lines, the agreement with conventional retention theory was more apparent than real. It can be seen in Equation (36) that the retention rate constant,  $\frac{K_R S}{\rho_w AU_0}$ , appears in both terms on the right-hand side. Since  $P_0$ ,  $t$ ,  $\rho_w$ ,  $A$ , and  $U_0$  are all known from the experimental conditions, a value of  $\frac{K_R S}{\rho_w AU_0}$  can be computed from both the slope and the intercept of the regression line. The true test of the simple theory is whether these values agree. Such a comparison is made in Table VI.

It is evident in Table VI that the value of  $\frac{K_R S}{\rho_w AU_0}$  determined from the intercept is consistently lower, by about 10%, than the value obtained from the slope. Thus, the simple, first-order retention theory does not completely hold. The fact that the value determined from the slope is always greater is in agreement with the finding that the presence of bound particles increases the rate of retention. The bound particle concentration decreases with increasing  $m$ , and the retention rate also decreases in this direction. The slope then depends not only on the retention rate constant but also on the rate of change of the rate constant. This can be easily shown. If the rate constant  $\frac{K_R S}{\rho_w AU_0}$  is taken to be a function of  $m$ , Equation (36) would take the form

$$\ln P' = \ln (K_R S P_0 t) - \frac{\int_0^m K_R S dx}{\rho_w AU_0} \quad (37)$$

and

$$\frac{d \ln P'}{dm} = \frac{1}{K_R S} \frac{dK_R S}{dm} - \frac{K_R S}{\rho_w AU_0} \quad (38).$$

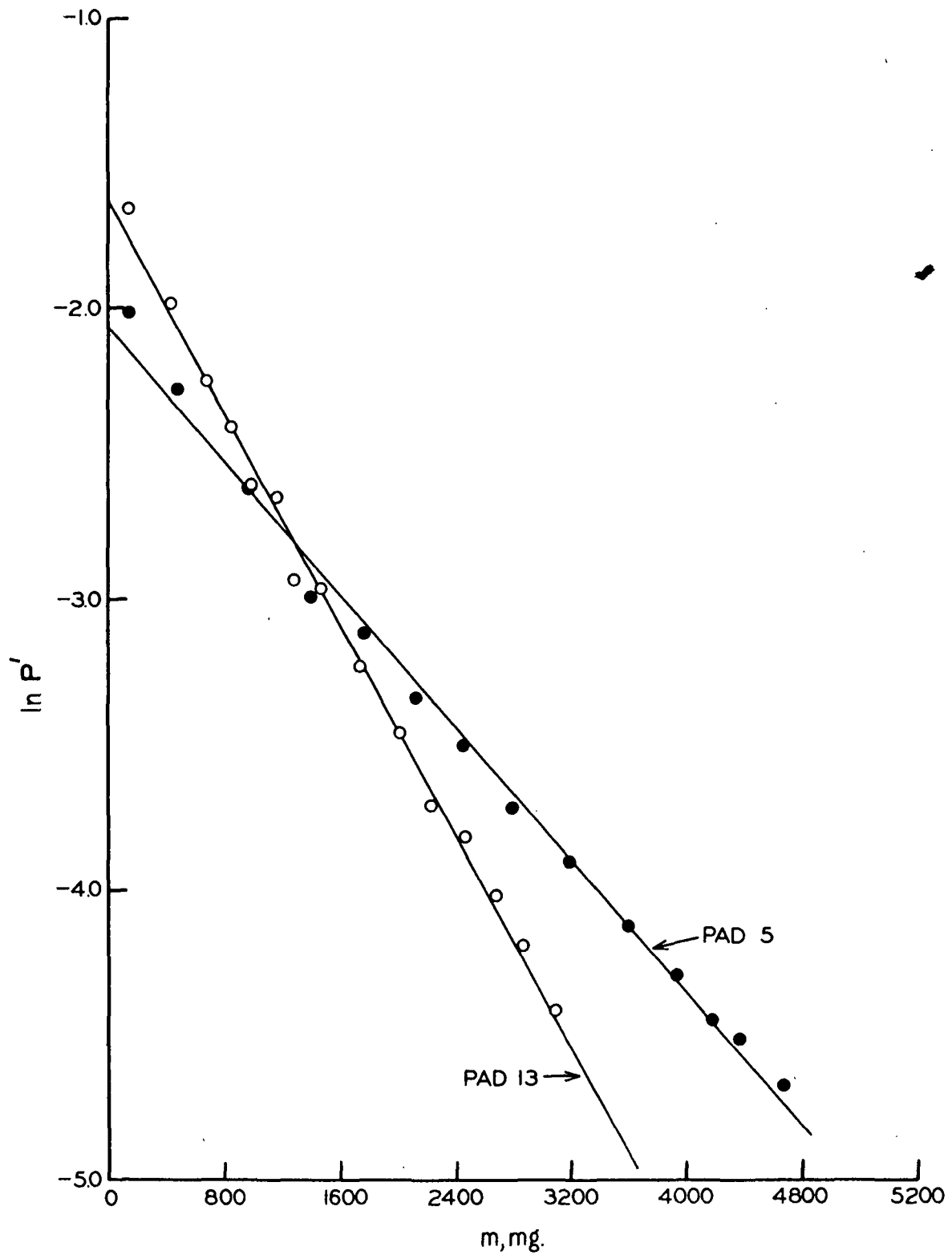


Figure 9. Conventional Retention Plots for Pads 5 and 13

Since  $\frac{dK_R S}{dm}$  is negative due to the decrease in bound particle concentration with increasing  $m$ , the slope is steeper than it would be with a constant value of the retention rate constant.

TABLE VI  
COMPARISON OF VALUES OF  $\frac{K_R S}{SEC.}^{-1}$ , COMPUTED FROM SLOPE  
AND INTERCEPT OF  $\ln P'$  vs.  $m$

Pad	Intercept	Slope x 10 <sup>4</sup>	$\frac{K_R S}{SEC.}$ (slope)	$\frac{K_R S}{SEC.}$ (int.)	$\frac{K_R S}{SEC.}$ (int.)	$\frac{K_R S}{SEC.}$ (slope)
5	-2.066	-5.719	26.1	23.0		0.88
6	-2.164	-5.245	23.9	20.9		0.87
7	-2.412	-3.879	17.7	16.3		0.92
8	-2.258	-4.585	20.9	19.0		0.91
7 Rpt.	-2.127	-5.306	24.2	21.7		0.90
8 Rpt.	-2.529	-3.574	16.3	14.5		0.89
9	-1.877	-6.820	31.2	27.8		0.89
10	-1.728	-8.052	36.7	32.3		0.88
13	-1.631	-9.072	41.4	35.6		0.86
14	-1.604	-8.653	39.5	36.6		0.93

#### DISCUSSION OF RATE ANALYSIS TECHNIQUES

A method for determining the retention rate from bound particle distribution measurements has been developed. The technique is most suitable when applied to constant-rate filtrations. The relationship between the retention rate and the final bound particle distribution is very direct in a constant-rate filtration. In addition, the free particle concentration is directly calculable from the bound particle concentration. These two factors make constant-rate filtrations applicable to the study of the functional dependence of the retention rate. Another factor in

favor of constant-rate filtrations is that the competing processes of attachment and removal tend to occur at opposite ends of the pad. This makes their separation feasible.

Rate analyses of permeation experiments are less straightforward. Retention behavior in a permeation experiment is time dependent. This time dependence complicates the analysis. In general, it is necessary to work with time-averaged quantities when analyzing permeations. Averaging can be avoided only if the retention rate is time independent. Since the bound particle distribution is inherently time dependent in a permeation, this means that averaging is avoided only when the retention rate is completely independent of the bound particle concentration. The results of this study indicate that  $\phi$  is dependent on  $\underline{P}'$ , and so average quantities must be used in analyzing permeations. Because of the averaging involved, permeation distributions are less sensitive to the retention rate. Rate analysis of permeations is useful for determining the trends of various parameters. It should not be used to determine the functional dependence of the retention rate because of the averaging involved.

The final bound particle distribution in a permeation represents an integral over the retention rate at each location in the pad. The distribution is integrally dependent on the retention rate, and this inherently makes the distribution insensitive to details. The integration process tends to smooth over significant features of the retention process. A good example of this process of smothering detail is the  $\ln \underline{P}'$  vs.  $\underline{m}$  plots in Fig. 9. Reasonable straight lines could easily be drawn through the data, thus apparently confirming traditional retention theory. Only by comparing the slope and the intercept could differences from the theory be found. The analysis of the average rate, on the other hand, showed up the nonideality of the process quite clearly. The fact that straight lines were obtained meant only

that free particle inventory dominated the retention process and that details tend to be smoothed out.

From the results of these studies, rate analysis of distributions from constant-rate filtrations appears to be a powerful tool in understanding retention phenomena. The retention of particles is basically a kinetic process, and the rate of retention is the most fundamental quantity which can be measured. The constant-rate filtration technique provides a simple measurement of the local retention rate,  $\phi$ , and local values of the free and bound particle concentrations,  $\underline{P}$  and  $\underline{P}'$ . In addition, since the free particle concentration is high where the bound particle concentration is low, and vice versa, the processes of attachment and removal tend to occur on opposite ends of the pad and are potentially separable.

A good many features of the retention process can be studied with this technique. If the retention rate can be separated into components of attachment and removal, the functional dependence of each on  $\underline{P}$  and  $\underline{P}'$  can be determined. The functional dependence determined in this manner could be enormously important in understanding more thoroughly the physicochemical mechanisms underlying the process. A start on this approach was made in this study, where the dependence of the retention rate on bound particle concentration was discovered. Much more needs to be done in the quantization of the retention rate.

The technique would be very applicable to studying the influence of colloidal variables. It would be highly desirable to know the extent to which colloidal variables control the retention rate and what part particle transport plays. It would be especially useful in examining the effects of additives on both attachment and removal.

## DISCUSSION OF RESULTS

### ATTACHMENT

The main result of the rate analysis of both the filtration and permeation experiments is that the attachment rate is not simple first order in free particles. Attachment is not adequately described by  $\varphi_A = \frac{K_A S}{P}$  where  $\frac{K_A S}{P}$  is a constant. The presence of bound particles augments the rate of attachment. This was shown in both the permeations and filtrations where the effective rate constant  $\varphi/P$  increased with increasing  $P'$ . The retention rate does appear to be first order in free particles, but the rate constant is dependent on  $P'$ .

$$\varphi_A = K_A (P') S P \quad (39).$$

The proportionality between the rate and the free particle concentration seems to be confirmed. Figure 9 strongly argues for this. The bound particle dependence is more complex.

The fact that the retention increases as the bound particle concentration increases would appear to indicate that particles are more easily retained on other particles than on the fiber surface. This may have serious implications for colloidal theories of retention based on the coflocculation of particles onto a fiber. The bound particle dependence of the retention does place a serious limitation on the usefulness of the collection efficiency concept. It is not at all clear how this bound particle dependence relates to particle transport. It would appear that the collection efficiency is best regarded as a semiempirical indicator of retention efficiency.

The retention rate determined from the constant-rate filtration was fitted to the form

$$\varphi_A = K_A S (1 - \gamma P' + \frac{\beta}{S} P'^2) P \quad (40).$$

In order to make this fit, it was necessary to restrict attention to the left of the maxima of the  $\varphi/P$  vs.  $P'$  plots. This was done by assuming that only attachment was significant to the left of the maximum. The results of this fit were presented in Table III. An attempt to use the average values of the three constants to fit the permeation data was unsuccessful. The reason was that the magnitudes of the constants were sufficiently large that the  $\partial P/\partial t$  term could not be neglected in the permeation equations. It then was impossible to get a solution.

The quadratic dependence of  $\varphi_A$  on  $P$  as shown in Equation (40) was suggested by the shape of the  $\varphi/P$  vs.  $P'$  plots and not by any theoretical considerations. A possible interpretation is given below. It is assumed that the attachment rate can be broken into two parts — the rate of attachment of particles onto the fiber surface and the rate of attachment onto other particles already bound. Then Equation (40) can be written as:

$$\varphi_A = K_A S (1 - \gamma P') P + K_A \beta P'^2 P \quad (41).$$

The first term represents attachment directly onto the fiber surface. This term decreases as the bound particle concentration increases because the bound particles cover part of the fiber surface. The more fiber surface covered by particles, the less available for direct attachment to the fiber. The second term represents attachment onto other particles. The quadratic dependence on  $P'$  is arbitrary, but it could be interpreted that a particle tends to attach to two or more particles. In that case, the attachment of particles onto bound particles would depend on the proximity of bound particles on the surface which could easily be proportional to the square of the bound particle concentration. If this interpretation is reasonable, then the ratio  $(\beta/S)P'_2/(1 - \gamma P')$  is a measure of the preference to attach to

other particles rather than to the fiber surface. In the filtration experiments, this ratio varied from about 0.007 near the mat surface to about 7 near the septum. If this interpretation is correct, then attachment onto other particles was quite significant in the filtration experiments.

#### REMOVAL

The factors governing the removal of particles from a fibrous sheet are not understood. Compared to particle removal, particle attachment is well known. The only definite fact known about particle removal is that it must have occurred in these experiments. The postulate of particle removal seemed the only possible way of explaining the pseudo-saturation and the large drop in the net retention rate at the septum end in the filtration experiments. On the basis of appearance, the permeation experiments do not suggest removal.

Since the free and bound particle concentrations are inversely related to each other in the constant-rate filtrations, and this tends to spatially separate attachment and removal, most of the information about particle removal was obtained from the four constant-rate filtration experiments. The most striking feature of particle removal was that removal set in suddenly and strongly on the septum end. Removal appeared to be negligible until a certain bound particle concentration was reached. Above a certain bound particle concentration, the rate of removal increased very rapidly.

Up to the present time, it has proved impossible to quantitatively measure the removal rate. This is due to the arbitrariness involved in separating the measured retention rate into attachment and removal. The removal rate could be calculated by difference from an assumed form of the attachment rate. For example, Equation (40) could be used for attachment; then,

$$-\varphi_D = \varphi - K_A S \left( 1 - \gamma P' + \frac{\beta}{S} P'^2 \right) P \quad (42)$$

where  $\varphi_D$  is the rate of removal. However, unless there is some reason for certainty about the form of the attachment rate, such a separation seems premature. It is definitely known that removal is not adequately described by  $\varphi_D = \frac{K_D}{S} P'$ . Such a function is too gradual in its onset. It does appear necessary to have a critical bound particle concentration in the removal rate. The simplest removal function that appears feasible is  $\varphi_D = \frac{K_D}{S} (P' - P'_{cr})$ , when  $P' > P'_{cr}$ , and  $\varphi_D = 0$  if  $P' < P'_{cr}$ . This has not been tested on the data because of the difficulties in incorporating such a discontinuous function into a regression analysis.

It is of interest to compare the evidence for a critical bound particle concentration obtained in the present study and the observation of so-called "saturation" in previous work (2). Such a comparison indicates that it is essentially the same. Thus, saturation (a sudden flattening of the bound particle concentration on the wire end in a filtration) is a manifestation of the existence of a critical bound particle concentration in removal. Saturation is the effect on the macroscopic particle distribution of the sudden inception of removal. It would be tempting to consider saturation to be an absolute phenomenon, with the fiber simply unable to retain any more particles. The name, saturation, tends to imply some such occurrence, and in this sense is misleading. Actually, the so-called saturation phenomenon must be considered to be dynamic in nature and would be more properly called pseudo-equilibrium. The whole retention process is a competition between attachment and removal, and a steady bound particle concentration can be maintained whenever these rates equal each other. The striking nature of the "saturation" distributions is their sudden onset, and this is due to the peculiar form of the removal rate.

It is very obvious that "saturation" is dynamic in nature. In the four filtration experiments, the bound particle concentrations at which the distributions leveled off was from 0.03 to 0.035. On the other hand, for permeation Experiments 5, 6, 7, 8, 7 Rpt., and 8 Rpt., performed under the same colloidal conditions and hydrodynamic stress levels (1 cm./sec. forming velocity), much higher values of  $\underline{P}'$  (from 0.10 to 0.13 near the pad surface) were obtained. Since bound particle concentrations three to four times as high as the "saturation" concentrations were obtained at the same colloidal and flow conditions, "saturation" cannot be considered to be anything but a dynamic interaction. The fact that "saturation" distributions were obtained only in the filtration experiments must be explained by factors affecting the balance between attachment and removal which are different in permeations than in filtrations. These differences are obvious. In the permeation, the free particle concentration is high where the bound particle concentration is also high. Thus, attachment and removal could both be present to a significant degree. In particular, because of the high  $\underline{P}$  values, attachment could maintain dominance even at large  $\underline{P}'$  values. In the filtration,  $\underline{P}$  values are highest at lowest  $\underline{P}'$  and vice versa. Thus, all of the factors tend to favor attachment on the surface end and removal on the wire end. The reason that these phenomena show up in the filtrations is that when removal begins to become dominant, the attachment rate is too small to overcome it because of the lower free particle concentration.

Even though "saturation" is a dynamic phenomenon, it remains a fact that removal sets in very strongly above a certain bound particle concentration,  $\underline{P}'_{cr}$ . Removal is not simply a power function of  $\underline{P}'$ , but rather seems to be expressed better as some function of  $(\underline{P}' - \underline{P}'_{cr})$ . It would appear that some particles are removed more easily than others. Once a certain amount of particles have been

retained, removal of particles becomes much easier and can occur at a relatively high rate. In order to shed some light on the possible nature of the critical bound particle concentration, it is useful to consider some work on particle removal previously described in the "Critical Review" (2).

The experimental data presented in Reference (2) are the only known data directly concerned with particle removal. In those experiments, radioactive, silver-tagged fines were used as particles in a system with classified fibers. A pad would be loaded with particles and then removal would be studied by passing fluid (without particles) through the pad at a fixed rate. The particles remaining in the pad were measured as a function of time by monitoring the radioactivity of the pad as a function of time. The results of these experiments are shown in Fig. 10. There were three main features of these results which are of interest. The first is that the removal process is definitely a rate process since the process occurred over a finite time period and at a decreasing rate. The shape of the curve looks much like an exponential to a  $-K_D t$  ( $e^{-K_D t}$ ) except for  $P'$  not going to zero as  $t \rightarrow \infty$ . The second main feature is that  $P'$  does not continually decrease to zero as time goes on, but rather seems to level off at some fixed value. The shape of the curve and the existence of a nonzero residual concentration suggest a rate of removal given by

$$\varphi_D = K_D (P' - P_{cr}) \quad (43).$$

The third main feature was that the residual was velocity dependent and the residual concentration decreased as the velocity increased. Hence,  $P_{cr}$ , certainly, and  $K_D$ , probably, are velocity dependent.

In general, the old results on removal tend to confirm the present findings. There exists some sort of critical bound particle concentration. Particles above the critical concentration are removed with relative ease. The older data indicate that this critical concentration is velocity dependent.

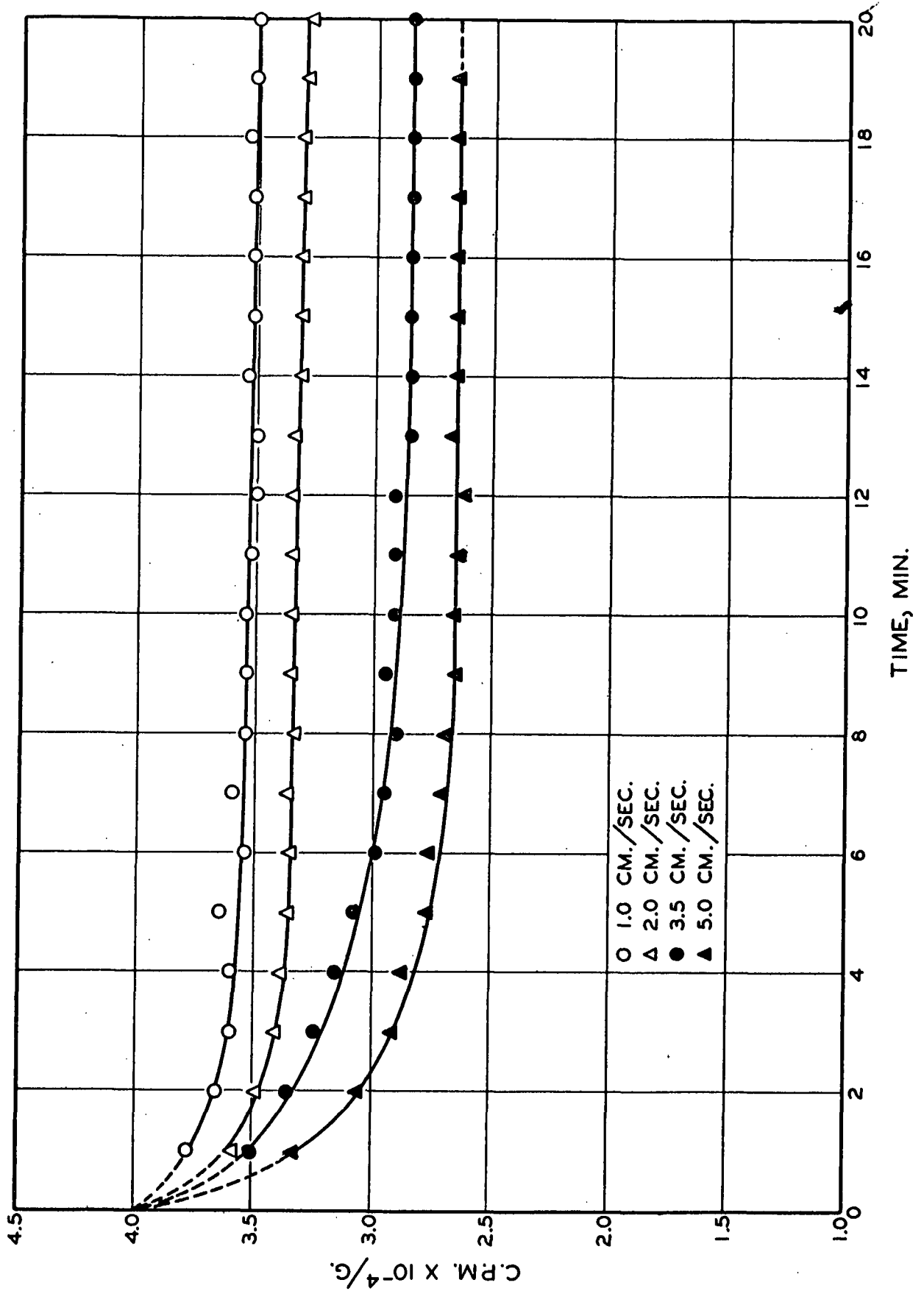


Figure 10. Removal of Particles by Shear Stress

## SUMMARY OF RESULTS

At the present time, no quantitative model or theory for describing the retention rate is available. Neither attachment nor removal is well understood. Bound particles play some sort of role in the attachment process. An increase in the bound particle concentration tends to increase the rate of attachment. Some success was obtained in fitting the attachment rate to the form

$$\varphi_A = K_A S (1 - \gamma P' + \frac{\beta}{S^2} P'^2) P \quad (44).$$

A tentative explanation of this form in terms of competing rates for attachment to the fiber surface and attachment to other particles was put forward. The first-order free particle dependence of the attachment rate seems to be well established.

Particle removal seems to increase strongly above some critical bound particle concentration. This critical concentration is undoubtedly shear dependent, and may also be dependent on ionic environment and other colloidal variables. The simplest form of a removal rate which is at all tenable is

$$\left. \begin{aligned} \varphi_D &= K_D (P' - P'_{cr}), & P' &> P'_{cr} \\ \varphi_D &= 0, & P' &< P'_{cr} \end{aligned} \right\} \quad (45).$$

There is reason to doubt that even this form is adequate. Addition of this type of removal rate to the kind of attachment rate proposed by Equation (44) will not predict an internal maximum in the bound particle distribution for a time-independent constant-rate filtration. In other words, with rate functions defined by Equations (44) and (45),  $dP'/d\underline{m}$  is  $\geq 0$  in a constant-rate filtration. However, in some high-velocity constant-rate filtrations performed on the dynamic drainage tester (3), internal maxima in the bound particle distributions were obtained. These would indicate that removal can become very complex at higher shear stresses.

### Tentative Hypothesis

A tentative hypothesis providing a qualitative explanation of the observed results can be put forward. Such a hypothesis must explain why a critical bound particle concentration exists for particle removal. It is reasonable to assume that removal is a strong function of the size of particles existing on the fiber surface. Particles are supposed to be removed when the stresses on the particle due to fluid shear overcome the attractive forces between particle and fiber. It appears likely that bigger particles are subject to greater amounts of stress. Thus, for a given shear (forming velocity), the larger particles could be expected to be removed.

It also appears reasonable to assume that particles can attach at either the fiber surface or onto particles already bound. This derives from the form of the attachment rate which was observed. If this is true, the attachment of free particles onto particles already bound will tend to build up larger sized particles on the fiber surface. Thus, as retention proceeds and the influence of bound particles on the attachment rate increases, larger sized bound particles will be formed.

The critical bound particle concentration could then be interpreted to be basically a critical bound particle size. The size of the bound particles would increase as the bound particle concentration increases until they reach a size where they can be removed by the prevailing shear stresses. The rate nature of the removal process could be due to the statistical fluctuations in shear level combined with the size distribution of the bound particles. If the particle-particle bonds in the large bound particles are stronger than the particle-fiber bonds, the entire large particle could be sheared off from the fiber. Then the removal of particles would not be confined to the incremental concentration greater than the critical ( $\underline{P}' - \underline{P}'_{cr}$ ) and negative values of  $\underline{dP}'/\underline{dm}$  could be obtained.

Up to the present time, it has not been possible to quantitize this hypothesis and test it against experimental data. To do so would require a treatment which includes size distribution of free and bound particles, with a cross-interaction through the retention rate. It remains simply a qualitative interpretation.

#### EFFECT OF SELECTED VARIABLES ON RETENTION

##### FINES AND BEATEN PULPS

###### Description of Experiments

Fines and beating were variables in all of the permeation and filtration experiments which have already been discussed. The conditions for the permeations were presented in Table V. For the filtrations, Pads 1 and 2 were formed with fines absent, and Pads 3 and 4 were formed with fines present.

The fiber which was used as a retention medium in all these experiments was a classified, bleached sulfite pulp, Weyerhaeuser Type S. Fines were prepared from the same fibers. Fines preparation involved dry grinding in a Wiley mill, followed by high shear in a Virtis homogenizer. After homogenization, a process of centrifugation and decantation was used to eliminate the larger size fines. Two batches of fines were prepared, the first being used only for Pads 7 and 8. All other experiments were performed with the second batch of fines. The size distribution of the second batch of fines was measured on a Coulter Counter. The results of this analysis are presented in Table VII.

For the experiments in which beaten pulps were used, a sufficient amount of original classified pulp was beaten for 15 minutes in a Valley beater at standard load. This beaten pulp was used directly for Experiments 11 and 12. A portion of beaten pulp was then reclassified on a Bauer-McNett classifier. The over-65-mesh fraction was then used as classified, beaten pulp in Experiments 13 and 14.

TABLE VII  
SIZE DISTRIBUTION OF FINES

Equivalent Spherical Diameter, $\mu\text{m}$ .	Number of Particles Larger than Stated Size
6.54	11
5.19	37
4.12	187
3.27	792
2.60	3,871
2.06	12,686
1.64	25,740
1.30	35,315
1.03	38,274

There are essentially no fines larger than 7.5  $\mu\text{m}$ ., and the peak of the distribution lies between 1 and 2  $\mu\text{m}$ .

### Results of Experiments

In order to determine the effect of fines on retention, some basis of comparison between the various experiments must be used. As has already been mentioned, the retention rate was not constant across the pads in these experiments. However, particularly with permeations, reasonably good straight lines were obtained when the data were analyzed according to the conventional retention theory. The value of the rate constant,  $\frac{K_R S}{m}$ , determined from the slope of these plots can be used as a measure of the average retention rate. Thus, the value of  $\frac{K_R S}{m}$  from the slope of  $\ln P'$  vs.  $m$  plots for permeations and  $\ln (\frac{P_{00}}{P} - P')$  vs.  $m$  plots for filtration can be used to measure the effect of fines. The exception is the experiments with whole, beaten pulp - 11 and 12. In these, the particle distribution

was unique, and they must be discussed separately. The summary of the effect of fines on retention is given in Table VIII.

TABLE VIII  
SUMMARY OF EFFECT OF FINES ON RETENTION

Pad	Experimental Conditions	$\frac{K_S}{R}$ , sec. <sup>-1</sup>
1	Filtration: no fines	12.3
2	Filtration: no fines	11.2
3	Filtration: fines in suspension	15.8
4	Filtration: fines in suspension	17.8
5	Permeation: no fines	26.1
6	Permeation: no fines	23.9
7	Permeation: fines in particle suspension	17.7
8	Permeation: fines in particle suspension	20.9
7 Rpt.	Permeation: fines in particle suspension	24.2
8 Rpt.	Permeation: fines in particle suspension	16.3
9	Permeation: fines in fiber suspension	31.2
10	Permeation: fines in fiber suspension	36.7
11	Permeation: whole beaten pulp - no added fines	-- <sup>a</sup>
12	Permeation: whole beaten pulp - no added fines	-- <sup>a</sup>
13	Permeation: classified, beaten pulp - no added fines	41.4
14	Permeation: classified, beaten pulp - no added fines	39.5

<sup>a</sup> Although it is impossible to get a reasonable slope for these distributions, the retention rate was higher in these experiments than in any of the others.

If the four filtration experiments are considered first, it can be seen that a relatively small but definite increase in the average retention rate was obtained when fines were present. Thus, fines improved retention in the constant rate filtrations.

The permeation experiments involving the artificially prepared fines (7, 8, 7 Rpt., 8 Rpt., 9, and 10) should then be compared with the permeations with no fines at all - 5 and 6. It can be seen that the effect of the fines depended on how they were introduced. When the mat was formed from fines-free pulp and fines were introduced into the particle suspension, a slight but definite reduction in retention occurred. When the mat was formed from a fiber-fines suspension and was then permeated by a fines-free  $TiO_2$  suspension, a significant increase in the overall retention was obtained. In both cases, the ratio of fines to fibers was maintained constant.

The strongest influence on the retention was obtained with beaten pulp, both before and after classification to remove the fines produced by beating. When the whole pulp was used, the bound particle distribution curve showed a distinct internal maximum. The bound particle distribution curve first increased and then decreased with increasing  $m$ . The distribution curves for the whole pulp (11 and 12) are shown in Fig. 11. The unique shape of these curves is due to the presence of the fines in the beaten pulp. After classification to remove the fines (13 and 14), the bound particle distributions showed the continual decrease in  $P'$  with increasing  $m$  normal for a permeation. It should also be noted that the value of  $P'$  obtained in Experiments 11 and 12 were the highest obtained in any of the experiments.

#### Discussion of Results

The effect of fines on retention depends on the three retention processes - fines onto fiber, particles onto fiber, and particles onto fines. Apparently, the

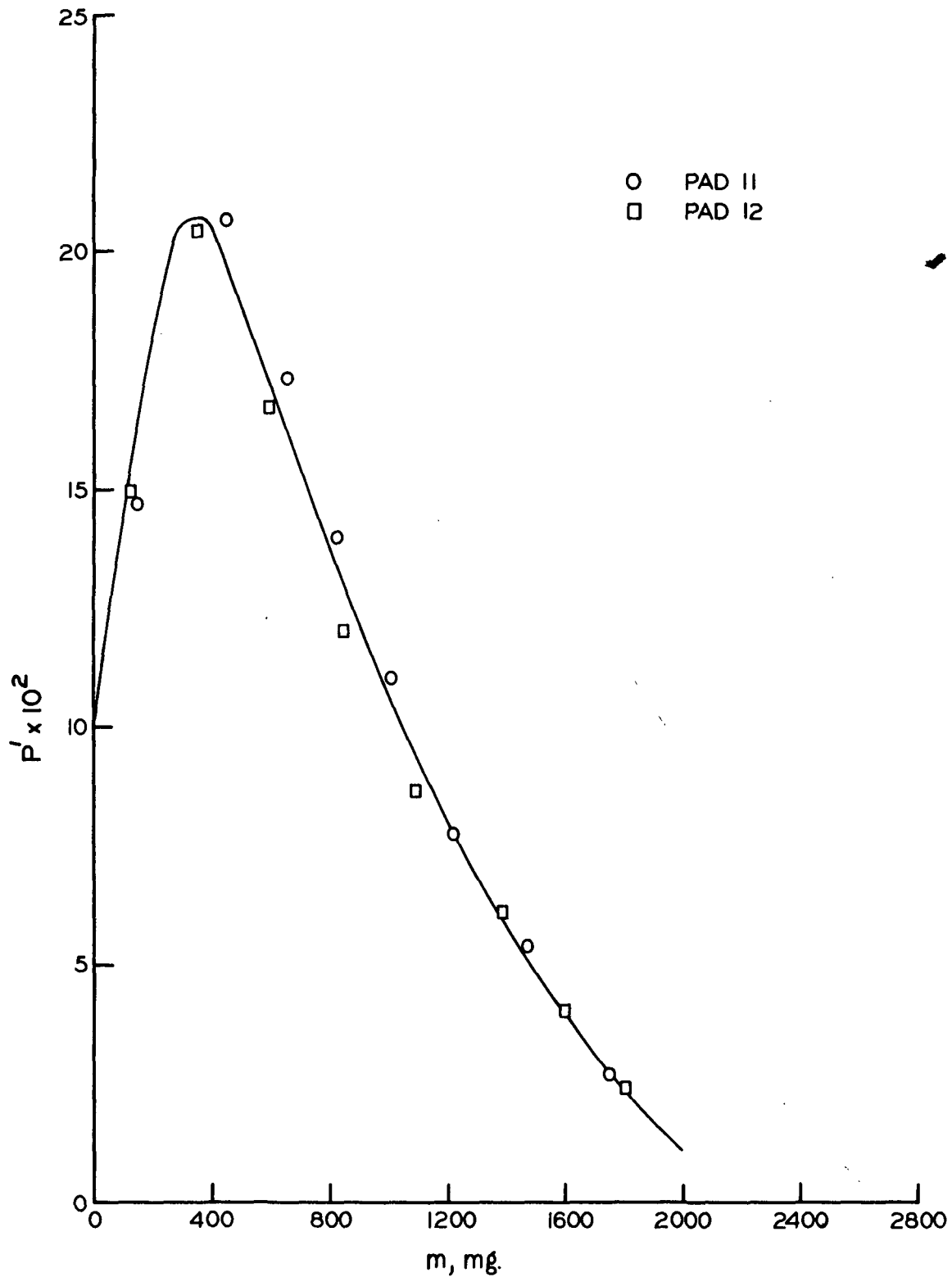


Figure 11. Bound Particle Distributions for Pads 11 and 12

best results are obtained when the fines have an opportunity to be retained by the fibers before particle retention occurs. An increase in retention effectiveness was found in the filtrations and in the permeations where fines were introduced during mat formation. In both cases, there was a good opportunity for fines to attach to the fiber surface. The increased surface area due to fines retention is apparently responsible for the increase in particle retention. When fines and particles were mixed together and then both permeated through a pad, retention was reduced. Apparently, a sufficiently large amount of particles were retained on the fines, and much of these fines were not retained by the fiber. In any event, it is clearly established that the mere presence of fines does not automatically result in improved retention.

The unique particle distribution obtained in Pads 11 and 12 can be explained in terms of the distribution of fines and the contribution of these fines to the total surface area of the pulp. Since the mat is formed by a filtration process, the fines concentration can be expected to increase from the surface toward the septum. Thus, the available surface area should increase in the same direction. This would tend to cause the retention rate to increase with increasing  $m$ . This is compensated for by the free-particle inventory. The free particle concentration will necessarily decrease as  $m$  increases, thus tending to cause the retention rate to decrease. The net result of these competing effects is a maximum in the bound particle concentration close to the mat surface.

The beating process itself increases the capacity of the fiber to retain even in the absence of the fines produced. This is clearly shown by Experiments 13 and 14 in which classified, beaten pulp was used. This is most probably due to the increase in the effective surface area of the fibers. There is reason to believe a proportionality exists between the effective retention rate constant,

$K_{RS}$ , and the hydrodynamic specific surface. Careful, systematic experiments would be required to demonstrate that a 1-to-1 correspondence exists between the hydrodynamic specific surface and the effective fiber surface for retention.

It is not known why the systems in which the artificial fines were used gave a relatively small effect compared to that obtained by beating. From the size distribution of the fines, their specific surface could be estimated to be on the order of  $10^6$  cm.<sup>2</sup>/g. The ratio of fines to fibers in these experiments was 0.25 g./10 g.; thus the specific surface of the fines per unit mass of fiber should have been on the order of 25,000 cm.<sup>2</sup>/g. Apparently, there was relatively little retention of the artificial fines. Why the artificial fines should have acted so differently from natural fines is not known. The experiments did demonstrate the complications which fines can introduce. They illustrate the complexity of the retention process on a paper machine. It is also clear that systematic experiments using the constant-rate filtration technique to study retention fundamentals should be performed on classified pulps.

#### PARTICLE SIZE

The size of the particles can potentially have a large effect on retention behavior. If this is the case, the particle size distribution is a significant parameter in any study of retention, and the theory of retention must be extended to include the effect of particle size. Particle size can be a very fundamental variable. The rate-controlling step could be size dependent. It is already known that particle transport rates, and even the particle transport mechanisms, are size dependent. Size could also be a factor in the physicochemical processes occurring at the fiber-particle interface. A few pages back, it was hypothesized that particle size may be very important in removal. Since all real particle systems consist of a distribution of particle sizes, the effects of such distributions on retention

must be examined. Most measurements of retention are macroscopic, e.g., the total mass of particles retained in a finite increment of the mat. If particle size is a significant variable, these macroscopic observations are subject to misinterpretation. For these reasons, a preliminary investigation of the effect of particle size on retention was made in this study.

#### Experimental Procedure

The size distributions of particles upstream and downstream of the pad in a permeation experiment were measured. Permeation was used to avoid the interference of the fibers in the particle size determination. In principle, the experiment was simple. Comparison of the particle size distribution upstream and downstream of the mat would supplement the data obtained from splitting the pad.

A Coulter Counter was used to measure the size distribution of the  $\text{TiO}_2$  particles in suspension. This is an electronic device which counts particles of particular sizes. The particles are suspended in an electrolyte and are caused to pass through a 30  $\mu\text{m}$ . aperture essentially one at a time. The change in electrical resistance between two electrodes on opposite sides of the aperture causes a signal to be put out which is proportional to the volume of the particle. The instrument has a counting circuit which can be set to count all signals greater than a given size. By varying this threshold setting and by calibrating against particles of known size, the number of particles in a very small aliquot greater than a preselected size can be counted. By running counts at several thresholds, a complete particle distribution curve can be rapidly measured.

The nature of the Coulter Counter introduced several complications in making the size distribution measurements. There were two major problems: the tendency of the aperture to plug and the need for a high-conductivity electrolyte. The first was mainly an operational problem and could be minimized by keeping the

apparatus and all fluids used very clean. The second was very troublesome because of the tendency for the  $\text{TiO}_2$  particles to flocculate in the electrolyte. The sensitivity of the instrument is increased by increased electrolyte conductivity, and best accuracy and range were obtained with a 4% (by weight) saline solution. This increased the difficulty with particle flocculation. Since the Coulter counts all particles it sees, not only the  $\text{TiO}_2$ , it was necessary to adopt an experimental procedure which excluded all extraneous particles and which minimized aperture plugging and particle flocculation in the Coulter Counter.

The following procedure was adopted. The flow system of the permeation cell was modified slightly so that a sample of the suspension which had passed through the pad could be accumulated and removed from the system without disturbing the permeation. The distilled water which was used in making up the suspension was passed through a Millipore filter to remove any extraneous particles. The suspension was then made up according to the usual procedure. The permeation proceeded in the usual fashion. A sample of the upstream suspension was taken at the start of the permeation. A sample of the downstream suspension was taken after the permeation had proceeded for 800 seconds. This allowed enough time to complete the size analysis of the upstream sample.

After the sample was taken, 171 cc. of suspension was put in the analysis beaker with 10 drops of hypochlorite-oxidized starch. The starch solution was prepared on the same day as the experiment and was passed through a Millipore filter to remove colloidal starch particles. The suspension plus starch was stirred gently and allowed to set for several minutes. Then 29 cc. of 24% NaCl solution (which also had been Millipore filtered) was added, and the size analysis begun immediately. About 10 minutes were necessary to obtain the complete distribution. The starch acted as a peptizing agent and prevented the  $\text{TiO}_2$  from flocculating in

the counter. Periodic checks of count stability at specific size levels were made to ensure against flocculation affecting the count.

The above procedure was used for both the upstream and downstream suspensions. The use of a large aliquot of suspension and addition of a fixed amount of concentrated salt provided for a reasonably large count of  $TiO_2$  particles and put the upstream and downstream count on a common basis. In addition, a blank run was made without any  $TiO_2$  present to provide a background count. The blank followed the same procedure as the suspension measurements.

#### Result of Experiment

The results of the experiment are presented in Table IX. The upstream particle size distribution was measured just before that start of the permeation, and again after the permeation was completed. The downstream size distribution was measured 800 sec. after the start of the permeation. Examination of the data in Table IX indicates that over a portion of the size region the blank count is higher than the count of particles measured downstream of the pad. This introduces a large uncertainty in interpreting the data. Since the blank was measured on a sample of liquid taken upstream of the pad before any  $TiO_2$  was introduced into the system, it was felt that the discrepancy could be due to extraneous particles in the water which are removed by the fiber mat during the permeation. It proved impossible to check this experimentally by running a downstream blank as well as an upstream blank. This was because a marked deterioration in the quality of the distilled water supply due to organic loading in the late summer prevented further experiments.

The crucial question with regard to the blank correction is to decide where the particles occurring in the blank come from. If their source is the starch solution or concentrated NaCl solution, a blank correction would have to be made.

On the other hand, if they are particles in the water which tend to be removed by the fiber mat, no blank correction need be made. Since the starch solution and the 24% saline are both filtered twice through a 0.43  $\mu\text{m}$ . Millipore filter, while the distilled water supply to the suspension is passed once through a 1  $\mu\text{m}$ . Millipore filter, it is reasonable to assume that the water is the main source of the blank. Hence, the blank is ignored in analyzing these data. It is felt that these data are reasonably representative of the actual behavior of the system. These are difficult experiments to perform. The one reported here was the only successful one out of three attempts.

TABLE IX  
PARTICLE SIZE DISTRIBUTION MEASUREMENTS

Size, $\mu\text{m}$ . <sup>3</sup>	Upstream $\text{TiO}_2$ , before	Upstream $\text{TiO}_2$ , after	Downstream $\text{TiO}_2$	Blank
3.23	124.5	209	88.5	--
2.29	163	216.5	120	144
1.614	251.5	299	161.5	--
1.145	342.5	463	222.5	309
0.807	588.5	677	339.5	--
0.573	1,050	1,253	510	639.5
0.404	3,119	3,388	786	--
0.286	11,349	12,276	2,064	2,029
0.202	25,540	26,865	3,020	2,232
0.143	55,986	55,650	4,800	3,406

The analysis of the effect of particle size on retention behavior is based on the simple first-order rate function, where the solution for free particles is

$$P = P_0 e^{-K_R S_m / \rho_w A U} \quad (46).$$

For particles of a particular size range,  $\sigma$ , this equation can be written

$$P_{\sigma} = P_{0\sigma} e^{-K_R(\sigma)Sm/\rho_w AU_0} \quad (47)$$

where  $P_{\sigma}$  is the mass of free particles in the  $\sigma$  size range per unit mass of fluid. If the density of the fluid and particles are constant, and the size range is small enough that the particles can be assumed of one particular size, then Equation (47) also holds when  $P_{\sigma}$  is replaced by  $N_{\sigma}$ , the number of particles per unit volume of fluid in the  $\sigma$  size range. A distribution function  $Q(\sigma)$  can be defined as follows.  $Q(\sigma)d\sigma$  = number of particles per unit volume lying in the size range  $\sigma$  and  $\sigma + d\sigma$ . Then Equation (47) can be written directly in terms of the distribution functions.

$$\ln \left( \frac{Q_0(\sigma)}{Q(\sigma)} \right) = \frac{K_R(\sigma)Sm}{\rho_w AU_0} \quad (48).$$

Thus, a plot of  $\ln \{ [Q_0(\sigma)]/[Q(\sigma)] \}$  vs.  $\sigma$  ought to give the size dependence of the effective retention rate constant. Equation (48) was the basic equation used in analyzing the effect of particle size.

The method used to work up the data was as follows. The raw data (number of particles vs. particle volume) were plotted on log-log paper and smooth curves were drawn through the points. All further work was done on these smooth curves. Two quantities were then defined as follows:

$$\Delta_{in} = Q_0(\sigma)\Delta\sigma \quad \text{and} \quad \Delta_{out} = Q(\sigma)\Delta\sigma$$

where  $\Delta\sigma$  was taken to be  $0.1 \mu\text{m}^3$ . As many values of  $\Delta_{in}$  and  $\Delta_{out}$  as were desired were calculated from the smooth curves by reading the number at  $\sigma$  and subtracting the number at  $\sigma + 0.1 \mu\text{m}^3$ . From these values the ratio  $\Delta_{in}/\Delta_{out}$  and then  $\ln(\Delta_{in}/\Delta_{out})$  was calculated at various  $\sigma$ 's. A plot of  $\ln(\Delta_{in}/\Delta_{out})$  vs.  $\sigma$  is given in Fig. 12.

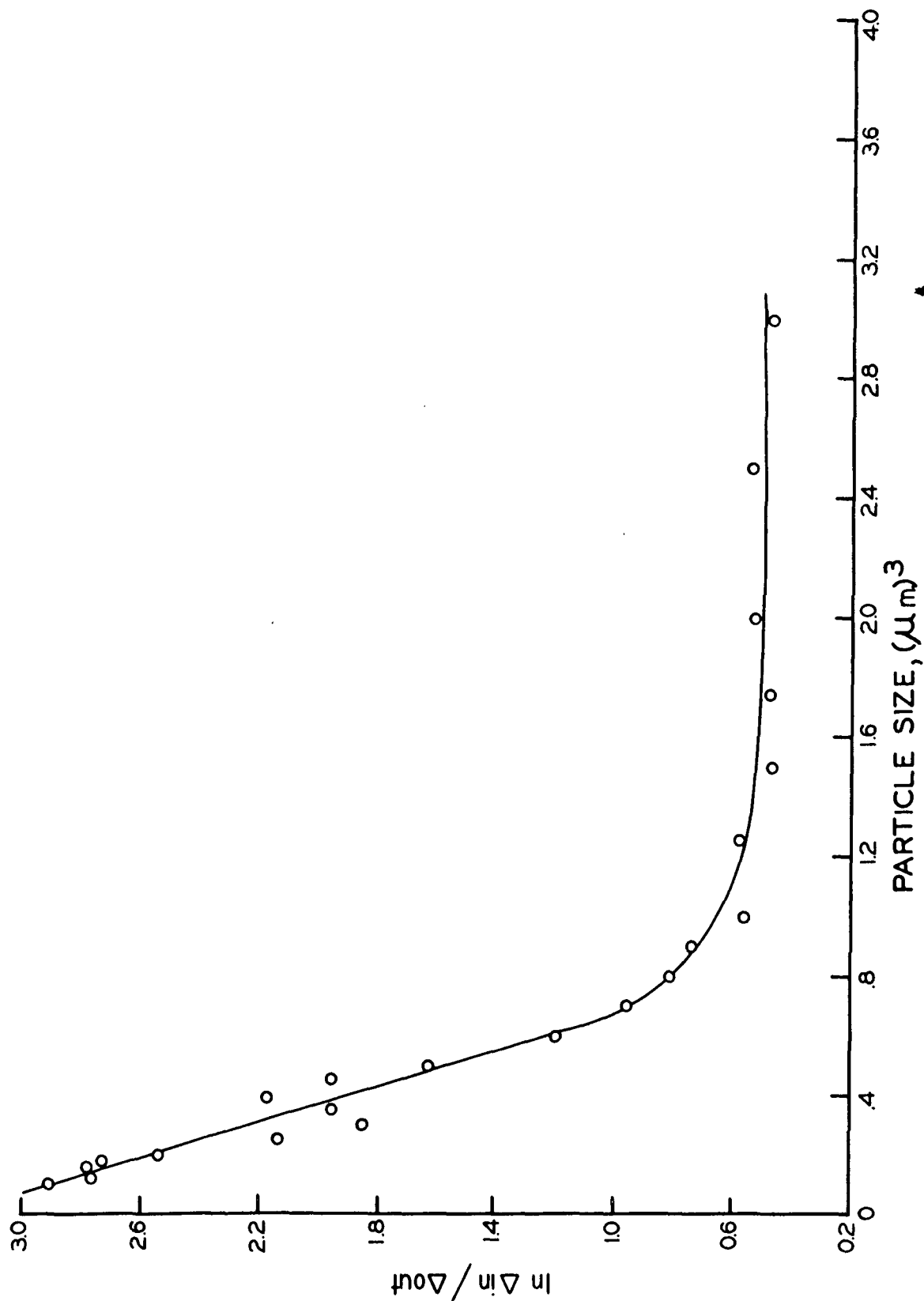


Figure 12. Effect of Particle Size on Retention Rate

Examination of Fig. 12 indicates that  $K_R(\sigma)$  increases sharply as the particle size is decreased. This increase is stronger than diffusion-controlled retention would give. This may be an indication that some removal of large particles in preference to small particles is occurring. The selective retention of small particles is clearly shown in Fig. 12. This curve conclusively shows sieving is not the retention mechanism in this system.

A good deal of information about the retention process can be obtained from measurements of the effect of retention processes on particle size distributions. The experiment discussed above is a relatively crude, initial attempt at incorporating size distribution measurements into retention studies. By refining the experimental techniques and by improving the analytical tools for handling particle size distributions a great deal more can be learned about retention.

#### FORMING VELOCITY

The data from which the effect of forming velocity is studied were presented last year in Report Two of this project (3). The data were taken on the dynamic drainage tester (DDT) and the experimental procedure is described in the old report. The data of interest were denoted as the A series. These were a series of constant-rate filtrations at fixed ionic levels and various values of the forming velocity. Forming velocity ranged from 8 to 35 cm./sec.

The particle distributions were highly curved, due in part to the prevalence of removal. Since only four points of the distribution curves were obtained, the rate-analysis procedure could not be used. Thus, a less sophisticated analytical method was required. The method used was to calculate an overall effective rate constant,  $K_{RS}$ , from the slope of an  $\ln(P_{\infty} - P')$  vs.  $m$  curve using

$$\ln (P_{\infty} - P') = - \frac{K_R S m}{\rho_w A U_o} + \ln (P_{\infty} - P'_o) \quad (49).$$

Linear regression lines of  $\ln (P_{\infty} - P')$  vs.  $m$  were run for the A series pads. Even though the data points were not extremely well fitted by the regression lines, the method is useful for determining the rough effect of forming velocity.

The results of the analysis are presented in Table X, and a plot of  $\ln \frac{K_R S}{\rho_w A U_o}$  vs.  $\ln U_o$  is shown in Fig. 13. All of the points for  $U_o > 10$  cm./sec. are reasonably well fitted to a straight line with a slope of about -0.6. The exception is the point at low velocity (8.23 cm./sec.), which is one full order of magnitude below the curve. From all appearances, this low-velocity pad is a valid point. It is not known whether the large difference between this point and the others is indicative of a change in attachment-controlling mechanism.

TABLE X  
EFFECTIVE RATE CONSTANTS FOR DDT DATA

Pad	Slope, mg. <sup>-1</sup> x10 <sup>4</sup>	$\frac{K_R S}{\rho_w A U_o}$ , sec. <sup>-1</sup>	$U_o$ , cm./sec.
1A1	-2.44	91.5	8.23
2A1	-2.91	195.5	14.7
3A2	-1.868	164.5	19.3
4A2	-1.304	144.0	24.2
5A1	-1.140	144.5	27.8
5A2	-0.957	121.5	27.8
6A1	-0.810	119.2	32.2
6A2	-0.849	125.2	32.2

The data at  $U_o > 10$  cm./sec. are well correlated by  
 $\frac{K_R S}{\rho_w A U_o} \propto U_o^{-0.6}$ .

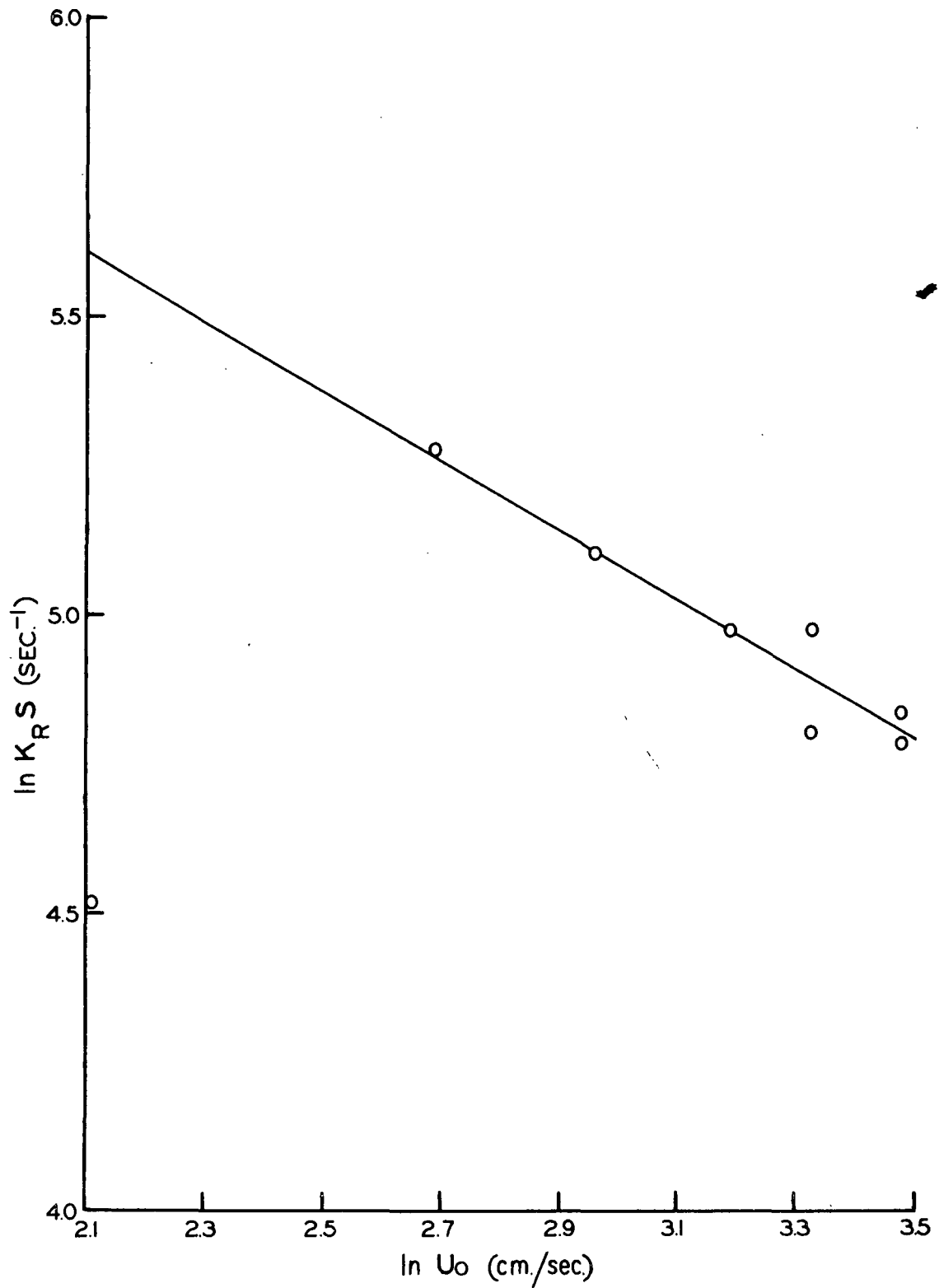


Figure 13. Effect of Velocity on Effective Retention Rate Constant

It is of interest that the effective rate constant can be represented by

$$K_R S \propto U_o^{-0.6} \quad (50).$$

In terms of the old collection efficiency concept, this would mean  $\underline{E}$  is proportional to  $\underline{U}_o^{-1.6}$ . This is a much more negative power than any particle transport mechanism would yield. The negative power dependence of  $\underline{K}_R S$  on  $\underline{U}_o$  is apparently due to the effects of particle removal. Since this method of getting  $\underline{K}_R S$  is such a crude way of handling the data, it is not possible to infer anything quantitative about removal from the power-law dependence of  $\underline{K}_R S$  on  $\underline{U}_o$ .

## GENERAL DISCUSSION AND CONCLUSIONS

### PRESENT STATE OF RETENTION THEORY

A comprehensive, quantitative theory of particle retention by fibrous mats is still a long way from realization. This study has uncovered some interesting facts about the retention process and should pave the way for further work in this area. The fundamental quantity in retention phenomena is the retention rate. This rate consists of two competing rates - that of attachment and that of removal. Present understanding of the attachment process is superior to that of removal.

#### Attachment

It is fairly well established that the attachment rate is first order with respect to the free particle concentration, at least for the hydrodynamic and colloidal conditions which were used. This is not a surprising finding. It is simply a quantization of the idea that the more free particles present, the greater the opportunity for some to be retained.

The attachment rate was also found to be a function of the bound particle concentration. In general, an increase in bound particle concentration led to an increased attachment rate at any given free particle concentration. This was a more surprising finding. The mechanism by which bound particles increase the rate of attachment is much more obscure than the interpretation of the first-order free particle dependence. The most apparent explanation is a preference for free particles to attach to bound particles rather than to the fiber surface. Some success was had in fitting a quadratic dependence on bound particle concentration to the attachment rate. This could be interpreted in terms of competing processes of attachment onto the fiber surface and onto other particles. The extent of applicability of the quadratic form is not known. More data are required to confirm such a dependence.

### Removal

The functional dependence of the removal rate is not presently known. The removal rate must be dependent on the bound particle concentration in some form since it is impossible to remove particles which are not bound to the fiber surface in the first place. The dependence of removal on bound particle concentration is not simply first order. Removal of particles seems to become much more important when a critical bound particle concentration is reached. The critical concentration appears to be a dynamic phenomenon which is dependent on the shear stress level in the pad. It is not a true saturation phenomenon in which the capacity of the fiber to hold particles is reached. The existence of the critical concentration means that not all bound particles are subject to removal at a given stress. This suggests examining the nature of the possible variations between bound particles. It is suggested that the critical bound particle concentration may be a manifestation of the size distribution of bound particles on the fiber.

### Limitations

Detailed knowledge of the retention rate and its components of attachment and removal is limited to a single forming velocity (1 cm./sec.) and a single colloidal condition ( $8.3 \times 10^{-4} M$  NaCl, pH 5.0, and  $TiO_2$  particles). Thus, any conclusions based on the forms of the rate functions must be considered tentative until confirmed over a wider range of parameters.

There were two major reasons why the range of parameters was so limited. The power of the rate-analysis technique in constant-rate filtrations was not realized until the experimental program was completed. When the power of the technique was realized, an attempt was made to apply it to the data obtained earlier and presented in Report Two (3). This attempt failed because the few data points per pad were insufficient to define the particle distribution curve with the required accuracy.

### Continuity

The applicability of the principle of continuity to retention behavior is firmly established. Treatment of the fiber mat as a continuum does not cause any serious difficulties. The use of the coordinate  $\underline{m}$  greatly simplifies the measurement and interpretation of retention behavior in a compressible fiber mat. The basic feature of compressibility, the spatial motion of the fibers in the mat, is completely taken care of by the coordinate  $\underline{m}$ . The major unaccounted-for feature of compressibility is the possible time and space dependence of the porosity,  $\epsilon$ . This will affect retention only if the retention rate itself is a strong function of porosity. The effect of fiber superficial velocity,  $\underline{U}_f$ , can be neglected. This is a minor factor compared to what is still unknown about retention.

The usefulness of the application of continuity principles to relate the measurable bound particle distribution to the fundamental retention rate is clearly established. The development of a simple technique for doing this opens the way for a greater understanding of the retention process.

### PRESENT NEEDS

#### Extension of Parameter Ranges

The analysis of the retention rate must be extended to cover a much wider range of parameters. The analysis must separate retention into attachment and removal in so far as possible. The parameters to be investigated must include the so-called colloidal variables as well as hydrodynamic variables. It is necessary to effect a marriage between the colloidal viewpoint and the hydrodynamic viewpoint of retention. There are many possible interactions between colloidal parameters and flow parameters. An example is the effect of the forming velocity on the thickness of the electric double layer, and hence on the repulsive barrier to

retention. Another example is particle removal. This involves a direct competition between a hydrodynamic shear stress and an attachment force which is physicochemical in nature.

The technique of analyzing the retention rate from the particle distribution in a constant-rate filtration is very suitable for an integrated study of colloidal and hydrodynamic variables. Such a study should include the effects of forming velocity, ionic environment, pH, and the use of alum and polymeric retention aids. It should be determined to what extent particle transport controls the rate of attachment, and if the theory of lyophobic colloids holds under the dynamic conditions of retention. It is critically important to differentiate between factors which influence the rate of attachment and factors which affect particle removal.

It must be demonstrated to what extent bound particles play a role in attachment. The quadratic dependence observed in the present study must be either confirmed or modified. A quantitative description of particle removal must be obtained. At the very least, a semiempirical function for the removal rate is necessary. The successful completion of the work discussed above is necessary before the retention theory can be realistically applied to the paper machine.

#### Particle Size

The effects of particle size on retention must be incorporated into the theory of retention. This would include the effects of size on attachment as well as removal. The more closely the retention problem is examined, the more it appears that particle size, and the distribution of particle size, is a very critical factor in retention behavior. Yet the effects of particle size have been generally neglected in retention studies. This knowledge gap concerning particle size must be closed.

The problem of particle size is twofold. An experimental problem exists concerning the measurement of particle size distributions under retention process conditions. The second problem is analytical and concerns the means of incorporating particle size distributions in a set of retention equations. Both are theory problems.

The experimental problem is basic and is essentially the reason why particle size has been a neglected parameter. The ultimate sizes of the particles are not necessarily germane to the retention process. Retention normally occurs under conditions which favor particle agglomeration. Thus, in general, it is necessary to measure the size distribution of particles in a dynamic, agglomerated system. The ideal method of measuring particle size distributions would be rapid, capable of measuring agglomerates without destroying them, and able to work directly in the particle environment. The Coulter Counter which was used in the present study does not meet all these requirements. The need for a highly conductive electrolyte in the Coulter Counter causes a good deal of difficulty with a particle system which tends to flocculate. To use a Coulter Counter for retention size distribution measurements would probably require modification of the instrument or of the measuring system. Other means of making the size measurements may be required.

The analytical problem involves deriving a set of retention equations which include the effects of particle size distribution. These equations would essentially replace  $\underline{P}$  and  $\underline{P}'$ , the free and bound particle concentrations, by particle size distribution functions for free and bound particles. These equations would involve three interrelated, independent variables -  $\sigma$ ,  $\underline{m}$ , and  $\underline{t}$  - instead of just  $\underline{m}$  and  $\underline{t}$  as at present. In the general form, the rate function would allow interactions between the free and bound particle distributions to account for such features

as particle flocculation, growth of bigger particles on the fiber surface, and selective removal of certain size ranges.

#### RELATION TO PRACTICE

The goal of studies of particle retention is to develop an understanding of retention fundamentals as an aid in improving retention on a paper machine. With regard to the paper machine, this reduces to providing answers to the following questions:

Does attachment occur primarily in the headbox, or during the sheet-forming process itself?

What is the rate-controlling step?

How can the rate of attachment be increased?

What level of shear stress removes the particles from the fibers and is this level exceeded on the paper machine?

Can resistance to removal be improved by the use of additives?

Answers to questions like these can best be provided from a better understanding of the nature of the retention process. Such an understanding is essential to obtaining optimum retention.

An immediate practical benefit would be obtained from the development of a simple retention behavior testing method applicable to machine conditions. Such a procedure could be used in the meanwhile as more fundamental knowledge is accumulated. It would remain useful as a control method even after retention has become more thoroughly understood. The constant-rate filtration technique looks promising as a possible testing method. It may be feasible for adaptation as a semiroutine test. A reasonable goal of any future work would be to develop a testing method to fill the present gap between simple handsheet tests and expensive mill trials.

### Particle Distributions on a Paper Machine

The ultimate test of any retention theory must be to predict the particle distributions which occur under actual papermaking conditions. The general form of these distributions have been adequately described by Groën (1). His findings were presented earlier in this report. In general, he found a relatively slight decrease in bound particle concentration proceeding from the top of the sheet toward the wire with a much sharper drop in particle concentration close to the wire. It is of interest to examine these distributions in the light of the present understanding of the retention process.

The dominant feature of the machine-made paper distributions is a decrease in  $P'$  with increasing  $m$ . This is exactly the opposite of what would be expected for a constant-rate filtration process. There are two possible suppositions to explain this decreasing dependence on  $m$  in terms of existing retention theory. One is to assume that essentially all of the attachment takes place in suspension, ahead of the wet end. The only significant action taking place on the wet end is the removal of particles due to drainage stresses and possibly washing at table rolls. Based on the known drainage conditions on the paper machine and the expected effect of forming velocity on removal, this is a reasonable interpretation of the experimentally measured distributions.

An alternative explanation assumes that significant attachment does occur on the wet end during sheet forming. The form of the final particle distribution is ascribed to the effect of the falling-rate-filtration nature of the sheet-forming process on the machine and the expected velocity dependence of the attachment and removal rates. All available evidence indicates that the importance of removal with respect to attachment increases with increasing velocity. Then a falling-rate filtration could conceivably lead to  $P'$  decreasing with increasing  $m$ . Rigorous

solutions to the retention equations for this case have not been developed because time effects cannot be neglected. Numerical solutions are premature until there is a better definition of the effect of velocity on attachment and removal.

It is impossible to choose between these two explanations on the basis of the experimental distributions alone. Yet it is very important to decide which actually describes the behavior on a paper machine. The reason is that the steps which would be taken to increase retention efficiency would be entirely different in each case. If attachment is essentially confined to the headbox, then better retention could be obtained simply by minimizing removal. On the other hand, if attachment occurs on the wet end, factors limiting the attachment rate would require adjustment. Thus, direct practical benefits would be obtainable if the particle distributions which occur on the paper machine can be explained.

#### CONCLUSIONS

The following statements summarize the major conclusions of the study.

1. A new technique involving mathematical analysis of the bound particle distribution curve from a constant-rate filtration has been developed. This technique allows a direct determination of local values of the retention rate as well as local values of free and bound particle concentrations. This technique should be a powerful tool in further studies of retention phenomena.
2. The retention rate is more complex than was previously suspected. The particle attachment rate is a function of bound particle concentration as well as first order in free particles. Preliminary indications suggest a quadratic bound particle dependence.

The removal rate is not a simple function of bound particle concentration. Removal becomes greatly increased when a shear-dependent critical bound particle concentration is exceeded.

3. The known complexity of retention phenomena was reinforced. In addition to effects of velocity and ionic environment previously known, the effect of fines and of particle size was shown to be important. This confirmed previous expectations.
4. The theory of retention has not yet progressed to the point where retention behavior on the paper machine can be predicted. The actual controlling phenomena on the paper machine remain subject to conjecture.

## NOMENCLATURE

$A$	= area of mat or sheet
$A_{\underline{i}}$	= coefficient in quadratic expansion
$a_0 - a_{\underline{t}}$	= regression coefficients
$B_{\underline{i}} - C_{\underline{i}}$	= coefficients in quadratic expansion
$E$	= collection efficiency
$K_A$	= attachment rate constant, $g. cm.^{-2} sec.^{-1}$
$K_D$	= removal rate constant, $sec.^{-1}$
$K_R$	= effective retention rate constant, $g. cm.^{-2} sec.^{-1}$
$L$	= distance from septum to mat surface, cm.
$M_{\underline{i}}$	= cumulative mass of fibers in first $\underline{i}$ layers, mg.
$m$	= fiber mass coordinate, cumulative from surface, mg.
$m_{\underline{i}}$	= mean $m$ of $\underline{i}$ th layer
$\Delta m_{\underline{i}}$	= mass of fibers in $\underline{i}$ th layer
$N_{\sigma}$	= number of $\sigma$ -sized particles per unit volume
$P$	= free particle concentration, mass particles/mass fluid
$P_0$	= free particle concentration in suspension
$P_{eq}$	= equilibrium free particle concentration
$P_{00}$	= total particle concentration, mass particles/mass fiber
$P'$	= bound particle concentration, mass particles/mass fiber
$P'_0$	= prepad retention; bound particle concentration in suspension
$P'_{eq}$	= equilibrium bound particle concentration
$P'_{cr}$	= critical bound particle concentration
$P'_{\underline{i}}$	= mean value of bound particle concentration in $\underline{i}$ th layer
$Q$	= particle size distribution function
$S$	= fiber specific surface, $cm.^2/g.$
$s$	= consistency, mass fiber/mass fluid

- $\Delta T_i$  = total mass of particles in ith layer, mg.
- $t$  = time, sec.
- $U_0$  = forming velocity, cm./sec.
- $U_{f,i}$  = fiber superficial velocity, cm./sec.
- $U_{w,i}$  = fluid superficial velocity, cm./sec.
- $U_{f,0}$  = fiber flux at septum, cm./sec.
- $U_{f,i}$  = fiber flux in suspension, cm./sec.
- $U_{w,i}$  = fluid flux in suspension, cm./sec.
- $x$  = dummy variable
- $z$  = position coordinate from septum, cm.
- $z'$  = dummy variable
- $\alpha_i$  = parameter which sets location of  $\underline{m}_i$
- $\beta$  = constant in assumed rate function
- $\gamma$  = constant in assumed rate function
- $\Delta_{in}$  = number of particles upstream of mat which lie between  $\sigma$  and  $\sigma + 0.1$
- $\Delta_{out}$  = same quantity downstream of mat
- $\Delta\sigma$  = particle size range,  $(\mu\text{m.})^3$
- $\epsilon$  = porosity
- $\epsilon'$  = porosity in suspension
- $\rho_f$  = fiber density, g./cc.
- $\rho_w$  = fluid density, g./cc.
- $\sigma$  = particle volume,  $(\mu\text{m.})^3$ ; also arbitrary size parameter
- $\varphi$  = retention rate,  $\text{sec.}^{-1}$
- $\varphi_A$  = attachment rate,  $\text{sec.}^{-1}$
- $\varphi_D$  = removal rate,  $\text{sec.}^{-1}$

Subscripts:

$\underline{i}$  =  $\underline{i}$ th fiber layer

$\underline{j}$  =  $\underline{j}$ th fiber layer

$\underline{N}$  = last fiber layer, wire side

$\sigma$  = the  $\sigma$  size range

Others:

$d$  = ordinary differential operator

$\partial$  = partial differential operator

$\overline{(\text{bar})}$  = time or space average

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LITERATURE CITED

1. Groën, L. J. Fundamental aspects of filler distribution in paper. In Formation and structure of paper (F. Bolam, ed.). Vol. II. London, Technical Section of British Paper and Board Makers' Association, 1962.
2. Han, S. T. The status of the sheet-forming process - a critical review. Appleton, Wis., The Institute of Paper Chemistry, Dec. 31, 1965.
3. Grace, T. M. Particle retention at high velocities in thin fiber mats. Progress Report Two, Project 2570. Appleton, Wis., The Institute of Paper Chemistry, May 10, 1967.

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APPENDIX I

DERIVATION OF RETENTION EQUATIONS

Assume that a fiber mat is being formed on a supporting septum from a system consisting of fibers, particles, and water. A spatial coordinate,  $z$ , can be defined with its origin at the septum. The mat grows in the plus  $z$  direction, and the suspension flows in the negative  $z$  direction. The process is assumed homogeneous in the other two space directions.

The retention rate,  $\varphi$ , can be defined as the net mass rate of particles becoming bound per unit mass of fibers. The dimensions of  $\varphi$  are mass of particles / (time x mass of fiber) or  $\text{time}^{-1}$ . With the retention rate describing the interchange between free and bound particles, differential material balances for fiber, water, free particles and bound particles can be formulated.

Application of the principle of conservation of mass to an incremental thickness of the mat results in the following equations.

$$\frac{\partial}{\partial z} \rho_f U_f = \frac{\partial}{\partial t} \rho_f (1 - \epsilon) \quad (51)$$

$$\frac{\partial}{\partial z} \rho_w U_w = \frac{\partial}{\partial t} \rho_w \epsilon \quad (52)$$

$$\frac{\partial}{\partial z} \rho_w U_w P = \frac{\partial}{\partial t} \rho_w \epsilon P + \rho_f (1 - \epsilon) \varphi \quad (53)$$

$$\frac{\partial}{\partial z} \rho_f U_f P' = \frac{\partial}{\partial t} \rho_f (1 - \epsilon) P' - \rho_f (1 - \epsilon) \varphi \quad (54)$$

where

- $\rho_f$  = fiber density,
- $\rho_w$  = fluid density (water),
- $U_f$  = superficial fiber velocity,

- $\underline{U}_w$  = superficial fluid velocity,  
 $\epsilon$  = interfiber porosity,  
 $\underline{P}$  = free particle concentration, mass/mass,  
 $\underline{P}'$  = bound particle concentration, mass/mass,  
 $\varphi$  = retention rate,  
 $\underline{t}$  = time, and  
 $\underline{z}$  = position up from system.

Equation (51) can be substituted into Equation (54) to yield

$$\rho_f U_f \frac{\partial P'}{\partial z} = \rho_f (1 - \epsilon) \frac{\partial P'}{\partial t} - \rho_f (1 - \epsilon) \varphi \quad (55),$$

and Equation (52) can be substituted into Equation (53) to give

$$\rho_w U_w \frac{\partial P}{\partial z} = \rho_w \epsilon \frac{\partial P}{\partial t} + \rho_f (1 - \epsilon) \varphi \quad (56).$$

If the two densities are constant (a reasonable assumption), Equations (51) and (52) can be combined to yield

$$\frac{\partial}{\partial z} (U_w + U_f) = 0 \quad (57)$$

with the solution,

$$U_w + U_f = U_0(t) \quad (58).$$

$\underline{U}_0$  can be interpreted to be the forming velocity and is at most a function of time.

Since fiber mats are in general compressible ( $\epsilon$  not constant), a fixed coordinate system is not very useful since it does not correspond to a specific layer in the mat. It is desirable to transform the retention equations to a coordinate system based on the mat itself. A convenient coordinate system to use is

the cumulative mass of fiber from the upper surface of the mat. This coordinate,  $\underline{m}$ , is defined in the following manner.

$$m = \rho_f A \int_z^L (1 - \epsilon) dz' = \rho_f A \int_0^L (1 - \epsilon) dz' - \int_0^z (1 - \epsilon) dz' \quad (59)$$

where  $\underline{L}(\underline{t})$  is the thickness of the mat at time  $\underline{t}$  and  $\underline{A}$  is the area of the mat.

In order to transform the continuity equations from the  $\underline{z}-\underline{t}$  coordinate system to the  $\underline{m}-\underline{t}$  coordinate system, the following transformation relations are required:

$$\frac{\partial}{\partial z} \rightarrow \left( \frac{\partial m}{\partial z} \right)_t \frac{\partial}{\partial m} = -\rho_f (1 - \epsilon) A \frac{\partial}{\partial m} \quad (60)$$

$$\frac{\partial}{\partial t} \rightarrow \left( \frac{\partial m}{\partial t} \right)_z \frac{\partial}{\partial m} + \frac{\partial}{\partial t} = \rho_f A \left[ \frac{d}{dt} \int_0^L (1 - \epsilon) dz - U_f + U_{f_0} \right] \frac{\partial}{\partial m} + \frac{\partial}{\partial t} \quad (61).$$

An overall fiber balance on the mat is used to determine the quantities within the brackets of Equation (61).

The fiber consistency,  $\underline{s}$ , is defined as the mass of fiber per unit mass of fluid in the suspension. The fiber flux in the suspension is

$$\rho_f U'_f = s \rho_w U'_w \quad (62).$$

If it is assumed that the suspension flows without slip, the porosity in the suspension is given by

$$\epsilon' = \frac{U'_w}{U'_0} = 1 - \frac{U'_f}{U'_0} = \frac{\rho_f}{\rho_f + s \rho_w} \quad (63)$$

and the fiber flux in the suspension is

$$\rho_f U'_f = \frac{s \rho_w \rho_f U'_0}{\rho_f + s \rho_w} \quad (64).$$

To be perfectly rigorous, the suspension fiber flux which should be used in the overall fiber balance is the flux relative to the surface of the mat. In that case,  $\underline{U}_o$  is replaced in Equation (64) by  $\underline{U}_o + (dL/dt)$ . However,  $dL/dt$  cannot be determined without a detailed knowledge of the porosity in the mat. For any reasonable suspension consistency,  $dL/dt$  will be very small compared to  $\underline{U}_o$ , and can thus be neglected.

The overall fiber balance on the mat is

$$\frac{s\rho_w\rho_f U_o}{\rho_f + s\rho_w} - \rho_f U_{f_o} = \frac{d}{dt} \int_0^L \rho_f (1 - \epsilon) dz \quad (65).$$

Substituting (65) into Equation (61) yields

$$\frac{\partial}{\partial t} + \rho_f A \left[ \frac{s\rho_w U_o}{\rho_f + s\rho_w} - U_f \right] \frac{\partial}{\partial m} + \frac{\partial}{\partial t} \quad (66).$$

Transforming Equations (55) and (56) gives

$$-\rho_f^2 U_f (1-\epsilon) A \frac{\partial P'}{\partial m} = \rho_f^2 (1-\epsilon) A \left[ \frac{s\rho_w U_o}{\rho_f + s\rho_w} - U_f \right] \frac{\partial P'}{\partial m} + \rho_f (1-\epsilon) \frac{\partial P'}{\partial t} - \rho_f (1-\epsilon) \varphi \quad (67)$$

$$-\rho_w U_w \rho_f (1-\epsilon) A \frac{\partial P}{\partial m} = \rho_w \epsilon \rho_f A \left[ \frac{s\rho_w U_o}{\rho_f + s\rho_w} - U_f \right] \frac{\partial P}{\partial m} + \rho_w \epsilon \frac{\partial P}{\partial t} + \rho_f (1-\epsilon) \varphi \quad (68).$$

Rearranging Equations (67) and (68) gives

$$\frac{s\rho_w \rho_f A U_o}{\rho_f + s\rho_w} \frac{\partial P'}{\partial m} + \frac{\partial P'}{\partial t} = \varphi \quad (69)$$

$$-\rho_w A \left[ U_o - \frac{U_f}{1-\epsilon} + \frac{\epsilon}{1-\epsilon} \frac{s\rho_w U_o}{\rho_f + s\rho_w} \right] \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f (1-\epsilon)} \frac{\partial P}{\partial t} + \varphi \quad (70).$$

These last two equations are the retention equations.

APPENDIX II

SPECIAL SOLUTIONS TO RETENTION EQUATIONS

The two retention equations are

$$\frac{s\rho_w\rho_fAU_o}{\rho_f + s\rho_w} \frac{\partial P'}{\partial m} + \frac{\partial P'}{\partial t} = \varphi \quad (71)$$

$$-\rho_w A \left[ U_o - \frac{U_f}{(1-\epsilon)} \frac{\epsilon}{(1-\epsilon)} \frac{s\rho_w U_o}{(\rho_f + s\rho_w)} \right] \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f(1-\epsilon)} \frac{\partial P}{\partial t} + \varphi \quad (72).$$

These two equations are the starting point in obtaining exact solutions for all three special cases.

The first case is for a constant-rate permeation with the retention rate taken to be first order in free particle concentration. In a permeation, the mat is formed first in the absence of particles. Normally, the mat is loaded to a constant porosity before being permeated with a suspension of particles. Since no fibers are present in the particle suspension,  $\underline{s} = 0$ . In addition, with the porosity constant or nearly constant,  $\underline{U}_f = 0$  or very nearly zero. Then, the retention equations become

$$\frac{\partial P'}{\partial t} = \varphi \quad (73)$$

and

$$-\rho_w AU_o \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f(1-\epsilon)} \frac{\partial P}{\partial t} + \varphi \quad (74).$$

As long as the conditions at  $\underline{m} = 0$  are constant (the boundary conditions) and  $\varphi$  and  $\underline{U}_o$  are time independent, there is nothing to cause  $\underline{P}$  to change with time. Thus,  $\partial P/\partial t$  can be neglected.

The retention rate is assumed to be

$$\varphi = K_R SP \quad (75)$$

where  $K_R$  is a retention rate constant and  $S$  = specific surface of fiber. Then, Equations (73) and (74) become

$$-\rho_w AU_o \frac{\partial P}{\partial m} = K_R SP \quad (76)$$

and

$$\frac{\partial P'}{\partial t} = K_R SP \quad (77)$$

with the boundary conditions  $P = P_o$  at  $m = 0$  and  $P' = 0$  at  $t = 0$ . The boundary conditions merely state that the free particle concentration at the surface of the mat equals the particle concentration in suspension, and that no bound particles are present until retention begins.

Equation (76) can be immediately integrated to yield

$$P = P_o e^{-K_R Sm / \rho_w AU_o} \quad (78).$$

Substituting (78) into (77) and integrating,

$$P' = K_R SP_o t e^{-K_R Sm / \rho_w AU_o} \quad (79).$$

The second case is for a constant-rate filtration with the same retention rate as in Case 1. In the constant-rate filtration ( $U_o = \text{constant}$ ), the mat-forming process occurs simultaneously with the retention process. The mat is formed from a suspension containing fluid, fibers, and particles. Thus,  $s$  has some finite value. If  $s$  is small compared to the consistency of the mat,  $U_f \ll U_o$  and  $\epsilon s \rho_w U_o / [(1-\epsilon)(\rho_f + s \rho_w)] \ll U_o$ . Furthermore, with  $s$  very small,  $s \rho_w / (\rho_f + s \rho_w) \approx s \rho_w / \rho_f$ . For this case,

Equations (71) and (72) reduce to

$$s\rho_w AU_o \frac{\partial P'}{\partial m} + \frac{\partial P'}{\partial t} = K_R SP \quad (80)$$

and

$$-\rho_w AU_o \frac{\partial P}{\partial m} = \frac{\rho_w \epsilon}{\rho_f (1-\epsilon)} \frac{\partial P}{\partial t} + K_R SP \quad (81)$$

with the boundary conditions  $\underline{P} = \underline{P}_o$  at  $\underline{m} = 0$  and  $\underline{P}' = \underline{P}'_o$  at  $\underline{m} = 0$  for all times  $\underline{t}$ . There is no initial condition since the mat does not exist until  $\underline{t} > 0$ . Since the suspension contains particles and fibers, retention by coflocculation can take place in suspension before the mat is formed.  $\underline{P}_o$  and  $\underline{P}'_o$  represent the free and bound particle concentrations in suspension, respectively. These are the concentrations which exist at the surface of the mat. If  $\underline{P}_o$  and  $\underline{P}'_o$  are constants and  $\varphi$  is time independent (at a given  $\underline{m}$ ), both time derivatives can be neglected. Then the equations become

$$s\rho_w AU_o \frac{dP'}{dm} = K_R SP \quad (82)$$

and

$$-\rho_w AU_o \frac{dP}{dm} = K_R SP \quad (83).$$

Combining (82) and (83) gives

$$\frac{d}{dm} (P + sP') = 0 \quad (84).$$

Therefore,

$$P + sP' = P_o + sP'_o = sP_{oo} \quad (85).$$

Equation (83) can be immediately solved, and again,

$$P = P_o e^{-K_R Sm / \rho_w AU_o} \quad (86).$$

Substituting (86) into (85),

$$P' = P_{\infty} - \frac{P_o}{s} e^{-K_R Sm / \rho_w AU_o} \quad (87)$$

or

$$P' = P'_o + \frac{P_o}{s} \left( 1 - e^{-K_R Sm / \rho_w AU_o} \right) \quad (88).$$

The third case is identical to Case 2 except that

$$\varphi = K_A SP - K_D P' \quad (89).$$

The retention equations become

$$s \rho_w AU_o \frac{dP'}{dm} = K_A SP - K_D P' \quad (90),$$

$$-\rho_w AU_o \frac{dP}{dm} = K_A SP - K_D P' \quad (91),$$

and

$$P + sP' = P_o + sP'_o = sP_{\infty} \quad (92).$$

Substituting (92) into (90) gives

$$s \rho_w AU_o \frac{dP'}{dm} = K_A S s (P_{\infty} - P') - K_D P' \quad (93).$$

This can be integrated with the boundary condition  $\underline{P}' = \underline{P}'_o$  at  $\underline{m} = 0$  to give

$$P' = \frac{K_A SP_{\infty}}{(K_A S + K_D/s)} \left[ 1 - e^{-(K_A S + K_D/s)m / \rho_w AU_o} \right] + P'_o e^{-(K_A S + K_D/s)m / \rho_w AU_o} \quad (94).$$

Since  $\underline{P}_{\infty} = \underline{P}'_o + \underline{P}_o/s$ , Equation (94) can be rewritten as

$$P' = P'_o + \frac{(K_A SP_o - K_D P'_o)}{(sK_A S + K_D)} \left[ 1 - e^{-(sK_A S + K_D)m / s \rho_w AU_o} \right] \quad (95).$$

With a retention rate of the form used in this case an equilibrium can be set up when the rate of attachment equals the rate of removal. At equilibrium,

$$K_A s P'_{eq.} = K_D P'_{eq.} = K_A S s (P_{oo} - P'_{eq.}) \quad (96).$$

Therefore,

$$P'_{eq.} = \frac{s K_A S P_{oo}}{s K_A S + K_D} = \frac{K_A S (P_o + s P'_o)}{s K_A S + K_D} \quad (97)$$

and

$$P'_{eq.} - P'_o = \frac{K_A S (P_o + s P'_o)}{s K_A S + K_D} - P'_o = \frac{K_A S P_o - K_D P'_o}{s K_A S + K_D} \quad (98).$$

Therefore,

$$P' = P'_o + (P'_{eq.} - P'_o) \left[ 1 - e^{-\frac{(s K_A S + K_D) m}{s \rho_w A U_o}} \right] \quad (99).$$

## APPENDIX III

PROCEDURE FOR OBTAINING  $\underline{P}' - \underline{m}$  DATA FROM INCREMENTAL  
 $\text{TiO}_2$  AND FIBER CONTENT

Bound particle distributions are defined by giving  $\underline{P}'$  as a function of  $\underline{m}$ . Experimentally, the quantities actually measured are  $\Delta T_{\underline{i}}$ , the mass of particles in the  $\underline{i}$ th layer of a delaminated pad, and  $\Delta m_{\underline{i}}$  the fiber content of the  $\underline{i}$ th layer. The following procedure was developed to reduce the  $\Delta T_{\underline{i}}$ ,  $\Delta m_{\underline{i}}$  data to sets of points of  $\underline{P}'$  and  $\underline{m}$ .

The average bound particle concentration in the  $\underline{i}$ th fiber layer starting from the mat surface is

$$\overline{P}_{\underline{i}} = \Delta T_{\underline{i}} / \Delta m_{\underline{i}} \quad (100).$$

If the cumulative fiber mass of the first  $\underline{i}$  layers is defined by

$$M_{\underline{i}} = \sum_{j=1}^{\underline{i}} \Delta m_j \quad (101),$$

Equation (100) can be written as

$$\overline{P}_{\underline{i}} = \frac{1}{M_{\underline{i}} - M_{\underline{i}-1}} \int_{M_{\underline{i}-1}}^{M_{\underline{i}}} P' dm \quad (102).$$

By the law of the mean, there then exists a value of  $\underline{m}_{\underline{i}}$  somewhere in the interval  $M_{\underline{i}-1} < \underline{m}_{\underline{i}} < M_{\underline{i}}$  at which  $\underline{P}'_{\underline{i}} = \overline{P}_{\underline{i}}$ . The problem of determining sets of  $\underline{P}'$  and  $\underline{m}$  then reduces to the determination of  $\underline{m}_{\underline{i}}$  for each  $\underline{P}'_{\underline{i}} = \overline{P}_{\underline{i}}$ .

The exact location of  $\underline{m}_{\underline{i}}$  in the interval will depend on the shape of the  $\underline{P}'$  vs.  $\underline{m}$  curve. This follows directly from Equation (102). A parameter,  $\alpha_{\underline{i}}$ , is defined by

$$m_{\underline{i}} = M_{\underline{i}-1} + \Delta m_{\underline{i}} / \alpha_{\underline{i}} \quad (103).$$

If  $\underline{P}'$  is a linear function of  $\underline{m}$ ,  $\alpha = 2$ . If  $\underline{P}'$  is curved,  $\alpha$  will have a different value. In order to proceed, the assumption is made that the  $\underline{P}' - \underline{m}$  curve can be fitted by a quadratic function over each interval:

$$P' = A_i x^2 + B_i x + C_i \quad (104).$$

Then Equation (102) can be written as

$$P'_i = \frac{1}{\Delta m_i} \int_0^{\Delta m_i} (A_i x^2 + B_i x + C_i) dx \quad (105).$$

Carrying out the integration of Equation (105) and equating it to Equation (104) with  $\underline{x} = \frac{\Delta m_i}{\alpha_i}$  yields

$$\alpha_i = \frac{B_i \pm \sqrt{B_i^2 + 4A_i \Delta m_i \left[ \frac{A_i}{3} \Delta m_i + \frac{B_i}{2} \right]}}{2 \left[ \frac{A_i}{3} \Delta m_i + \frac{B_i}{2} \right]} \quad (106).$$

In order to use Equation (106) to calculate  $\alpha_i$  [from which  $\underline{m}_i$  is obtained by Equation (103)], the coefficients  $\underline{A}_i$  and  $\underline{B}_i$  must be known. These are determined by fitting the quadratic function to the three sets of points -  $(\underline{P}', \underline{m})_{i-1}$ ,  $(\underline{P}', \underline{m})_i$ , and  $(\underline{P}', \underline{m})_{i+1}$ . At the two extreme ends of the pad, the last three points are used. Thus, at the surface, Sets 1, 2, and 3 are used, and at the septum, Sets N-2, N-1, and N are used. The equations for the coefficients are:

$$A_1 = \frac{\overline{P}'_1}{(m_2 - m_1)(m_3 - m_1)} - \frac{\overline{P}'_2}{(m_2 - m_1)(m_3 - m_2)} + \frac{\overline{P}'_3}{(m_3 - m_1)(m_3 - m_2)} \quad (107),$$

$$B_1 = \frac{-\overline{P}'_1(m_2 + m_3)}{(m_2 - m_1)(m_3 - m_1)} + \frac{\overline{P}'_2(m_1 + m_3)}{(m_2 - m_1)(m_3 - m_2)} - \frac{\overline{P}'_3(m_1 + m_2)}{(m_3 - m_1)(m_3 - m_2)} \quad (108);$$

for the intermediate layers,

$$A_i = \frac{\overline{P'_{i-1}}}{(m_i - m_{i-1})(m_{i+1} - m_{i-1})} - \frac{\overline{P'_i}}{(m_{i+1} - m_i)(m_i - m_{i-1})} + \frac{\overline{P'_{i+1}}}{(m_{i+1} - m_i)(m_{i+1} - m_{i-1})} \quad (109),$$

$$B_i = \frac{-\overline{P'_{i-1}}(m_{i+1} + m_i - 2M_{i-1})}{(m_i - m_{i-1})(m_{i+1} - m_{i-1})} + \frac{\overline{P'_i}(m_{i-1} + m_{i+1} - 2M_{i-1})}{(m_{i+1} - m_i)(m_i - m_{i-1})} - \frac{\overline{P'_{i+1}}(m_i + m_{i-1} - 2M_{i-1})}{(m_{i+1} - m_i)(m_{i+1} - m_{i-1})} \quad (110);$$

and for the last layer,

$$A_N = A_{N-1} \quad (111);$$

$$B_N = \frac{-\overline{P'_{N-2}}(m_N + m_{N-1} - 2M_{N-1})}{(m_{N-1} - m_{N-2})(m_N - m_{N-2})} + \frac{\overline{P'_{N-1}}(m_{N-2} + m_N - 2M_{N-1})}{(m_N - m_{N-1})(m_{N-1} - m_{N-2})} - \frac{P'_N(m_{N-1} + m_{N-2} - 2M_{N-1})}{(m_N - m_{N-1})(m_N - m_{N-2})} \quad (112).$$

All of the values of  $\overline{P'_i}$  are directly calculated from the original data by Equation (100). In order to start the procedure, an initial set of values of  $\underline{m}_i$  are needed. These are obtained by assuming  $\alpha = 2$ . Then the various values of  $\underline{A}_i$  and  $\underline{B}_i$  are computed,  $\alpha_i$  is determined, and a new set of  $\underline{m}_i$ 's obtained. This procedure is then repeated until each value of  $\underline{m}_i$  agrees with its previous value within 1 mg.

APPENDIX IV

PROCEDURE FOR RATE ANALYSIS OF FILTRATIONS

For a constant-rate filtration, the two key relationships are

$$\varphi = s\rho_w AU_o \frac{dP'}{dm} \quad (113)$$

and

$$sP' + P = sP_{oo} = P_o + sP'_o \quad (114).$$

The rate analysis procedure determines local values of  $\varphi$ ,  $\underline{P}$ , and  $\underline{P}'$  from the bound particle distribution data. This procedure is described as follows.

The basic data are the set of  $(\underline{P}', \underline{m})$  points obtained from the raw data by the procedure described in Appendix III. The first step is to fit these points to a fourth-order polynomial,

$$P' = a_o + a_1 m + a_2 m^2 + a_3 m^3 + a_4 m^4 \quad (115).$$

The five regression coefficients were determined from a least-squares fit of the data. The program which determined the coefficients also plotted the curve and the original data points so that the goodness of the fit could be judged. In all cases, excellent fits with no snaking were obtained. All further calculations were done in terms of the polynomial, Equation (115).

For any given experiment,  $\underline{P}_{oo}$ ,  $\underline{s}$ ,  $\underline{\rho}_w$ ,  $\underline{A}$ , and  $\underline{U}_o$  were known from the initial suspension make-up and the forming conditions. At any desired  $\underline{m}$  within the range of the original data,  $\underline{P}'$  is calculated from (115). The free particle concentration is calculated from

$$P = s(P_{oo} - P') \quad (116).$$

The retention rate,  $\varphi$ , is found from Equation (113) with

$$\frac{dP'}{dm} = a_1 + 2a_2m + 3a_3m^2 + 4a_4m^3 \quad (117).$$

$\varphi$  is, of course, calculated at the  $\underline{m}$  values which were used to calculate  $\underline{P}'$ .

APPENDIX V

PROCEDURE FOR RATE ANALYSIS OF PERMEATIONS

In the case of permeations, the analysis is made in terms of time-averaged quantities. The key relationships are:

$$\bar{\varphi} = P'/t \quad (118)$$

and

$$\bar{P} = P_o - \frac{1}{\rho_w AU_o t} \int_o^m P' dx \quad (119).$$

The ratio of these two quantities was widely used in the data analysis:

$$\frac{\bar{\varphi}}{\bar{P}} = \frac{\rho_w AU_o P'}{\rho_w AU_o t P_o - \int_o^m P' dx} \quad (120).$$

The basic distribution data were fitted to a polynomial by the procedure described in Appendix IV. All calculations were based on the polynomial.

$$\int_o^m P' dx = m(a_o + \frac{a_1 m}{2} + \frac{a_2 m^2}{3} + \frac{a_3 m^3}{4} + \frac{a_4 m^4}{5}) \quad (121).$$

At any particular  $m$ ,  $P'$  was calculated from Equation (115),  $\bar{\varphi}$  from Equation (118),  $\bar{P}$  from Equation (119), and  $\bar{\varphi}/\bar{P}$  from (120).