A STUDY OF THE COLLOIDAL AND PHYSICAL PHENOMENA
RELATING TO FREENESS AND STOCK DRAINAGE

A thesis submitted by

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INTRODUCTION AND PRESENTATION OF PROBLEM

The freeness tester in its various forms was designed in response to a demand for an instrument which would measure the "wetness" of pulp prepared for the paper machine. The terms "freeness," "slowness," and "wetness" have long been used in the paper industry to describe one of the properties or conditions of a pulp. These terms have been more or less loosely used, although their meaning is generally understood. They attempt to describe the drainage of water from fibers while they are being felted into a sheet of paper. A "free" pulp allows rapid drainage, whereas a "slow" pulp retards the drainage of water from the fibers. "Freeness" and "slowness" are therefore antonyms. "Wetness," on the other hand, is a more general term including both ends of the scale of measurement.

Since the rate of drainage of water from stock suspension is directly connected with allowable machine speed and, also, since freeness is used to indicate the condition of the pulp, an investigation of the factors controlling the drainage of water from stock could be of decided value. Moreover, existing testers have been found lacking as a measure of the rate of drainage or of the condition of the stock.

The property of freeness has been specifically defined many times, usually in terms suited to a particular freeness tester. This thesis attempts to describe freeness with respect to drainage of stock on a Fourdrinier wire. Since existing testers have faults inherent in the instruments in the light of this definition of freeness, the design of an instrument which simulates drainage of stock on a wire is demanded.

Thus, this study will have a three-fold purpose;

1. The development of an instrument for the study of drainage.

2. A study of existing testers.

3. An investigation of some of the factors affecting drainage.

HISTORICAL REVIEW

The drainage of water from a stock suspension has long been recognized as a characteristic of great importance but its measurement in numerical terms has been rather difficult. For a number of years the inability of any simple freeness test to fully characterize a pulp has become more and more accepted. If the freeness test accurately describes the rate of drainage of water from fibers as those fibers are being felted on the wire of a Fourdrinier machine, the test has definite value as a measure of one nonfundamental pulp property. However, there still exists in the industry an exaggeration of the value and meaning of freeness and a tendency to accept the freeness value as indicative of a definite stock condition. The freeness test is used in the mill as a beating control and to prophesy the behavior of stock on the machine and in the laboratory, in combination with laboratory refining equipment, to predict the behavior of a pulp in the beater room and on the machine.

ORIGIN AND DEVELOPMENT OF FREENESS TESTING

A survey of the development of freeness testing gives a hint of the difficulties encountered in attempting to measure the drainage of water from stock. Good discussions of the development of freeness testing are given by Clark (1) and Green (2).

In 1907 Klemm (3) was granted a German patent for the first sedimentation tester. This device is essentially a graduated glass tube covered by a wire screen on one end and a quick opening cap. The volume occupied by the completely drained fibers is used to indicate the degree of beating. Klemm thus takes advantage of the fact that beaten fibers form a more compact sheet than unbeaten fibers.

Skark (4) pointed out the disadvantages of the Klemm tester. He stated that the instrument works best on free stocks but is of doubtful value on slow stocks. A slow stock, it was pointed out, has a very long drainage time, and forms a meniscus at the surface, making it difficult to read the volume. He then described his own instrument, which consists of a vertical cylinder with a wire cloth on the bottom. The outflowing water is discharged into a graduate. The total volume of outflow is measured at definite time intervals. Skark (5) later offered a recording mechanism to plot automatically the curve of discharge volume versus time for his apparatus.

In 1913, Schopper (6) described a new apparatus for determining the degree of beating. This instrument (patented by Schopper and Riegler) has, as its most important part, a cone with two discharge orifices of different size which are placed at different levels. The sudden rush of water with free pulps is discharged from both orifices, whereas with a slow pulp almost all of the water is discharged from the smaller, lower one. In this way a means was provided for separating the water which drains rapidly from that which drains more slowly. The volume of the rapidly drained water is recorded as a numerical indication of the degree of beating and the rate of drainage.

The same principle was used by Green (7) in his original tester which he has since modified several times. The principle and operation have remained the same, although the dimensions and, hence, the scale of values have been changed.

In 1915, the use of the Mullen tester as a freeness tester was suggested by Cyster (8). The diaphragm is removed, the glycerol chamber filled with pulp, and the pressure required to drive the water through the pulp pad is determined.

Fishburn and Weber (9) published a paper in 1916 describing a drainage tester for groundwood pulp. The operation of this tester embodies measuring the time for the discharge of a given volume. A tester similar to the Fishburn-Weber apparatus was described (10) in 1917, and, in the same year, Kress and McNaughton (11) proposed the use of a homemade tester of the same type. They stated that the reliability of the instrument as an indication of the beating treatment is exceedingly questionable. Their study pointed out the limitations of this type of tester. The main limitation was felt by most workers to be overcome by the invention of the divided-funnel type tester. This is best expressed by Green (12) in the following statement: ".... then the Schopper-Riegler patent was published. A very simple trick had been devised by these men in Austria whereby the elusive end point of the draining test, with which we have been struggling, was made definite and extremely delicate."

In 1919, the Canadian Forest Products Laboratories undertook the design of a standard freeness test. This group made a study of freeness testing and as a result adopted the Schopper-Riegler principle. According to Cameron (13), the chairman of the committee in charge of this program, it was decided that no other instrument had sufficient advantages over the above type with which the industry was familiar. The Canadian freeness tester, which was designed as a standard tester by this group, followed the general lines of the Green and Schopper-Riegler instruments. Both the Green and Canadian testers are designed to give a greater distinction between well beaten pulps. A description of the standardized apparatus is given by Cameron (14).

Williams (15) brought out his first freeness tester in 1920. This instrument was based on the divided-funnel principle. In 1925 Williams (16) brought out his "50-50 tester" which was again of the same type but of slightly different construction. The instrument was again modified in 1927 (17) to give a larger range of values and a better distinction between pulps. Williams, since then, has brought out a slowness tester of the sedimentation or drainage-time type. This instrument, the Williams precision tester, is described by Davis (18).

Boehm (19) modified the Schopper-Riegler instrument by increasing the total volume. This was shown to give the instrument a greater sensitivity for very free stocks. Thus Boehm's modification of the divided-funnel type has done for the higher range of freenesses what Green had already accomplished for the more thoroughly beaten stocks.

A different type freeness tester was introduced by Campbell (20) in 1927. This tester allows water to flow by gravity under a constant head through a layer of pulp on a wire. The water builds up to a definite level above the pulp pad depending upon the resistance of the pad to the flow of water through it. This instrument was redesigned by Carpenter and Schafer (21) in such a way that the water level over the pulp pad was kept constant and the rate of flow through the pad was measured. An equation has been worked out to express the rate of variation of flow, and constants of the equation define the characteristics of the pulp.

The Paper Makers' Association of Great Britain and Ireland developed a standard sheetmaking apparatus and specified a standard method of sheet forming and strength testing. They also suggested a method for determining freeness with this instrument. According to Clark (22), the use of the British sheetmaking equipment for determining the time of drainage of a pulp is accurate, and the results have been found to be more in accord with results on the paper machine than determinations by any other method. Campbell (23) discussed the use of drainage time on the British sheet machine as a freeness measurement. He later proposed the determination of a drainage factor by the use of the drainage time of two test samples of different weights. This factor is determined by dividing the difference of the times of drainage (for two definitely different readings) by the difference in the weights of the samples. The quotient expressed as seconds per gram is far less affected by the loss of fines than the straight drainage time. This method is also explained by Sankey (24), who urged the adoption of the British methods. The determination of drainage time and drainage factor has now been tentatively accepted as a TAPPI standard as an addenda to the sheet making standard procedures.

Gartshore (25) claimed that the freeness test does not indicate running conditions on the paper machine. He proposed a tester embodying a suction of 5 cm. of mercury acting beneath the wire. His instrument gives a wetness figure defined as the time interval from the beginning of drainage to the disappearance of water through the pad. Campbell (26) criticized the method, in that it duplicates the effect of suction boxes rather than the drainage prior to this point. He stated that the drainage test as run on the British sheet machine with 3 cm. of mercury vacuum is fairly comparable with the Gartshore test. However, this objection is in direct contradiction to his article (27) in which he considers the forces exerted by the machine to cause water removal. In this article Campbell calculated an effective suction of about 20 cm. of water acting through the wire and effecting drainage before the suction boxes are reached.

Besides the above-mentioned testers there are several designs of instruments for the estimation of the degree of beating in the beater room. There are also several devices for automatic freeness recording. Many workers have expressed freeness in terms of pulp constants of one sort or another, which they have derived through a mathematical treatment of some type.

The drainage-type tester is generally conceded to be, excluding the human error in determining the end point, the more reliable tester. The divided-funnel type tester is considered to be more convenient and faster to operate, although it is, at best, even more empirical than the drainage type. However, its proponents state that it has a wider range of sensitivity and a definite and sharp end point. Green (2) pointed out that the drainage testers have a limited range of sensitivity without changing testing conditions. He, however, admitted that the divided-funnel type could be improved for very free or very slow pulps by a slight modification of testing conditions. The divided-funnel type tester is felt to be a standardized form which will allow different laboratories to duplicate results. Campbell (23) pointed out, and many others in the field agree, that the British sheet machine drainage time is more nearly in accord with drainage on the paper machine than any other tester. The pressure causing drainage on the machine (produced chiefly by the suction effect of the table rolls) is more nearly duplicated by the British sheet machine than by any of the freeness testers.

Both types of testers are felt to have errors which cause deviation in results from actual machine behavior. The following deviations from machine conditions have been mentioned: high head, passage of fines through the wire (the amount of fines passed through the wire is insufficient when the head-box stock is being tested, and is too large if jordan stock is being tested; jordan stock is essentially the same in composition as the finished paper, whereas head-box stock contains also the fine material which passes through the wire on the machine and is added in the white water), nonuniformity of the suspension concentration (floating and settling of stock), compression head above the pulp pad, absence of suction beneath the wire, long period of drainage, consistency at the end point far below that of drained stock on the machine, and the resistance to drainage and flow offered by the instrument itself. One fault found with freeness testing in general has been the inversion of results between two types of testers. A pulp may appear to be freer than another on one tester and slower on a second tester. Comparative charts of the readings at different stock conditions on the different testers have been made, but their value is partially lost because of this characteristic of the various instruments.

VARIABLES AFFECTING DRAINAGE

There are a great number of variables which affect the rate of drainage of water from fibers felting on a wire. Many of these have been investigated or at least recognized. These variables are most readily classed as machine or experimental variables and as stock or furnish variables. The former class includes such factors as temperature, head above the wire, consistency, sheet weight, wire size, effective suction pressure--time, machine speed, number and size of table rolls, size of the breast roll, and the relative position of the apron and the breast roll--, the shake of the machine, the head above the slice, the amount of fines passed through the wire, and the amount of reuse of white water. The furnish variables include the following: degree and character of refining, fiber size distribution regarding length and width, fibrillation, wet flexibility of the fibers, wet compressibility of the pulp pad, distribution of fines, time of standing of the stock, the "hydration" of the stock, and the effect of added materials such as electrolytes, fillers, rosin, starch, etc.

Operational Variables

The effect of temperature on freeness and drainage has been the subject of many studies. Almost all investigators have agreed that freeness varies with temperature in a manner almost entirely accounted for by the change in viscosity of the suspending medium. Davis (28) has shown that the change of freeness with temperature is chiefly due to the viscosity change, although he feels the shrinkage of fibers with heat has a slight effect. Smith (29) had advanced this theory as early as 1919. He believed that the fiber volume is decreased by heat and the capillary openings are thus enlarged. Freeness values thus show an increase with temperature slightly greater than that due to viscosity changes alone.

Reuse of white water is discussed by Brawn (30). He showed that the decrease in freeness may be caused by the flour in the white water and stated that, on the machine, this is partially offset because of the freeness increase due to the increased temperature through the reuse of white water.

Campbell (31) has pointed out the general effect of head on drainage. He stated that the property of pulp measured by a freeness test is its resistance to the flow of water. This property varies with the pressure causing the flow and with the time during which the pressure is operating. Such variation of this property, he stated to be indicative of the character of the pulp.

It is known that the table rolls of the Fourdrinier machine cause an effective suction pressure acting under the wire. Thus, the head causing drainage consists not only of the head above the wire but also of the effective suction acting on the under side of the wire.

Consistency and sheet weight are known to be important factors in the drainage of water from pulp. Worm and Davis (32) have shown that the drainage time on the Williams precision (drainage type) tester varies linearly with the sheet weight. Investigations have been made also of the effect of weight on freeness as measured by the divided-funnel type testers. Nomographic charts have been prepared and are available for the effect of sheet weight variations on all testers. Sankey (24) and Campbell (23) have pointed out that the effect of sheet weight on the British sheet machine drainage time is not proportional to the weight, although the relation is linear. The drainage time has been shown to be proportional to the sheet weight minus a constant. This has been attributed to the fact that capillary flow does not start until a closed fiber mesh is formed.

The mesh size of the wire used on the paper machine is known to have a decided effect on the rate of drainage. Specht (33) has shown that the amount of open area on the wire on the paper machine was not as important in regard to drainage as the size and number of the openings. In an investigation of different wires in a Schopper-Riegler tester he found that the construction of the wire plays a relatively greater part in the initial flow than it does in the final freeness, which is believed to be a function of the stocks used. However, on the machine, the passage of a large amount of fines through the wire exaggerates the effect of wire size.

Furnish Variables

The condition of the furnish or of the fibrous suspension as it goes to the freeness tester or to the headbox on the paper machine is the most important consideration in the rate of drainage of water from the suspension. The degree to which the fibers are cut, fibrillated, and hydrated determines, in a major part, the drainage characteristics of the pulp. Certain properties which are the result of the beating operation are also important. Among these are the zeta potential of the pulp and, hence, the presence of added materials, the fines distribution of the pulp, the flexibility of the fibers, and the compressibility of the pulp pad. The amount of short fibrous material in the original pulp and the percentage of easily shortened or easily hydrated fibers are also very important. This means that the resistance of the original pulp or of any fraction of it to physical treatment during stock preparation is of great importance in the behavior and drainage characteristics of the pulp after treatment.

Fiber dimensions and distributions are generally considered to be a prime consideration in drainage behavior. Bachman (34) stated that freeness deals with fiber length chiefly. He went so far as to say that freeness has nothing to do with drainage on the machine. According to Brown (35), slowness increases as fiber length decreases, but from a papermaking standpoint fiber length has a negligible effect on drainage rate. All early work on this subject was carried out on fractions of different fiber length which were obtained by fractionation of a pulp in equipment similar to the Bauer-McNett classifier. Brown, in his work, produced short fibers from long fibers separated by classification of the original pulp. In this way, the effect of the different chemical and physical properties of the shorter fibered material present in the original pulp is eliminated as a variable. However, Brown stated that the amount of short fibrous material and the percentage of easily shortened or hydrated fibers in the original pulp are still of importance in drainage characteristics. Guild and Mills (36) stated that the fiber length has little effect on drainage except for the fine flour which clogs the wire.

The importance of the flexibility of the fibers or of the compressibility of the pulp pad which, for practical purposes, are synonyms, has been pointed out by Campbell (37). He determined a constant--a numerical term indicative of specific resistance of the pulp--which he felt to be indicative of the drainage characteristics. The ratio of these constants, as determined on two different testers, he called "relative compressibility" and considered it to be a measure of pulp quality. He later (31) showed that the specific resistance of a pulp varies with pressure and with the time during which the pressure is applied.

For years the hydration of pulp on mechanical treatment has been a subject of discussion. Whether this phenomenon is chemical or physical, there is no doubt but that both fibrillation and chemical hydration tend to increase greatly the drainage time of a pulp. The general subject of hydration is discussed in a separate section.

Electrokinetic phenomena are of decided importance in any study of freeness or drainage. According to Stamm, (38), Kanamura and others have shown that the zeta potential of a pulp increases on beating or refining. The potential is felt to control the effect of the addition of ions, size, fillers, etc., to a pulp furnish. In fact, Yorston (39) believed the effect of pH (observed by many workers) to be a function of positive ion concentration and of the valence of these ions rather than of pH alone. Adams, Simmonds, and Baird (40), among others, have concurred with his views.

HYDRATION AND REFINING

The nature of hydration in the papermaking sense, as connected with the refining of stock, is little understood. It is felt that refining action upon the fibers takes three courses: fiber cutting, fibrillation, and actual hydration. In this discussion, however, the term "hydration," unless otherwise specified, will be reserved to describe the action occurring when processing a pulp in a beater or some similar mechanical device for the refining of pulp.

Many theories have been advanced concerning the nature of hydration. These theories can be classified into three groups: chemical, physical, and physico-chemical. Evidence from time to time has given current preference first to one theory and then to another. The true solution will probably embody a combination and modification of all three. Excellent summaries of the work carried out in this field, as well as complete bibliographies on the subject are available, including those by Bialkowsky (41), Bell (42), Simmonds (43), Campbell (44), and Strachan (45).

Early investigators considered that a chemical change occurred on beating, with the formation of a gelatinous cellulose hydrate compound, which acts as a mucilage. This compound is thought to cause the greasy feel, the slowness of the stock, and the subsequent bonding of beaten fibers. Others postulated the formation of an insoluble hydrolytic decomposition product. However, chemical analysis shows no apparent change in alpha-, beta-, and gamma-cellulose contents during beating. On the other hand, it has been shown that the addition or presence of low molecular weight celluloses facilitates beating action. Kress and Bialkowsky (46) have found that cellulose must swell in the medium used for beating if strength and hydration are to be obtained. Low molecular weight celluloses may thus accelerate the swelling of fibers rather than catalyse the actual beating action.

Strachan is the foremost exponent of the physical theory of hydration. This theory disregards any need for a chemical substance to explain hydration but attributes the hydrating action to the intertwining and bonding of the small fibrils formed by the beating process. The bonding is presumed to be due to the forces of cohesion between colloidal surfaces. This cohesive force is increased as the film of water between the fibers decreases and the cellulose surfaces come closer together. The physical theory emphasizes the structural changes of the fiber which take place on beating.

The physico-chemical theory is a compromise view proposed by Campbell, which combines the fibrillation theory of the physical concept with the formation of a hydrated layer of cellulose in contact with water. Thus, the attraction of the fibers in water suspension for each other is thought to be lessened due to this hydrated cellulose layer. Under these conditions, water can more readily enter the structural lattice and cause swelling. Beating disrupts the structure even further and also frays and crushes the fibrils.

PRESENTATION OF DATA

DEVELOPMENT OF APPARATUS

A great number of freeness studies have been carried out although, almost without exception, they have been made with instruments on which the drainage of water from fibers varies decidedly from drainage on the paper machine. Therefore, these investigations have not been concerned with drainage as it occurs on the Fourdrinier wire but rather with drainage as measured by the particular instrument used. For practical purposes freeness should be defined as that property of a pulp which determines the rate of drainage of water from this pulp on the wire of a Fourdrinier paper machine. In order to carry out a study of such a property, an instrument was demanded which would more closely simulate the drainage on the paper machine.

The operating conditions of existing freeness testers differ from actual conditions on the paper machine in the following ways: a high pressure head above the wire; absence of a suction leg beneath the wire; a long time of drainage; a possible settling or floating of stock and hence a nonuniform suspension; a low initial consistency; a low consistency at the end point; a high sheet weight; in the amount of fine material passed through the wire; and in the resistance of the instrument itself to drainage. An instrument was designed which corrects these faults and more closely approximates the conditions of drainage on the paper machine.

Instrument Design

Three important requirements had to be considered in the design of the instrument: The factors affecting drainage must be variable. The time of drainage must be accurately measurable. The testing conditions must approximate machine conditions as closely as possible. A variation of the different factors is necessary to permit a study of the effect of these factors, and the selected definition of freeness must be satisfied to make the study at all valuable.

The use of a low head above the wire, a low sheet weight, and a suction head under the wire necessarily means a very short time of drainage. Thus, the value of this instrument depends on an accurate measurement of this time. This has been accomplished through photoelectric means. A beam of parallelized light is reflected from the suspension surface. Then a photoelectric measurement of the sudden decrease in specularly reflected light or of the sharp increase in diffusely reflected light as the pulp pad goes "dry" serves to automatically time the drainage. A discussion of the instrument design falls naturally into three sections: (1) the design of a drainage instrument with a low resistance to drainage and with a variable suction pressure acting under the wire; (2) the design of an optical system to measure the time of drainage photoelectrically under testing conditions which duplicate machine conditions; and (3) the design of an electrical system to record automatically the short time of drainage under these conditions.

Drainage Instrument Design. A schematic sketch of the drainage instrument is given in Figure 1. As can be seen in this sketch, the body

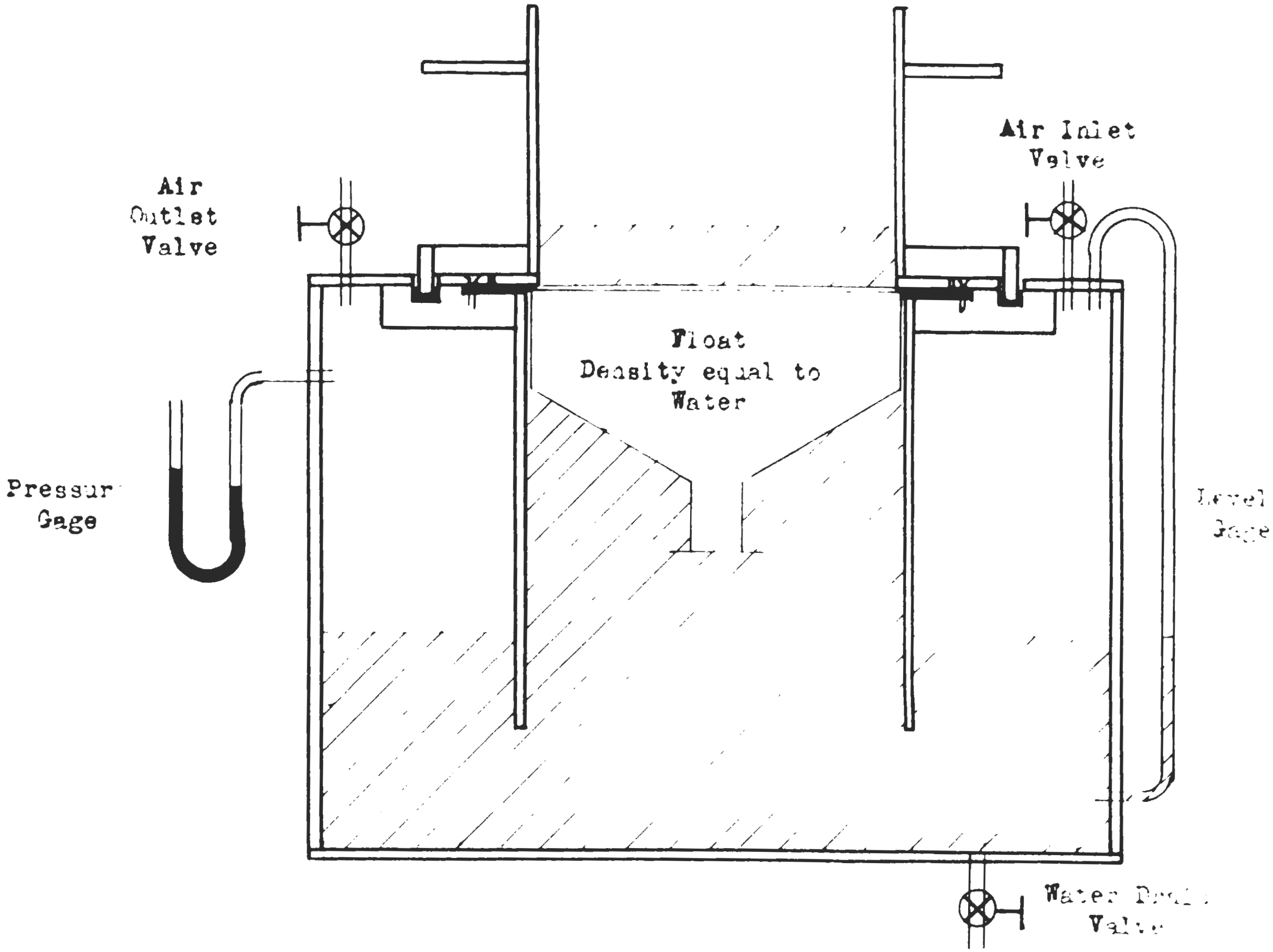


FIGURE 1

DIAGRAMMATIC SKETCH OF

THE DRAINAGE INSTRUMENT

of the instrument is made up of a cylinder closed at the bottom and attached by an annular ring to a shorter inner cylinder at the top. Water seals the lower end of the inner cylinder and forms an airtight chamber. A wire mounted on a removable annulus covers the top of the inner cylinder. The cylindrical upper section, which is removable to allow the wire to be cleaned, is placed above the wire across the inner cylinder. A mercury seal prevents leakage of the stock suspension between the upper and lower sections.

A piston, adjusted to the density of water and, hence, behaving dynamically as a volume of water equal to its own volume, fits inside the inner cylinder. Air pressure, applied in the outer cylinder, forces the piston to move with the column of water up the inner cylinder and to form a seal against the annular rubber gasket directly under the wire. A slight excess pressure is applied to offset the head caused by the stock which is to be added to the upper section. The piston prevents the stock mixture from diffusing through the wire and mixing with the water below, and also ensures streamline flow after drainage has started.

With the piston in position, the sample is placed in the upper section and diluted to the correct head above the wire. As the air outlet valve is opened and the air pressure released, the water leg beneath the wire immediately becomes a suction leg acting on the under side of the wire. The stock suspension above the wire acts as a positive head. The sum of the two or the composite head is opposed by the resistance of the pulp to drainage of water through it, and by the inertial force.

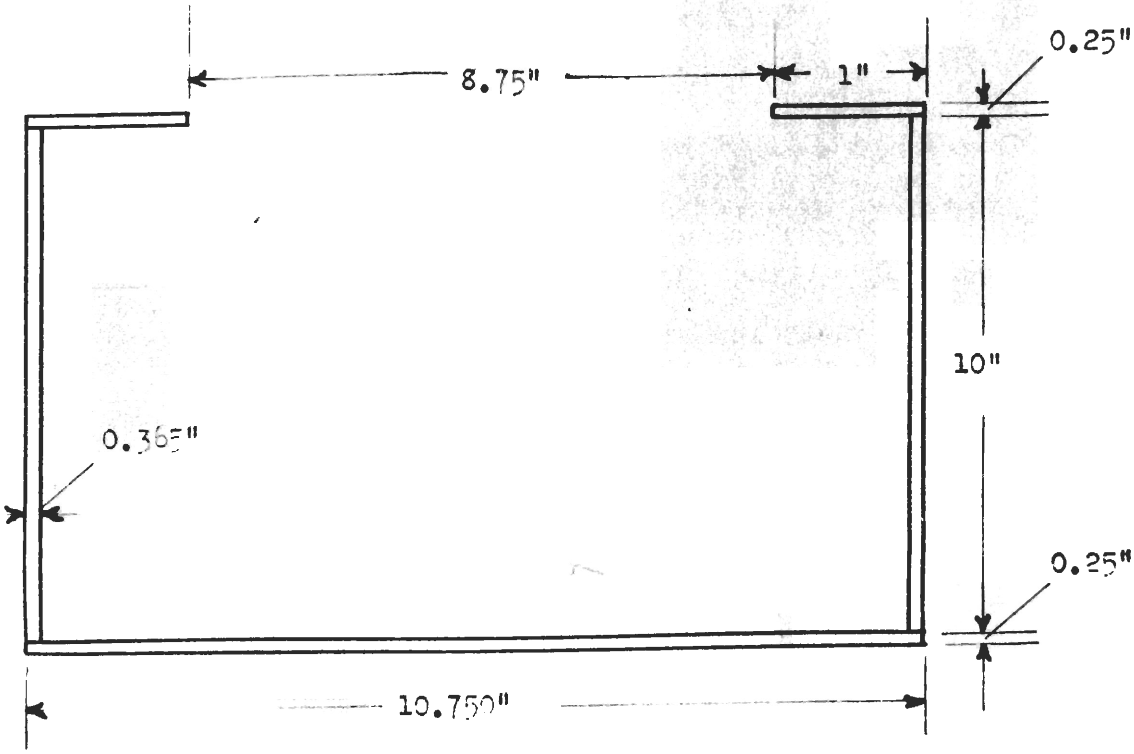
All the instrumental variables can be readily changed. The pressure head, sample weight, and temperature are easily adjusted. The wires are detachable and can be interchanged. The suction head can be varied simply by changing the water level in the outer cylinder.

With this design it is possible to make three important observations: (1) time of drainage; (2) water retained by the pulp after free drainage is complete; and (3) the amount of fiber passed through the wire.

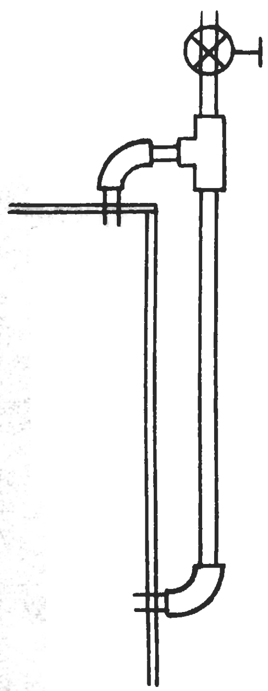
The instrument was made entirely of brass. The various parts of the instrument were machined separately and assembled by sections. These sections will be discussed individually.

Figure 2 illustrates the outer shell section of the instrument. The cylinder is a 10-inch length of 10-inch pipe which was soldered on to a 12 by 12-inch plate of one-quarter inch brass. Four adjustable legs of one-half inch steel were screwed into the corners of the plate. An annular ring of one-quarter inch brass was screwed and then soldered to the upper edge of the cylinder. The various valves and gages were added to this section after the instrument was assembled. A water drain cock was set into the bottom plate. The other valves and gages were placed in the upper annular ring. With the exception of the air outlet valve, one-quarter inch pipe and fittings were used for these valves and gages.

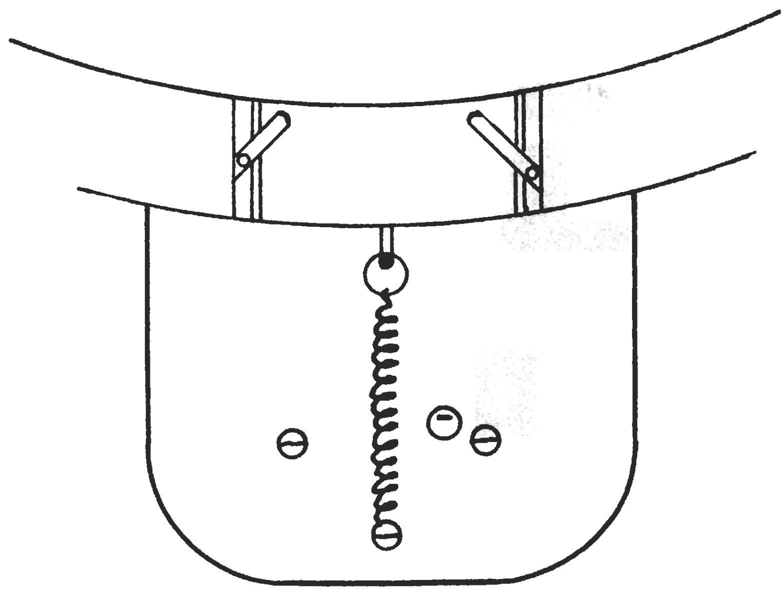
The water inlet valve and the level gage were combined as shown in Figure 2. A nipple and a right angle elbow were placed in the



Main Shell



Water Inlet Valve
and Level Gage



Air Outlet Valve

FIGURE 2

annular ring and also in the side of the cylinder below the inner cylinder level. The upper elbow was connected by a nipple to a T fitting. The glass sight tube was dropped through the T into the elbow below and made fast with litharge. The water inlet valve was screwed into the upper side of the T fitting. The air pressure manometer gage was fastened with litharge into a right angle elbow. Both the level gage and the air pressure gage were fitted with ruled backboards. The air inlet valve was also screwed into the upper annular ring.

The air outlet valve represented a serious problem in design. This valve had to open and exhaust the entrapped air in less than 0.01 of a second to attain the desired accuracy. A spring-actuated plate valve was selected as most suitable for the requirements. Two empirical formulas were used to calculate the area of the opening required to exhaust in the desired time the maximum possible volume of air causing a positive pressure. A one square inch opening was concluded to be more than sufficient.

An opening two inches long by one-half inch wide was cut in the upper annulus and a flat brass plate cut to cover this. These two pieces of the valve were ground together with emery powder. Two guides were placed at either side of the valve and two leaf springs carried from these to the cover in order that a tight seal be formed with the oil lubricant.

A platform at the level of the valve was mounted on the side of the outer shell. A screw eye was mounted in the back side of the valve cover and attached by a spring to a post at the outer edge of the platform. The valve cover was held in the closed position against the spring pressure by a brass rod passed through a hole in the platform and through the eye in the valve cover. When this rod is removed, the valve opens and drainage starts. Two posts were placed at the back of the platform to catch the valve cover as it opened.

When the valve is completely open, it closes a switch which starts the timers. The time of opening of the valve was measured by an electric timer and found to be less than one 0.01 second. Since the air takes 0.01 of a second or less to exhaust, the valve opens in less than this time, and the timing of drainage begins after the valve is completely open, the over-all error is less than 0.01 second.

Figure 3 shows the design of the center section, composed of a 7-inch length of standard 5-inch pipe, whose inner diameter was increased by 0.2 of an inch. This pipe was screwed into a standard 5-inch brass flange, which was machined as indicated. The deep slot formed the mercury seal for the upper section; the shallow cut held the one-eighth inch rubber gasket which was held in its position by a brass annulus screwed to the flange. The entire center section was screwed together and then soldered to the annulus of the outer section. The assembled sections were tested for leaks and the instrument was made airtight.

As is indicated, the wire was soldered on a removable brass annular ring which lies on the rubber gasket and is centered by the annulus which fixed that gasket in place. Several different mesh wires were mounted on annular rings which are interchangeable.

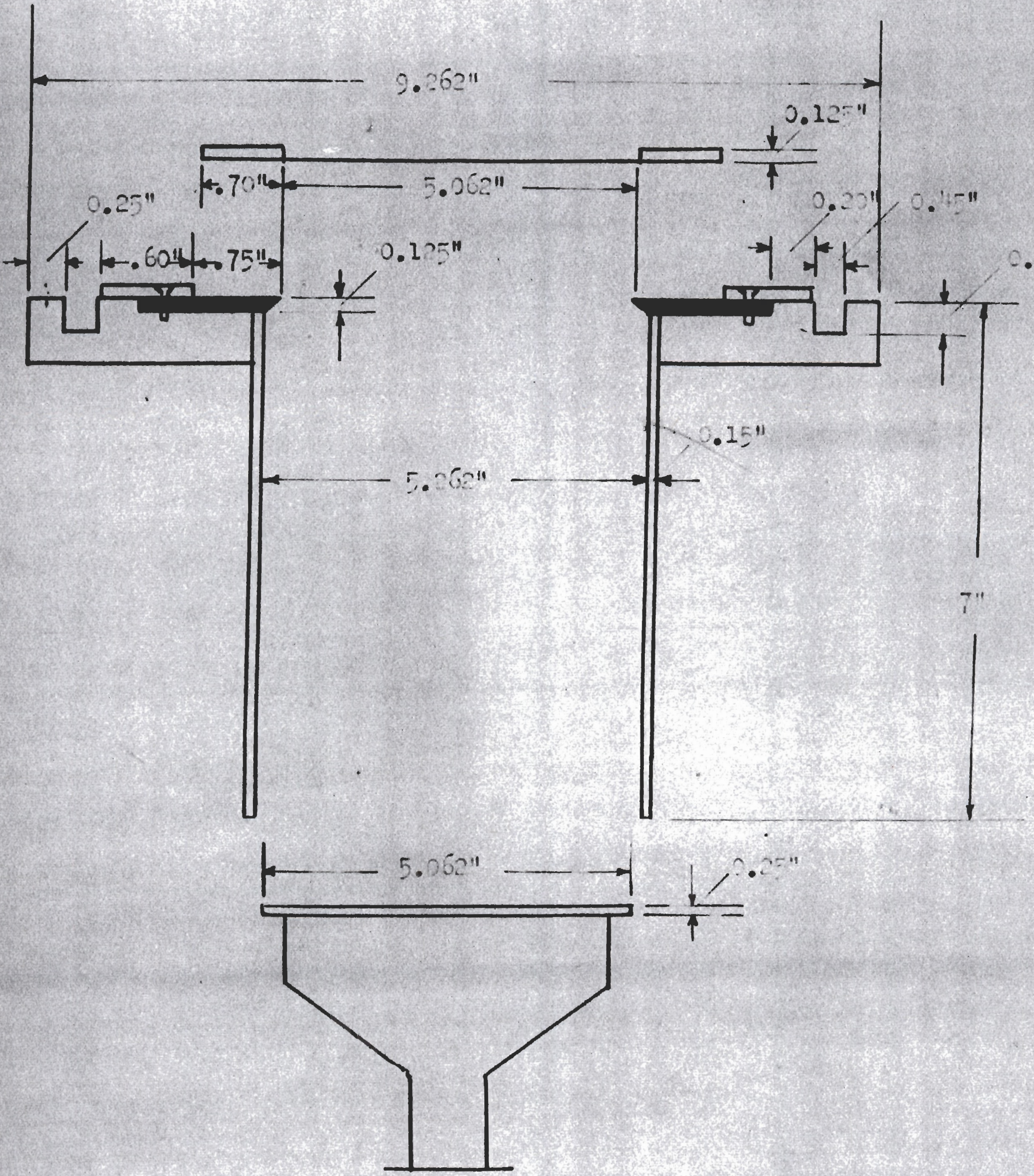


FIGURE 3

CENTER SECTION

The float section fitted inside the cylinder and was made of sheet copper with a top of brass plate. It was balanced by a brass counterweight at the bottom. Additional weights to adjust its density were added to the float. In order to remove the float after the instrument was assembled, the annulus holding the rubber gasket in position had to be unscrewed and the rubber gasket removed.

The upper section is illustrated in Figure 4. This consisted of a 4-inch piece of 5-inch pipe screwed into a flange which had been cut as shown. A piece of 8-inch brass pipe was sweated on to the outside edge of the machined flange. The protruding edge of this pipe dipped into the mercury seal in the deep slot of the center section. Two handles were attached to the upper section to assist in removing it from the instrument. This section is held merely by its own weight on the center section after the wire is in place. It is centered by the slot of the mercury seal.

Optical Design. The optical system, which was made in a unit to prevent any need of refocusing, is illustrated in Figure 5. The suspension is illuminated by a parallelized light beam at right angles to the surface. The light from a concentrated filament, clear-glass, 100-watt bulb is passed through a condensing lens, through a piece of plane glass at 45 degrees to the beam, and to the surface. As long as a water surface is present, the light is specularly reflected, but when the pulp fibers began to go "dry," a diffuse reflection is obtained. Two methods of determining the end point are possible. The photocell housing can be used interchangeably in two positions depending on whether

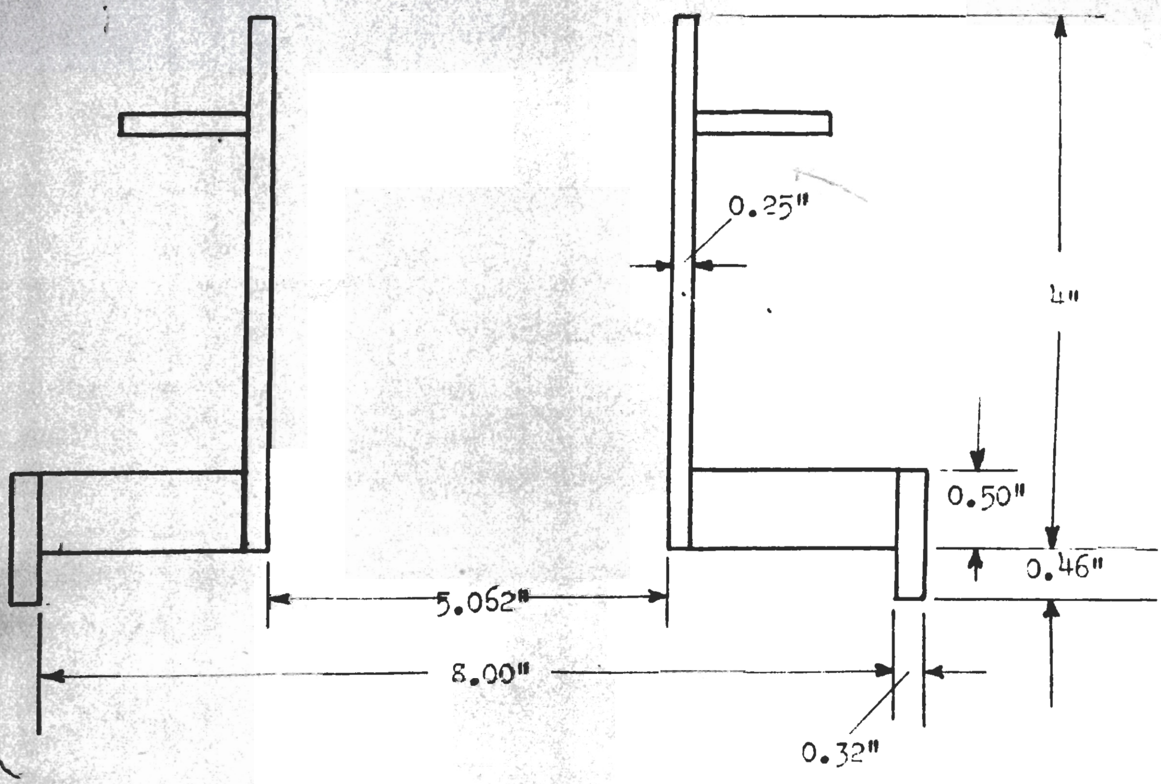


FIGURE 4

UPPER SECTION

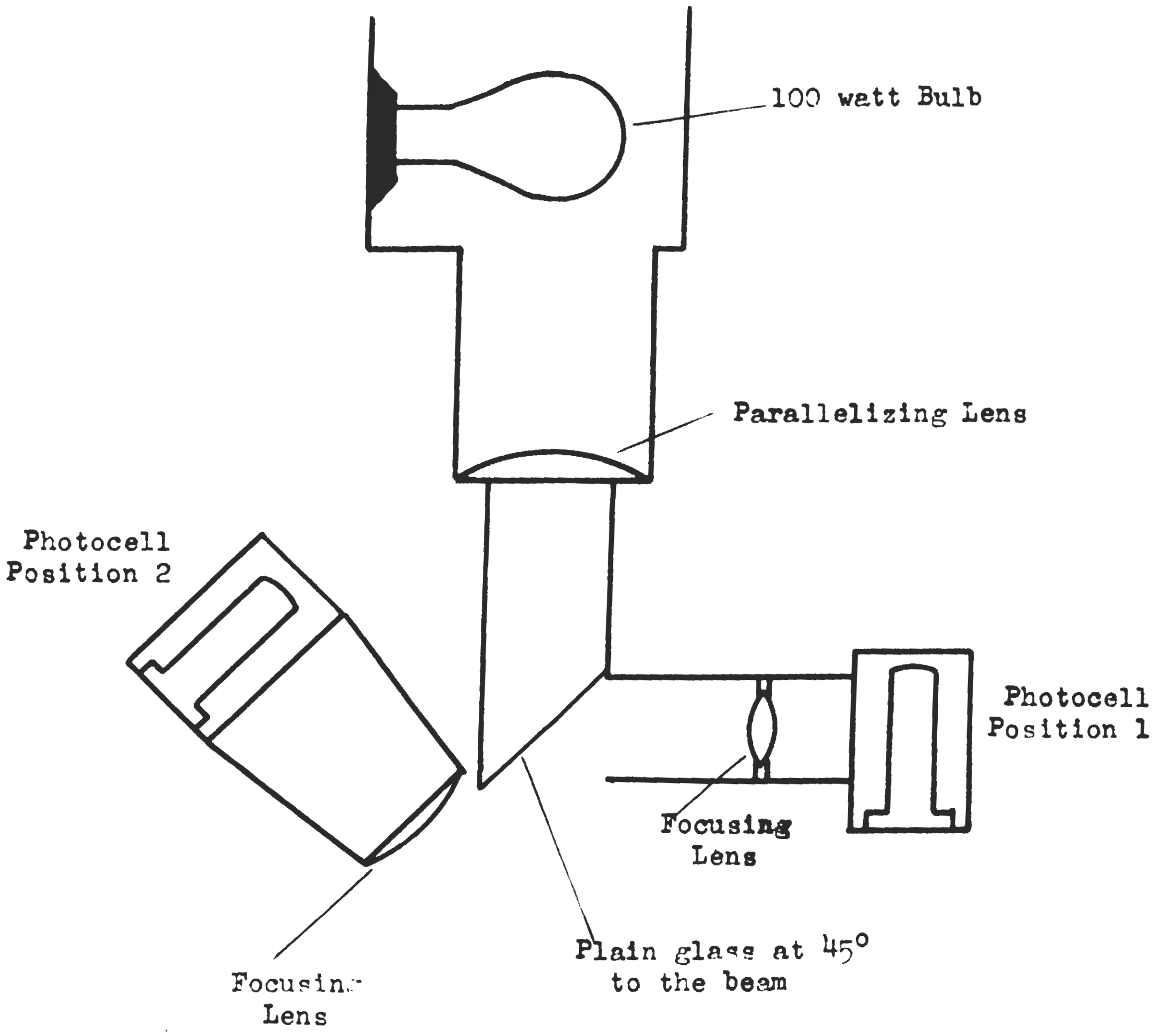


FIGURE 5

OPTICAL DESIGN

the increase in diffusely reflected light or the decrease in specularly reflected light is used to detect the formation of a dry sheet.

The specularly reflected light is reflected directly back toward the light source and is partially reflected off the glass to photocell position 1. Thus the photocell in position 1 "sees" the sudden drop in specular reflection as the fibers break through the water surface. In position 2, the photocell "sees" the increase in diffuse reflection as the pulp pad forms. In both positions the reflected light is focused by a lens on to the photocell. In position 2, there was an iris diaphragm built into the instrument to allow adjustment of the amount of light impinging on the photocell.

Electrical Design. Several amplifier designs were constructed and rejected before one was found which satisfied the demands of the instrument. The accepted design is shown in Figure 6; the amplified photocell current operates a double-throw relay in the outer circuit which, in turn, actuates the electric timers.

Two electric timers, made by the Standard Electric Time Company, one with an accuracy of 0.01 of a second and the other with a long totalizing time, were connected to the poles of a double-pole relay in the outer circuit. In this circuit there was also a microswitch which was attached to the under side of the platform of the air outlet valve. The actuating lever of the switch was placed through a hole in the platform and the valve cover closed the switch at the moment when the valve opening was completely uncovered. Thus, when the valve was opened and drainage started, the circuit was closed and the timers started automatically.

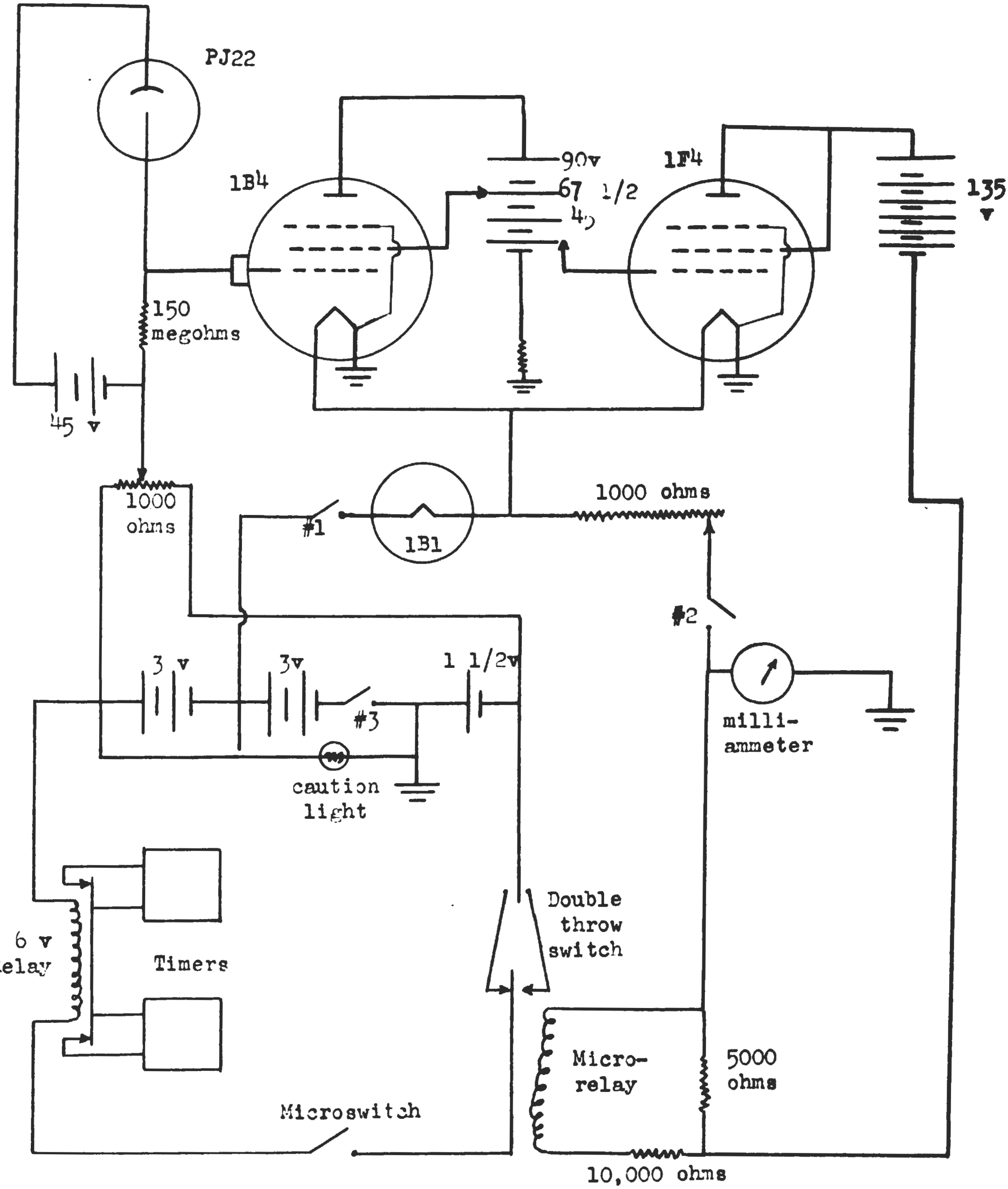


FIGURE 6

AMPLIFIER CIRCUIT

Switches 1 and 3 connected the amplifier itself while switch 2 controlled a bucking current by which the amplified photocurrent could be adjusted to a definite value. It was found simpler, however, to adjust the photocurrent level by the bias voltage control. The double-throw switch across the poles of the double-throw microrelay was necessary if the same amplifier was to be used for the diffuse as well as the specular end point. If photocell position 2 were used, the outer circuit should be closed when the photocurrent was very low and should break when the amount of light reaching the photocell reached a certain value. The opposite is true if the specularly reflected light was seen by the photocell.

Instrument Operation and Technique

As was mentioned earlier, it was hoped to use this instrument to investigate these factors: the time of drainage of a pulp suspension, the water retained by the pulp after drainage, and the amount of fine material passed through the wire. However, the measurement of only one of these proved worthwhile. The amount of water retained in the pulp after drainage was complete, did not vary beyond experimental error with the degree of beating or the type of pulp. The fines passed by the instrument were not sufficient to make their measurement practical. A technique, however, has been developed by which the time of drainage can be accurately measured.

Not only was the amount of water left in the pulp sheet after drainage nearly a constant value, regardless of the degree of beating, but also the application of a positive pressure on the sheet resulted in a nearly constant water content. A device was arranged by which a suction pressure was applied to the formed sheet. As in the other cases, no appreciable deviation in the final water content was found between different samples.

Instrumentally the apparatus allowed the duplication of machine conditions for all variables but one: the passage of fines through the wire. The head, sheet weight, suction head, wire size, temperature, time of drainage, consistency, etc., can all be kept within the paper-making range. The amount of fines passed through the wire, however, was found to be far below machine conditions. The amount passed was only in the order of two per cent or less for the most highly beaten chemical pulps and less than five per cent for groundwood. If machine chest stock were being tested, it would be desirable to have a very slight loss in fines, because this stock has almost the same composition as the finished paper. However, headbox stock contains, in addition to the fibers in the finished paper, the fine material which passes through the wire on the machine and is returned to the headbox with the white water.

The problem then is to determine whether it is necessary to select conditions which duplicate the machine concerning the passage of fines and to add this amount of fines to the sample before testing, or whether it is best to select conditions which show the lowest loss of fines. In an attempt to answer this question, samples of white water, headbox stock, jordan stock, and wet broke were obtained from a commercial machine running 16-pound (17x22--500) bond over a 70-mesh wire at 470 feet per minute.

From the consistency of the headbox stock, the white water, and the wet broke, the amount of fines going through the wire can be calculated. This value was found to be 22.1 per cent. Headbox stock was tested using a series of different sized wires on the instrument until the same fines passage was obtained. To equal the amount of fines passed by a 70-mesh wire on the machine, a 20-mesh wire was necessary on the instrument. Furthermore, the nature of the fines passed was entirely different. Drainage times were run on a sample of jordan stock to which was added a known amount of fiber from the white water, and on another sample to which was added the same amount of fines separated from headbox stock by the instrument. The drainage times were as follows:

TABLE I

EFFECT OF FINES ON DRAINAGE

Sample		Drainage Time sec.
Jordan stock	1.00 gram	0.29
Jordan stock White water fines	0.80 gram 0.20 gram	0.58
Jordan stock Instrument fines	0.80 gram 0.20 gram	1.28

A microscopic examination of the fines samples substantiated these data. The fines obtained from the instrument appeared only slightly shorter than the whole headbox stock, whereas the fibers in the white water were very short. The high fines loss through the relatively fine wire of the machine and the difference in the nature of these fines from those obtained on the instrument can be attributed to four possible factors on the machine: the effect of the shake; the high suction on the machine: the downward velocity due to the head behind the slice; and the washing-out effect of water carried back to the under side of the wire by the table rolls.

The development of the technique for testing took three paths. First, the end point had to be selected; second, the electrical circuit had to be modified to the point of greatest sensitivity; and third, the actual testing technique had to be developed.

As was discussed in the design of the optical equipment, the completion of drainage was indicated by a sudden decrease in the specularly reflected light from the suspension surface or by an increase in diffusely reflected light from the fiber mat. Both end points were used for a great number of different freeness samples. The specular end point, which indicates the point where fibers first break through the water surface, and the diffuse end point, which indicates the formation of a dry sheet, seemed to remain in a fixed proportion regardless of the degree of beating.

The specular end point appeared to have a better accuracy over the entire freeness range, although it gave poorer duplication for very slow pulps. The diffuse end point seemed to have the same magnitude of variation for all freenesses, which made the end point very unreliable for free pulps. In addition, the change of the amount of specularly reflected light at the end point was far less gradual than the change in the diffusely reflected light.

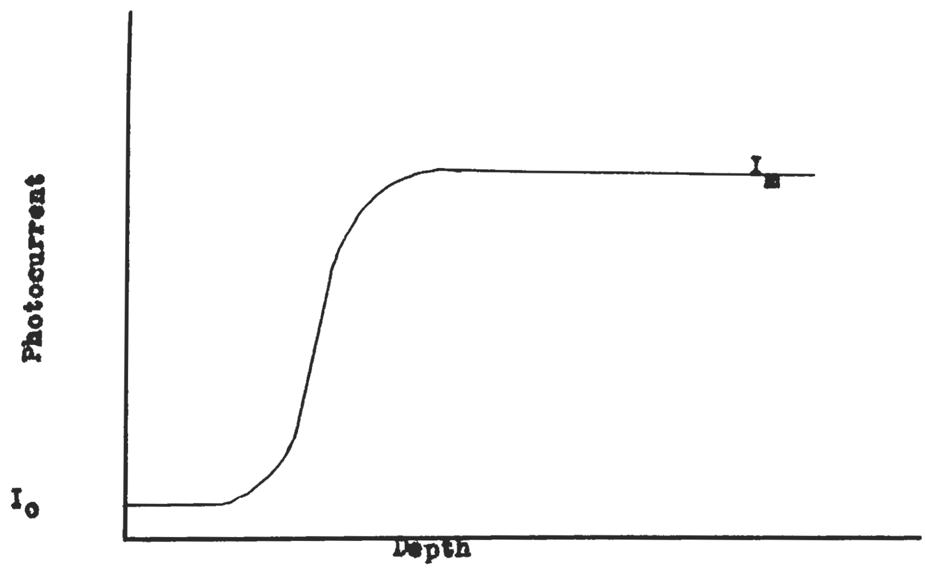
Furthermore, it was shown that the end point based upon diffuse reflection was somewhat dependent upon the absorption and scattering coefficients of the pulp tested, whereas the specular end point was not. The change of absorption coefficient and scattering coefficient with wavelength was used to show this. Two pulps were studied, one of which showed a large variation of scattering coefficient and only a small change of absorption coefficient with wavelength and a second which had a large absorption coefficient change and a small change in scattering coefficient. Filters which passed only light of certain wavelength bands were placed in the beam incident on the pulp. Thus the scattering and absorption coefficients were effectively changed. The time of drainage as measured by the increase in the diffusely reflected light changed considerably with this treatment, but the drainage time measured by the decrease in specularly reflected light was not affected.

Since the end point which depends upon the sudden decrease of specularly reflected light is sharper, less dependent upon the optical properties of the pulp, and more accurate over the entire range, and since there appears to be a fixed ratio between the drainage times by the two methods of determining the end point, the photocell will be used in the position in which it "sees" the decrease in the specularly reflected light as the fibers break through the water surface.

The electrical circuit was modified in such a way as to increase the sharpness of the end point and the reproducibility of the method. To make an allowance for the difference in the reflectance of different samples, it was necessary to adjust the amplifier to the same final photocurrent value--that is, the difference in the reflectance of the wet pulp pad was taken into account and its effect removed by the amplifier adjustment. The change of photocurrent with depth above the wire can be assumed to have a curve similar to that sketched in Figure 7. The maximum current I_m was set by the saturation current of the amplifier. As was discussed above, the same I_o was used for each sample. Thus, to get the sharpest end point, the point at which the relay operates should be adjusted to the sharpest slope of the curve. This was done by adjusting the resistances in series and in parallel with the microrelay.

FIGURE 7

PHOTOCURRENT vs. DEPTH



In order to satisfactorily operate the tester under the conditions desired, experimental technique had to be developed which would permit duplicate runs to accurately check each other. A small sample weight, a low head, and a short time are all desirable but all tend to exaggerate any errors in experimental technique.

A small sample weight of about one gram, equivalent to a basis weight of 55 pounds (25x40--500), was most desirable. Using a one-inch head above the wire, then means a consistency of 0.286 per cent. It appeared to be difficult at first to obtain any degree of reproducibility under these conditions. However, after several changes in technique had been made, it appeared possible to obtain good duplication of results.

It was found that if the pulp sample was made up to volume, dispersed, and then added to the tester, the results showed less variation than if the samples were dispersed in the instrument. A volume of 350 cc. is equivalent to a one-inch head above the wire. The wire itself was buckled just enough to make the position of the wire in the tester of decided importance. Furthermore, bubbles are easily trapped under the wire. If this happens, the suction leg can break and the effective suction is not at the desired value.

To use the instrument at different temperatures, additional weights are necessary to make the density of the float equal to that of water at these temperatures. Standard number eight brass washers, weighing approximately 0.64 gram, were used to adjust its density. The necessary number of washers are given in Table II. The relative change in weight with temperature agrees with the density change of water.

TABLE II

FLOAT CALIBRATION

Temperature °C.	No. of Washers
10	23
15	22
20	21
25	19 1/2
30	18
35	16
40	14
45	11
50	8
55	4 1/2

The instrument was calibrated for the drainage time of water alone with all wires from 50- to 80-mesh; however, the wire size had little effect. The drainage time was longest for the finest wire and shortest for the coarsest, but the largest change was only 0.03 second. Table III shows the change of drainage time with suction pressure and with pressure head for a 50-mesh wire.

TABLE III

VARIATION OF DRAINAGE TIME OF WATER WITH SUCTION HEAD AND PRESSURE HEAD
50-mesh Wire

Suction Head in.	Drainage Time in Seconds Pressure Head in Inches				
	1/4	1/2	1	2	3
1/2	0.15	----	----	----	----
1	0.14	0.18	----	----	----
2	0.13	0.16	0.20	0.28	0.36
3	0.12	0.14	0.19	0.25	0.32
4	0.12	0.14	0.18	0.21	0.27

Testing Procedure

The water in the tester was adjusted to the desired temperature and the density of the float to the density of water at that temperature. After the wire was placed in position, air pressure was applied to force the piston tight against the rubber gasket. The water level was adjusted so the final level in the outer cylinder would give the desired suction leg when drainage started. The water in the upper section was removed by suction, during which care was taken to remove all the air bubbles beneath the wire. Surface tension of the water prevented air from going back again.

A sample containing 1.00 gram of fiber (oven-dry basis) was diluted to 350 cc. and then dispersed. The optical unit was swung into position, the clocks moved to zero, and the light turned on. The sample was added and the air-release valve opened, the clocks started, and the reading automatically given. This reading was disregarded and the amplifier adjusted to a photocurrent reading of 0.20 milliampere. The optical system was then swung aside, the upper section taken off, and the wire removed, cleaned, and replaced. The above procedure was then repeated and this time the data were recorded. If a series of runs is being made on the same pulp, the photocurrent may be adjusted from the previous sample.

Using the above procedure, good reproducibility can be obtained. The data of Table IV show the order of reproducibility obtained with pulps varying from very free to very slow stocks. These data were collected on a bleached sulfite pulp beaten in the 1 1/2-pound Valley laboratory beater for the indicated times.

TABLE IV

ACCURACY OF DRAINAGE TIME DETERMINATION
Average of Ten Readings

Beating Time min.	Schopper-Riegler Freeness cc.	Drainage Time sec.	Average deviation from the average %
5	845	0.56	4.5
10	810	0.70	3.6
30	700	1.31	3.3
40	460	3.28	2.0
60	305	7.77	1.4
90	145	26.4	1.7

STUDY OF EXISTING TESTERS

Numerous interconversions of freeness scales for the different testers have been made by other workers. These conversion charts, however, are not absolute. In many cases an actual inversion of results for two pulps has been shown to occur with different testers. That is, one pulp may appear freer than another in one tester and yet may appear to be the slower pulp on a second tester. Furthermore, the difference in the amount of fines passed by the different testers tends to throw some doubt on the reliability of converting from one freeness scale to another.

The commonly accepted procedures for the different testers were used in this study. The Schopper-Riegler instrument employed was the model with the automatic cone lifting device. It uses 1000 cc. of stock at 20° C. containing two grams of pulp. The Canadian standard and the Green tester both use three grams of pulp in a liter at 20° C. The three above testers are of the divided-funnel type. The volume of free or rapidly draining water from the upper outlet is used as a measure of the rate of drainage.

The Williams "Precision" tester is, in effect, a graduated glass cylinder with a wire mesh bottom. Water at 25° C. is placed in the tester until the level is at the lower mark. A liter of stock at 25° C. containing three grams of pulp is then added, the suspension well mixed, and the time for one liter to drain recorded as the slowness. Drainage is affected by a small suction leg and care must be taken to avoid trapping air beneath the wire.

Drainage time and drainage factors were also obtained on the British sheet machine, using TAPPI Standard T 205 m-40.

The Inversion of Results Between Testers

During this investigation, a number of examples of the inversion of results between testers were found. Two of these, for groundwood and sulfite pulps, are compiled in Table V to illustrate the disagreement between testers. Inversion of results are not limited to these pulps but were found also between two groundwood pulps, two different sulfite pulps, a sulfite and a kraft pulp, etc. The selected examples are, however, more striking, and thus better illustrate the inversion of results between testers. The results are the average of three values.

Example 1 shows the inversion between the different types of testers. The groundwood pulp appears considerably slower than the sulfite on the Schopper-Riegler, Canadian, and Green type testers but freer on the Williams tester and the British sheet machine. The data shown in example 2 indicate that this inversion does not occur only between testers of the Schopper-Riegler type and the drainage type. In this example, the sulfite pulp appears to be slightly freer than the groundwood on the Schopper-Riegler instrument and somewhat slower on the Green and the Canadian standard testers. The Williams and the sheet machine values, on the other hand, show the sulfite to be a far slower pulp than the groundwood.

Until the inversion between instruments of the divided funnel type (example 2 above) was discovered, it was felt that the inversion

TABLE V

INVERSION OF RESULTS BETWEEN TESTERS

Example 1

Freeness Tester	Groundwood Pulp	Sulfite Pulp
Schopper-Riegler	225 cc.	285 cc.
Green	50 cc.	59 cc.
Canadian	65 cc.	77 cc.
Williams	487 sec.	500 sec.
British sheet machine		
Drainage time	36 sec.	70 sec.
Drainage factor	74 sec./g.	630 sec./g.

Example 2

Freeness Tester	Groundwood Pulp	Sulfite Pulp
Schopper-Riegler	265 cc.	275 cc.
Green	56 cc.	53 cc.
Canadian	70 cc.	68 cc.
Williams	410 sec.	539 sec.
British sheet machine		
Drainage time	31 sec.	70 sec.

might be merely a problem of instrumentation. However, with this possibility removed, the inversion of results could be due to any of several factors. The most obvious among these is the possibility that the drainage volume vs. time curve differs for different pulps. If this were true, it would be possible that a pulp with a long total drainage time could have a very rapid drainage at first, thus resulting in a higher freeness by the divided-funnel method. Other factors which might cause the inversion of results include the amount of fines passed by the instrument, the temperature of testing, the consistency of the sample, the sample weight per area of wire, and the head used above the wire.

Shape of the Drainage-Time Curve. As was pointed out above, the inversion of results between testers could be easily explained if the curve of drainage volume plotted against time differed with different pulps. If this should occur, a study of drainage should be a study of the entire curve rather than of the total drainage time. Therefore, a thorough investigation was made of the shape of the drainage volume vs. time curve.

The Williams tester is a graduated glass cylinder and thus can be readily used to obtain the curve of volume drained plotted against time. Bleached sulfite pulp was taken to the same total Williams drainage time by several different methods; pebble milling, beating in a sharp or dull Valley 1 1/2-pound laboratory beater, and mixing with groundwood pulp. The time of drainage for each 100 cc. drained on the Williams tester was recorded for these pulps. Motion pictures were also taken of the drainage and the time of drainage at each volume checked by that means. The curves of the different pulps were identical within experimental error.

Curves were obtained in the same way for a number of different types of pulp and compared with beaten sulfite pulp at the same total drainage time. Among these tested were groundwood (both beaten and unbeaten), kraft, overbleached sulfite, sulfite-groundwood combinations, sulfite fibers which had been shortened by hand cutting, etc. All gave curves of the same shape as that of a sulfite pulp which had the same total drainage time. These experiments cover the range from very free to very slow stocks.

It was concluded, therefore, that neither the method of beating, the type or condition of the pulp, nor the fiber length of the pulp affected the curve of drainage volume vs. time. However, Bachman (34) pointed out that the drainage volume vs. time curve on the Williams tester differed between pulps. His data were sketchy and incomplete, however, and his work could not be duplicated. Clark (1) pointed out that Skark, in some of the early work done on freeness testing, had also indicated a difference in the shape of this curve between pulps. This difference Skark felt to be due to fiber length.

Since data had been presented which indicated that the drainage-time curve differed between pulps and the above data were thought to have disproved this, an investigation was made of the factors which might have caused a change in the curve. Temperature and sample weight, if varied, naturally affected the total drainage time. However, variation of either of these factors did not change the shape of the drainage volume vs. time curve from that ordinarily obtained.

It was found, however, that it was a very simple matter to trap a bubble of air beneath the wire of the tester. Since there is a small suction leg affecting drainage on the Williams tester, the presence of an air bubble beneath the wire can entirely change the shape of drainage vs. time curve. A bubble trapped beneath the wire sometimes allows the suction leg to break entirely and the water to drain from the instrument. An example of these effects are shown graphically in Figure 8. The same effect was noted on other samples. The data are given in Table VI. If a freer sample than that given in this study were measured with air trapped beneath the wire, it is easily seen that the shape of the curves would be definitely different.

TABLE VI

EFFECT OF ENTRAPPED AIR ON DRAINAGE-TIME CURVE
Williams Tester

cc. Drained	No Air Bubble	Air Bubble	Suction Leg Broken at 700 cc. Drainage
200	4.3	4.4	4.5
300	10.3	10.3	10.4
400	20	23	23
500	34	38	37
600	52	58	57
700	76	87	88
800	104	126	135
900	141	170	208
1000	183	224	305

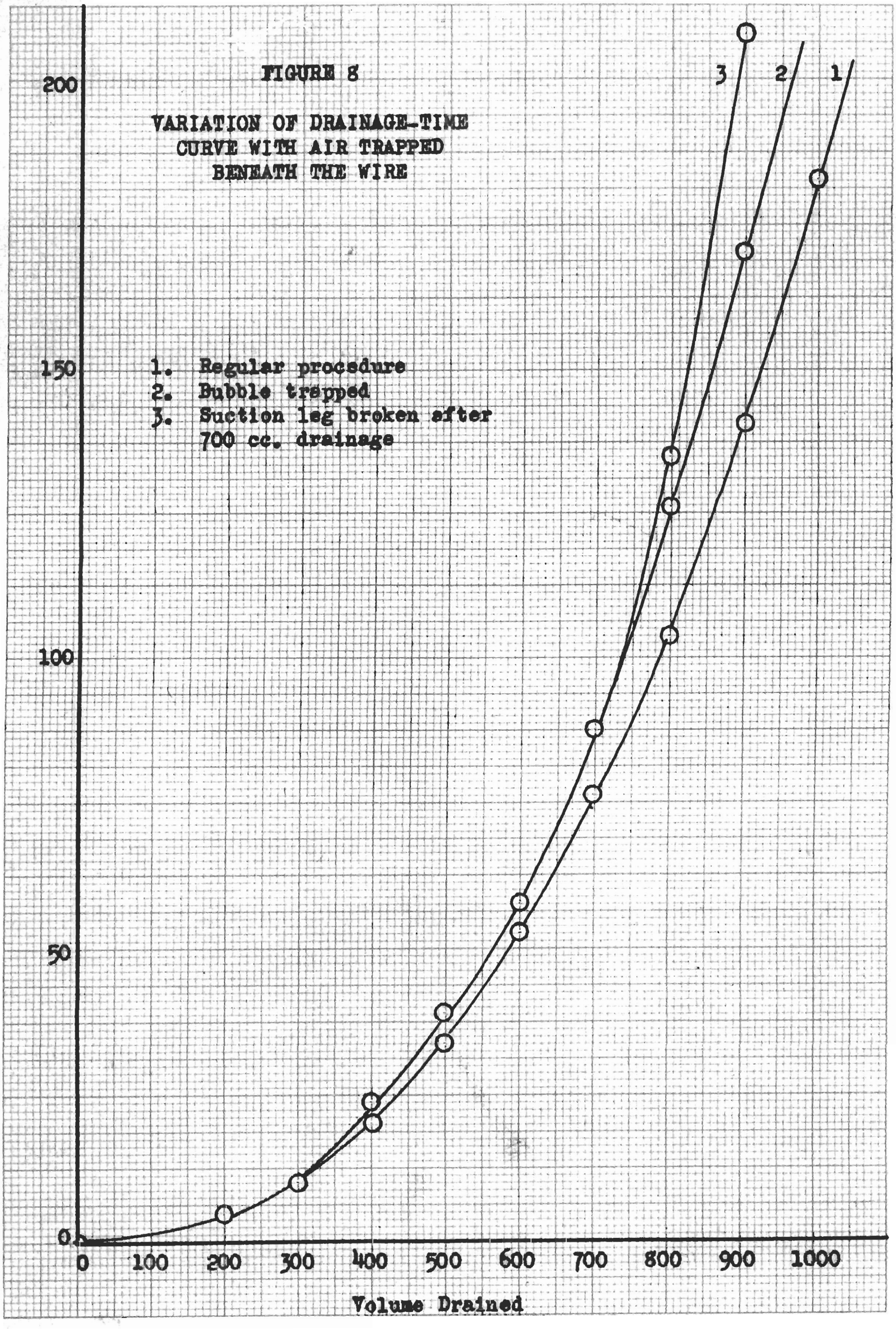


FIGURE 8
VARIATION OF DRAINAGE-TIME
CURVE WITH AIR TRAPPED
BENEATH THE WIRE
1. Regular procedure
2. Bubble trapped
3. Suction leg broken after
700 cc. drainage
3
2
1
200
150
100
50
0
0
100
200
300
400
500
600
700
800
900
1000
Volume Drained

Since the inversion of the results between testers could be accounted for by a change of the very early portion of the drainage curve, this was also investigated. The first drainage from the pulp could fill the cone of the inverted funnel quickly and give, apparently, more free water. Motion pictures were taken of the early portion of the drainage curve on the Williams tester, for samples which were known to invert their relative freeness when tested on different testers. No differences in the shapes of the curves were found.

Fines Passed by the Instrument. It was thought that the amount of fines passed by the different testers through the wire might explain the inversion of results. A sample of groundwood and a sample of beaten sulfite which were known to show inversion of their relative freeness were tested on all the freeness testers. The percentage of the sample passing through the wire was determined. The data are collected in Table VII.

TABLE VII

FINES PASSED BY THE INSTRUMENTS

Tester	Groundwood pulp Freeness	Groundwood pulp Fines %	Sulfite pulp Freeness	Sulfite pulp Fines %
Williams	410 sec.	1.5	539 sec.	0.8
Schopper-Riegler	265 cc.	1.6	275 cc.	0.7
Canadian	70 cc.	1.8	68 cc.	0.6
Green	56 cc.	1.5	53 cc.	0.6
British sheet machine drainage time	31 sec.	6.7	70 sec.	0.8

The change in the amount of fines passed through the wire is small in the case of all testers except the British sheet mold. The amount of fines do not change enough to account for the inversion of results between testers. In the case of the British sheet mold the relatively high fine loss with groundwood may partially account for the very low drainage time with this pulp.

Difference in the Testing Procedure with Different Testers. The testing procedures of the different testers differ in only three major respects. These are the temperature of testing, the sample weight per area of wire, and the head causing drainage. Table VIII shows the variation between the testing condition on different testers.

TABLE VIII

CONDITIONS OF TESTING

Tester	Diameter cm.	Wire Area sq.cm.	Sample Weight g.	g./sq.cm.	Total Volume cc.	Head in.
Schopper-Riegler	11.3	100	2	0.0200	1000	3.92
Canadian	10.1	80	3	0.0582	1000	4.91
Green	10.1	80	3	0.0582	1000	4.91
Williams	8.1	51.5	3	0.0374	1200	9.16
British	16.0	200	1.2	0.0060		

The following tests were run on a groundwood pulp and a sulfite pulp which showed freeness inversion between testers: all regular freeness testers, Williams test at 20° and 25° C., Williams test at standard weight per unit area and at the weight per unit area of the Schopper-Riegler test, Williams test using total head equal to Schopper-Riegler test, Williams test under complete Schopper-Riegler conditions, and Schopper-Riegler test using the same weight per unit area as the Williams procedure. The data are tabulated in Table IX.

TABLE IX

EFFECT OF VARYING TESTING CONDITIONS
ON INVERSION OF FREENESS

Tester	Groundwood Pulp	Sulfite Pulp
Schopper-Riegler (S.-R.)	253 cc.	283 cc.
Green	52 cc.	71 cc.
Canadian	64 cc.	69 cc.
British	30 sec.	60 sec.
Williams		
Standard	483 sec.	512 sec.
20° C.	513 sec.	636 sec.
g./sq.cm. = S.-R.	161 sec.	182 sec.
Head = S.-R.	119 sec.	106 sec.
S.-R. conditions of head and areal density	78 sec.	70 sec.
S.-R.		
Areal density equal to that of Williams	107 cc.	130 cc.

These data show the cause of the inversion between testers. Variation of temperature and of weight per area of wire does not affect the relative positions of the pulps. When the head in the Williams tester was changed to that of the Schopper-Riegler tester, however, the freeness values took the same relative positions they originally had in the Schopper-Riegler tester. The inversion of results thus appears to be caused by the different heads used in testing.

The head was systematically varied on the Williams tester for samples of groundwood and sulfite pulps. The times of drainage for the two pulps and the ratio of the two are given in Table X.

TABLE X

EFFECT OF HEAD

Head in.	Drainage Time in Williams Tester, seconds Groundwood	Sulfite	Ratio
9.18	162	178	1.10
8.41	150	152	1.01
7.65	135	122	0.91
6.88	113	96	0.88
6.12	93	81	0.87
5.35	73	62	0.85
4.59	54	45	0.83
3.82	41	31	0.76

Thus it can be concluded that the inversion in the relative freenesses of two pulps between different testers is due to the different behavior of the two pulps under different heads. This effect may be caused by the difference in the degree that the two pulps are compressed under different heads or by the difference in the resistance of the first portion of the fiber mat laid down to compression because of the increased fiber-water friction at the higher velocity of flow.

Since the same effect would be expected with an increased total head as with an increased pressure head, the suction head under the wire was varied in the laboratory instrument developed for this investigation and the head above the wire was kept constant. Two samples one groundwood and one sulfite which showed inversion of the relative freeness values, were tested in the drainage tester using different suction legs under the wire. Aside from the suction head, which was varied as shown in Table XI, the standard testing procedure was used.

TABLE XI

EFFECT OF SUCTION ON INVERSION OF RESULTS

Suction Head Inches	Drainage Time, seconds Groundwood	Sulfite	Ratio
2	9.27	9.06	1.02
3	6.84	7.08	0.97
4	5.24	6.17	0.85
5	5.11	5.81	0.88

Here, again, the relative freenesses invert with change of head causing drainage. Thus the two pulps show what may be thought to be a different degree of compressibility with pressure.

Since this variation of compressibility with pressure is of decided importance, a study was made to determine how this property changed with refining. A bleached sulfite pulp was refined in all the available types of laboratory refiners. A 1 1/2-pound Valley laboratory beater was sharpened with coarse graphite mixed with the pulp. Standard beater runs were made according to Institute Method 403 on the sharpened beater and on a normal beater. A standard pebble mill run (Institute Method 404) was made. The pulp was also refined in the Morden Stockmaker and in the Lampén mill.

The procedure followed for the Morden Stockmaker was: 90 grams of bleached sulfite (oven-dry) in 2000 cc. of water were disintegrated in the British disintegrator for 600 revolutions on the counter, and rinsed into the charging pan with 750 cc. of water; 1000 cc. of water were then placed in the Morden, and the charge added with 750 cc. of water. The stock was circulated for two minutes from the time charging was started. Then the rotor was lowered, the instrument run the desired time, and the rotor lifted. The sample was then collected from the sampling opening.

The following procedure was used for the Lampén mill: 40 grams of oven-dry pulp were soaked for four hours in 2000 cc. of water and disintegrated for 600 revolutions on the counter in the British disintegrator. The pulp was then filtered, redispersed in 1000 cc. of water, added to the mill, and beaten the desired time. Following beating, the fiber was disintegrated in 2000 cc. total volume in the British disintegrator for 7500 revolutions.

The effect of these different methods of beating on the compressibility of the pulp is given in Table XII. Relative compressibility

TABLE XII

EFFECT OF REFINING TREATMENT ON RELATIVE COMPRESSIBILITY

Time of Refining min.	Drainage time, seconds 6-inch Suction Head	2-inch Suction Head	Relative Compressibility
	Sharpened Valley Beater		
0	0.27	0.45	0.60
10	0.48	0.78	0.62
25	1.02	1.72	0.59
45	3.40	5.66	0.60
60	11.14	18.26	0.61
	Normal Valley Beater		
0	0.25	0.43	0.57
10	0.40	0.67	0.60
25	0.82	1.41	0.58
45	2.67	4.48	0.60
60	8.00	13.84	0.58
	Pebble Mill		
10	0.49	0.66	0.74
30	0.47	0.74	0.63
45	0.51	0.80	0.64
60	0.76	1.17	0.65
90	1.12	1.95	0.59
	Morden Stockmaker		
1/2	0.52	0.79	0.66
1	0.67	1.14	0.59
2	0.85	1.50	0.57
4	1.66	3.03	0.55
	Lampén Mill		
30	0.82	1.37	0.60
60	1.81	3.01	0.60
90	3.75	6.14	0.61

is a term selected to express the ratio of the drainage times obtained, using six inches and two inches suction pressure, respectively.

These data indicate the following conclusions concerning relative compressibility: neither the degree nor the method of refining have a pronounced effect; the same furnish, whether beaten with sharp or dull tackle, will nearly equal values; and any difference is caused by a variation in the pulp itself.

An investigation of the difference in relative compressibility between different types of pulps was therefore made. Samples of kraft, soda, groundwood, and sulfite pulps were beaten in the laboratory Valley beater. No particular beating procedure was used. The drainage time at the different suction heads were obtained and the relative compressibility calculated. These data are compiled in Table XIII.

TABLE XIII

RELATIVE COMPRESSIBILITY OF DIFFERENT PULPS

Pulp	Drainage Time, seconds 6-inch Suction Head	 2-inch Suction Head	Relative Compressibility
Kraft	3.94	5.55	0.71
Soda	5.81	11.62	0.50
Sulfite	2.72	4.38	0.62
Groundwood	13.61	29.58	0.46

The relative compressibility differs considerably between pulps. Thus the relative compressibility of a pulp seems to be due to the character of the original pulp rather than the physical refining treatment to which it has been subjected.

Effect of the Inversion of Results Between Testers

The fact that the relative drainage time of different pulps changes with head is of utmost importance. There can be no universal interconversion between the different freeness scales since, as has been shown, the testers have different heads acting to cause drainage. Nor can any of the existing testers be used to prophesy the relative drainage rates of different stocks upon the paper machine. Although the total head on the machine (including both the head above the wire and the effective suction head) is unknown, it is probably not the same as that on any of the testers. However, if the same furnish is used, any of the existing testers would be expected to give a relative measure of the rate of drainage on the machine.

The existing testers actually give a relative measure of freeness when freeness is defined in terms suited to that particular tester. But in the light of a definition of freeness as that property of a pulp which controls the drainage of water from a pulp suspension on the wire of a Fourdrinier paper machine, it is obvious that the testers leave much to be desired.

To get an absolute relative scale of drainage time, it is necessary, in the light of the foregoing data, to determine the drainage time under conditions of head equal to those of the paper machine. This means the use of an instrument similar to the one developed in this investigation. Therefore, to obtain a relative measure of drainage on the machine, the effective suction acting under the wire must be known. Since it is considered to vary with machine speed, number of table rolls, and the relative position of the apron and the slice, the determination of the true relative machine drainage would be a difficult one. However, if the effective suction in one condition of operation can be determined, the use of this suction leg for all operational conditions of the machine would give a much closer approximation to the true relation of the drainage behaviors of the different stocks than is obtained on any existing tester.

The effective suction pressure on a paper machine was actually determined on an experimental paper machine. Two pulps of different nature were used which were known to have different relative compressibilities. These pulps were run over the machine at constant machine speed, the same headbox consistency, and the same basis weight. The consistency selected was one which allowed the sheet to go dry on the wire before the suction boxes. The distance from the end of the apron to the break was measured and from this and the machine speed, the effective drainage times and the ratio between the two were calculated.

The drainage times of the two pulps were determined at different suction pressures and the ratio between the two pulps calculated. The data of the machine operation and the instrumental data are given in Table XIV.

The change of drainage ratio with head is shown in Figure 9. This curve extrapolates to a drainage ratio for the two pulps equal to that obtained on the machine at a suction head of about fourteen inches. This effective suction head acting on the machine must be due to more

TABLE XIV

MACHINE DRAINAGE TIME DETERMINATION

	Sample 1	Sample 2	Ratio
Machine speed	84 ft./min.	85 ft./min.	
Headbox consistency	0.665%	0.660%	
White water consistency	0.043%	0.042%	
Percentage of fines	6.5%	6.4%	
Distance to "break"	3.67 ft.	7.58 ft.	
Effective drainage time	2.62 sec.	5.36 sec.	2.04

Laboratory Instrument--Drainage Time, seconds

Suction Head inches			
2	1.50 sec.	4.98 sec.	3.32
3	1.28 sec.	3.54 sec.	2.76
4	1.12 sec.	2.92 sec.	2.61
5	0.96 sec.	2.44 sec.	2.54
6	0.83 sec.	2.06 sec.	2.48
7	0.79 sec.	1.92 sec.	2.43

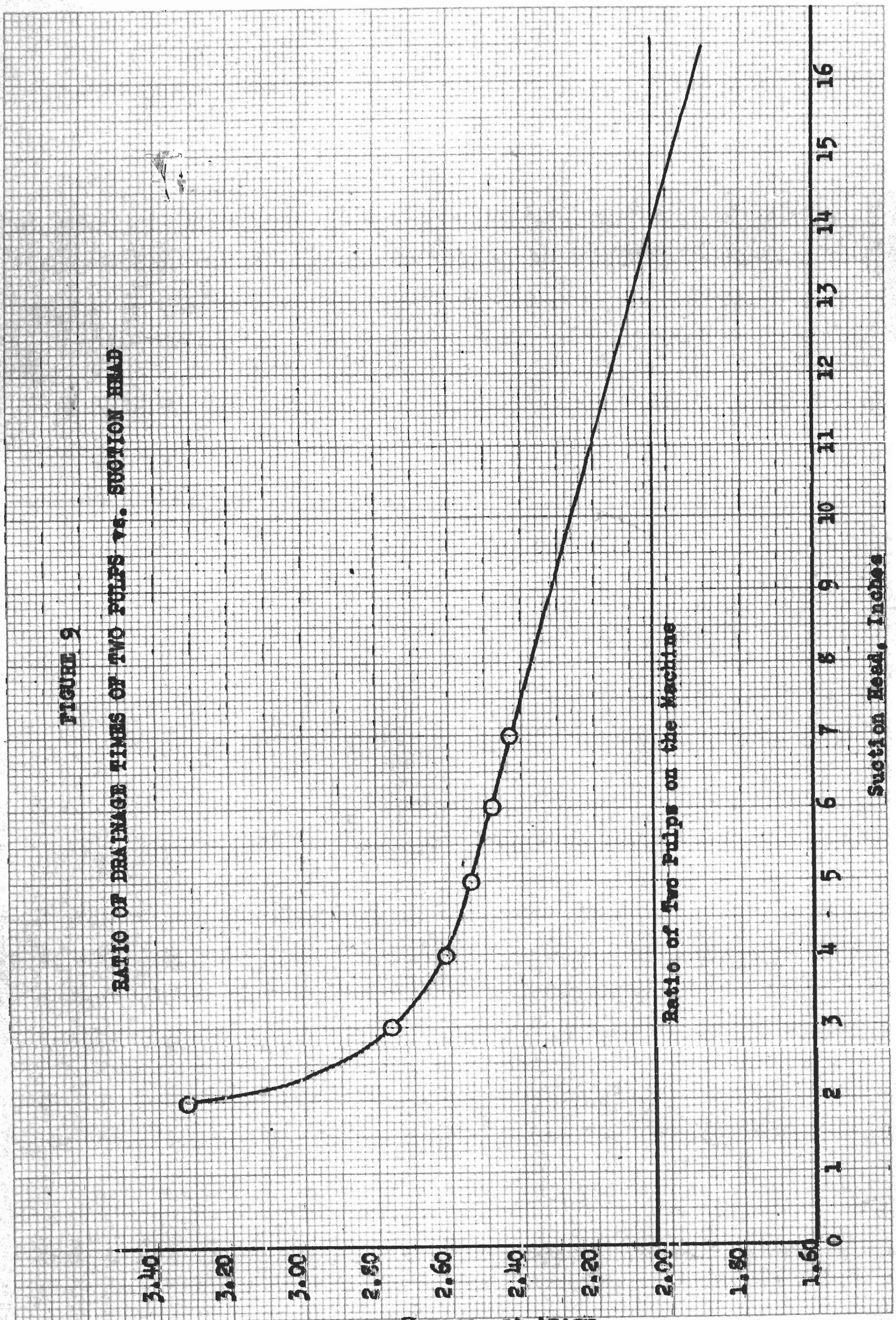


FIGURE 9

RATIO OF DRAINAGE TIMES OF TWO PULPS vs. SUCTION HEAD than merely the true suction head. It undoubtedly is also affected by the other machine variables.

The duplication of the ratio of machine drainages by the instrument was shown for some unbeaten sulfite pulp. The ratio of the drainage times on the machine determined in the above way for a sample treated with locust bean gum and an untreated sample was 1.28 in one case and 1.23 in a second. On the instrument the ratios were 1.22 and 1.20, respectively. The ratio on the instrument did not vary with suction head beyond experimental error. This was expected because the same stock was used. Thus, the relative drainage time between two pulps checks quite closely on the machine and on the instrument.

Interconversion of Freeness Scales

Although it has been shown that interconversion of freeness scales are exact only for the pulp used in their determination, Table XV was prepared for bleached sulfite stock to indicate how the drainage times determined on the instrument developed during this investigation compares with the freeness and slowness values as determined on existing testers. The relationship between the values obtained on existing testers and the laboratory instrument for one pulp is graphically illustrated in Figure 10. Since these relationships will not hold absolutely for any other pulp, only the actually measured points are included. None have been approximated from curves in order to give a complete chart over the entire range. All data listed are the average of three separate determinations.

TABLE XV

INTERCONVERSION OF FREENESS SCALES
Bleached Sulfite Pulp

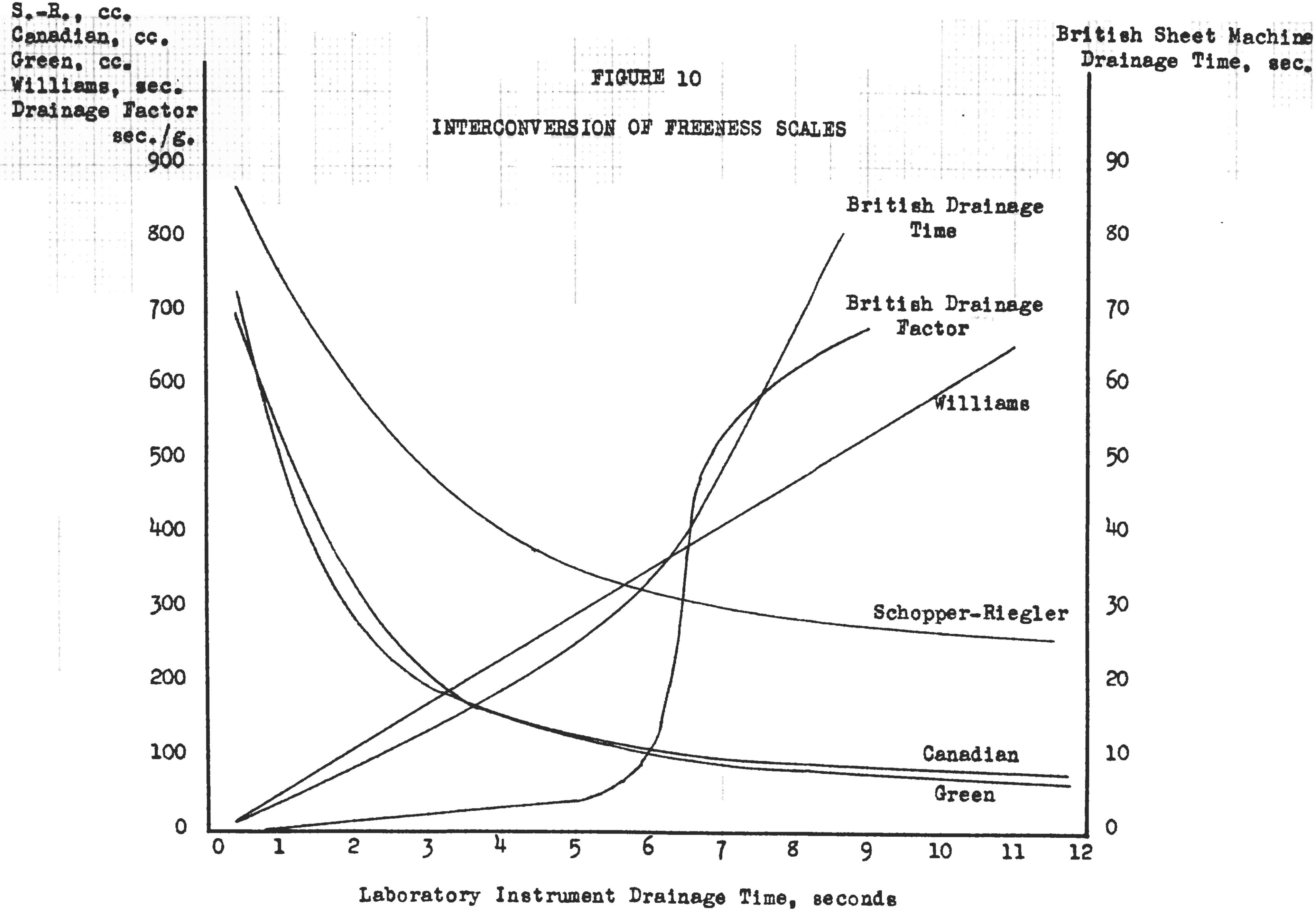
Tester	Beating Time, minutes				
	0	2	5	10	15
Schopper-Riegler, cc.	860	850	845	810	778
Canadian, cc.	710	705	700	610	560
Green, cc.	680	680	675	580	580
Williams, sec.	14.8	16.1	18.5	30	45
British,					
Drainage time, sec.	4.0	4.1	4.2	4.3	4.9
Drainage factor, sec./g.	0.58	0.76	1.03	2.05	4.80
Laboratory instrument, sec.	0.41	0.48	0.57	0.66	0.81

Tester	Beating Time, minutes				
	20	25	30	35	40
Schopper-Riegler, cc.	730	724	700	505	465
Canadian, cc.	470	455	430	220	190
Green, cc.	510	490	468	230	186
Williams, sec.	65	75	77	164	187
British,					
Drainage time, sec.	5.7	6.8	6.9	11.9	15.4
Drainage factor, sec./g.	5.92	7.42	8.38	20.8	29.8
Laboratory instrument, sec.	1.15	1.28	1.31	2.62	3.28

Tester	Beating Time, minutes				
	45	50	60	75	90
Schopper-Riegler, cc.	328	318	292	175	120
Canadian, cc.	120	102	98	53	43
Green, cc.	110	93	87	41	18
Williams, sec.	328	404	479	1042	1935
British,					
Drainage time, sec.	30.5	45.7	63.9	188	387
Drainage factor, sec./g.	76.8	518	616	---	---
Laboratory instrument, sec.	5.71	6.82	7.77	18.72	36.62

FIGURE 10

INTERCONVERSION OF FREENESS SCALES



The samples of beaten pulp were obtained by a standard beater run (Institute Method 403) in the 1 1/2-pound Valley laboratory beater. The standard testing procedures were used for all instruments. A sample weight of one gram, a one-inch head above the wire, and a suction leg of three inches were used in the laboratory instrument.

As can be seen in Figure 10, the values obtained on the laboratory instrument show a general proportionality with those obtained on the drainage type testers. The Williams values show almost a straight-line relationship with the laboratory instrument. The drainage value on the British sheet machine varies somewhat from a straight-line function of the instrument drainage time, whereas the drainage factor has a very peculiar relationship to instrument drainage. The more empirical, divided-funnel type testers, as would be expected, gave values generally proportional to each other but these values had a definitely nonproportional relation to determinations made on the laboratory instrument.

EFFECT OF THE VARIABLES OF DRAINAGE

The drainage of water from fibers felting on a wire is affected by a great many variables. These drainage variables divide themselves readily into two classes; machine or experimental variables, and stock or furnish variables. The former class includes such factors as temperature, wire size, head above the wire, effective suction head, consistency, and the sheet weight. Among the stock variables are the degree and nature of refining, fiber length, fiber width, fibrillation of the fibers, distribution of fines, wet compressibility of the pulp pad, the hydration (either chemical or colloidal) of the stock, and the effect of added material such as electrolytes, fillers, rosin, starch, etc.

Operational Variables

Head Causing Drainage. The effect of the head causing drainage has already been discussed. It was shown that the ratio between drainage times at different heads differs between pulps, and also that the ratio between two different heads could be considered constant for any one pulp, regardless of the treatment given that pulp.

The head causing drainage includes both the head above the wire and the suction head below the wire. Tables XVI and XVII show the effect of variation of pressure head and suction head, respectively, on the ratio of the drainage times for a very free and a very slow pulp. The entire range of pulp freeness has been covered and the same results are shown throughout the drainage time scale. The drainage time measurements refer to the laboratory instrument. A three-gram sample, a temperature of 20° C., and a 50-mesh wire were used. The head below the wire was kept at three inches for the data expressed in Table XVI and a positive head of two inches was used for the data in Table XVII. The data given are the average of five determinations, and drainage times are corrected for the drainage time of plain water.

The data agrees with that shown previously. The effect of head, either pressure or suction, on drainage time is not affected for a given pulp by the degree of beating.

TABLE XVI

EFFECT OF PRESSURE HEAD

Free Stock			Slow Stock		
Pressure Head in.	Drainage Time sec.	Percentage of 2-inch Reading	Pressure Head in.	Drainage Time sec.	Percentage of 2-inch Reading
1.0	0.46	26	1.0	63.1	31
1.5	1.00	57	1.5	118.1	59
2.0	1.76	100	2.0	201.6	100
2.5	2.43	139	2.5	269.3	134
3.0	3.10	176	3.0	356.4	178

TABLE XVII

EFFECT OF SUCTION HEAD

Free Stock			Slow Stock		
Suction Head in.	Drainage Time sec.	Percentage of 3-inch Reading	Suction Head in.	Drainage Time sec.	Percentage of 3-inch Reading
2	2.07	121	2	236.0	119
3	1.70	100	3	199.3	100
4	1.50	88	4	170.8	85
5	1.42	83	5	159.3	80

Effect of Temperature. Table XVIII illustrates the effect of temperature on drainage time. Again only the data for a free stock and a slow stock are included. The same effect was obtained for the entire scale of drainage time. The calculated drainage time was calculated from the 20° C. reading and the proportional viscosity change with the change in temperature. A three-gram sheet, two-inch pressure head, 50-mesh wire, and a three-inch suction head were used in this series of determinations. The drainage time is not corrected for the drainage time of water, because that is also affected by viscosity.

TABLE XVIII

EFFECT OF TEMPERATURE

Free Pulp			Slow Pulp		
Temp. ° C.	Drainage Time sec.	Calculated Time sec.	Temp. ° C.	Drainage Time sec.	Calculated Time sec.
10	2.61	2.57	10	260.8	264
15	2.28	2.25	15	220.4	230
20	1.98	1.98	20	203.1	203
25	1.77	1.76	25	182.6	180
30	1.63	1.57	30	160.3	161
35	1.52	1.41	35	148.7	145

The data indicate that the change in drainage time due to a change in temperature can be considered, for all practical purposes, proportional to the change in the viscosity of water.

<u>Effect of Weight</u>. The instrument developed for this investigation is not suited for a study of the effect of a variation in weight on drainage time. The end point is determined automatically when the sheet does "dry." Since the volume occupied by the fibers varies with weight, the instrument measures the drainage of a volume of water which, therefore, would change with the weight of pulp used.

Studies of the effect of sample weight on drainage time were carried out on both the British sheet machine and on the Williams instrument. These data are given in Tables XIX and XX, and are illustrated in Figures 11 and 12. Two pulp samples with different freeness were studied for the British sheet machine and three for the Williams.

TABLE XIX

EFFECT OF WEIGHT ON BRITISH SHEET MACHINE DRAINAGE TIME

Sample 1		Sample 2	
Weight g.	Drainage Time sec.	Weight g.	Drainage Time sec.
0.242	4.3	0.405	4.5
0.687	25	0.696	8.4
0.952	46	0.700	8.6
1.067	56	1.093	20.3
1.172	67	1.213	24.3
1.333	82	1.531	35.3
1.424	91	1.687	40.0
1.895	139		

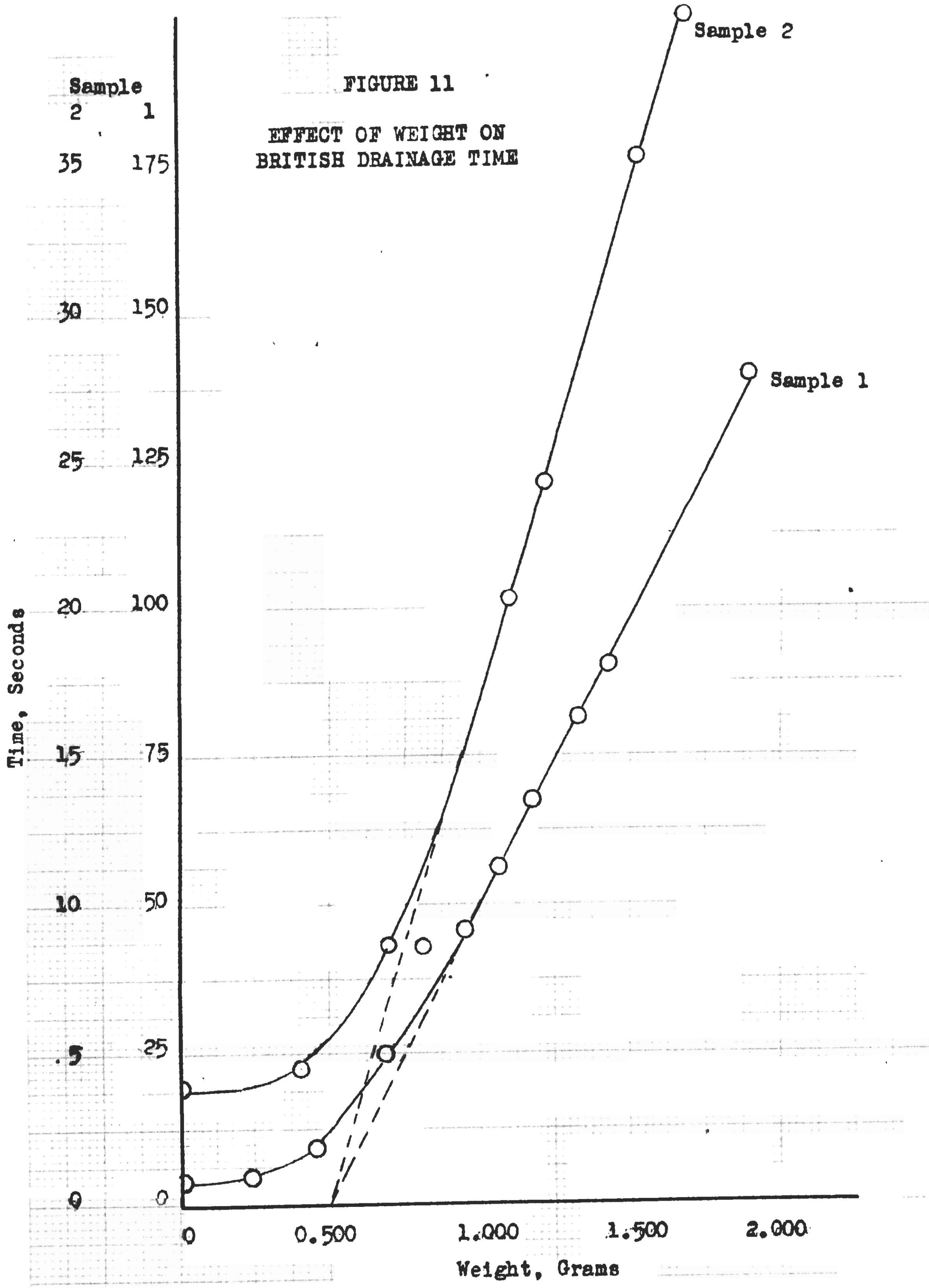


FIGURE 11
EFFECT OF WEIGHT ON
BRITISH DRAINAGE TIME
Sample
2 1
35 175
30 150
25 125
20 100
15 75
10 50
5 25
0 0
Time, Seconds
Sample 2
Sample 1
0
0.500
1.000
1.500
2.000
Weight, Grams

The curves for the effect of weight on the British sheet machine seem to be linear functions of weight. However, they appear proportional to the weight minus a constant rather than to the weight alone. The straight lines extrapolate to a value of one-half gram. This is in agreement to the data found by Sankey (24), Campbell (23), and others.

TABLE XX

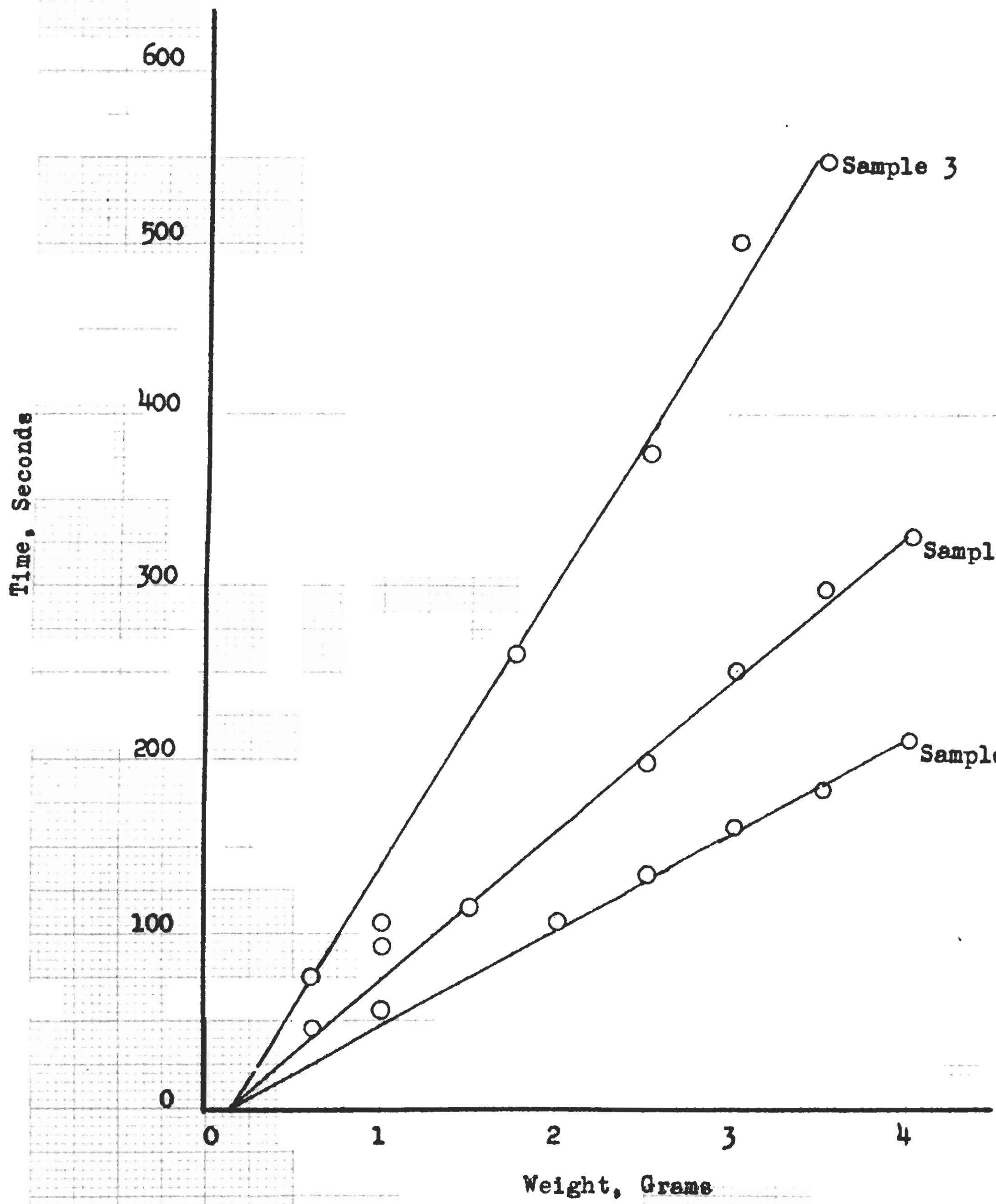
EFFECT OF WEIGHT ON THE WILLIAMS DRAINAGE TIME

Weight g.	Drainage Time, seconds		
	Sample 1	Sample 2	Sample 3
0.6	--	47	77
1.0	57	93	107
1.5	--	116	---
1.75	--	---	262
2.0	107	---	---
2.5	134	198	378
3.0	162	251	501
3.5	183	298	547
4.0	212	328	638

With the Williams tester a linear function of drainage time with weight was also obtained. The drainage time was again proportional to the weight minus a constant but in this case the constant was about one-eighth of a gram. Since the area of the wires on the two testers are also in a ratio of four to one, the statement seems justified that a certain thickness of pulp pad must be obtained before a capillary effect sets in and an indication of the true drainage through a fiber

FIGURE 12

EFFECT OF WEIGHT ON
WILLIAMS DRAINAGE TIME



mat is obtained. It appears that this necessary pad thickness is equivalent to about 0.25 gram per 100 sq. cm.

Effect of Wire Size. Four different wire meshes were used in the instrument; 50, 60, 70, and 80. In all cases the effect of varying the wire used in the instrument on the drainage time was very small. The amount of fines passed by the wires was in all cases of the order of one per cent, and no apparent difference in the amount of fines passed was evident between the different wires. On the paper machine, the effect of the wire used would be of relatively greater importance because, as was seen earlier, the amount of fines going through the wire on the machine is far greater than on any instrument.

Stock Variables

Fiber Length. The majority of the studies which have been made of the effect of fiber length on drainage have been rather unscientific. The different fiber length samples have been obtained by fractionation of the original pulp in an instrument similar to the Bauer-McNett classifier. Thus, the effect of the different chemical and physical properties of the different fiber length fractions of the pulp, as well as the effect of the fiber length change itself, was evidenced in the results.

To avoid this, the original pulp was classified by the regular Bauer-McNett procedure, and the longest fibers were separated. These fibers were made into sheets on the Noble and Wood sheet machine and pressed to 65 per cent moisture content. This moisture content was selected because it is known that no appreciable fiber-to-fiber bonding occurs with more than 60 per cent moisture still present in the sheet. The sheets were cut on a cutting board into four different widths: 1/16-inch, 3/16-inch, 1/4-inch, and 3/8-inch; the uncut sample was also studied. These samples were dispersed with a slowly rotating "Lightnin" stirrer. In this way any fibrillation of the fiber was avoided.

The above procedure was carried out on two samples of bleached sulfite pulp, one of which had been merely slushed for five minutes in the 1 1/2-pound Valley laboratory beater and a second which had been beaten for sixty minutes in the laboratory beater according to the standard procedure. The drainage times and freenesses were run on all the existing testers and on the laboratory instrument. (The standard procedure was used: 1-gram sample, 20° C., 1-inch head above the wire, 3-inch suction head, and 50-mesh wire. Because of the low drainage time of the unbeaten pulp, a second drainage test of this pulp was also run using a higher sample weight (2.5 grams).) The average fiber length was also determined. These data are given for both the unbeaten sample and the beaten sample in Table XXI.

The fiber length determinations were made by a projection method. A sample of fiber was dispersed by the addition of locust bean gum. The image of the suspension was projected at a known magnification on a screen. The length of each of two hundred fibers was determined and the average fiber length calculated.

It is evident that average fiber length _per se_ has only a small effect upon drainage time. Drainage time increases with a decrease in

TABLE XXI

EFFECT OF FIBER LENGTH

Unbeaten Sulfite Pulp

	Sample Number				
	1	2	3	4	5
S.-R.	870 cc.	865	870	867	865
Canadian	750 cc.	750	750	735	725
Green	695 cc.	700	695	705	700
Williams	10.0 sec.	10.9	12.8	13.0	13.0
Laboratory instrument					
1 gram	0.28 sec.	0.32	0.30	0.37	0.39
2.5 grams	0.84 sec.	0.87	0.89	0.93	0.96
Fiber length	2.84 mm.	2.47	2.09	1.76	1.21

Beaten Sulfite Pulp

	Sample Number				
	1	2	3	4	5
S.-R.	370 cc.	370	375	372	367
Canadian	123 cc.	120	118	123	117
Green	94 cc.	92	92	90	90
Williams	335 sec.	349	350	351	357
British	48 sec.	46	43	42	40
Laboratory instrument	5.18 sec.	5.34	5.49	5.87	6.08
Fiber length	2.03 mm.	1.86	1.56	1.24	0.93

fiber length but not to a degree which has any importance in papermaking.

These samples differed in their average fiber length but were made up of all length fibers in different distributions. To check on the effect of a more limited distribution of fiber length, the prepared samples of unbeaten pulp were mixed together and fractionated. Drainage times were run on the various fractions. Fiber length determinations were not run but as seen in Table XXII, the above data were corraborated.

TABLE XXII

EFFECT OF FIBER LENGTH ON DRAINAGE TIME

On Screen	Drainage Time sec.
20	0.30
35	0.33
65	0.34
150	0.46

To show that samples obtained by fractionation were of decidedly different drainage time, a groundwood pulp was classified in the Bauer-McNett instrument. The drainage times of the original pulp and of the various fractions are shown in Table XXIII.

TABLE XXIII

EFFECT OF FRACTIONATION

	Drainage Time sec.
Whole pulp	11.56
On 35-mesh	0.32
On 65-mesh	0.55
On 150-mesh	11.52

Since none of the fractions show a drainage time equal to that of the original pulp, the high drainage time of the original pulp seems to be due to the finest material in the pulp, that which is collected on the 150-mesh screen plus that passed through the 150-mesh screen of the classifier. This agrees with other data available.

The effect of fiber length upon the decrease of freeness with beating was investigated. Standard beater runs were made on bleached sulfite pulps whose initial fiber length had been changed. Dry lap pulp was cut by hand into four different width strips referred to in Table XXIV. as samples 1, 2, 3, and 4. The cuts were made across the length of the pulp to give the greatest change in fiber length. Fiber lengths were run on the initial pulps after the five-minute slushing period by the method previously described. A Schopper-Riegler freeness and drainage times on the Williams tester and the laboratory instrument were run at every beating interval.

The results show that the shorter fibers are more readily degraded in the beater. The fibers which had been shortened by cutting undoubtedly fibrillate much more readily than the uncut fibers; this probably accounts for this phenomenon.

<u>Specific Surface</u>. Since the fibrillation of a pulp has been thought to be of decided importance in the drainage behavior of a pulp, an investigation of the degree of fibrillation and its effect on drainage should be made. Fortunately a rapid method for the estimation of the surface area of pulp has recently been developed. This method which is

TABLE XXIV

EFFECT OF FIBER LENGTH ON THE CHANGE OF FREENESS WITH BEATING

Test	Beating Time, minutes 0	5	15	30	45	60
	Sample 1					
S.-R.	860 cc.	850	770	680	310	286
Williams	15 sec.	19	47	91	348	580
Laboratory instrument	0.45 sec.	0.53	0.79	1.50	5.98	8.31
Fiber length	2.61 mm.					
	Sample 2					
S.-R.	865 cc.	855	765	665	300	254
Williams	15 sec.	20	49	105	360	616
Laboratory instrument	0.45 sec.	0.54	0.81	1.84	6.40	9.14
Fiber length	2.07 mm.					
	Sample 3					
S.-R.	860 cc.	850	765	605	290	205
Williams	16 sec.	23	50	115	409	834
Laboratory instrument	0.43 sec.	0.55	0.85	1.95	6.83	12.61
Fiber length	1.72 mm.					
	Sample 4					
S.-R.	860 cc.	850	750	500	272	175
Williams	16 sec.	23	54	176	482	1662
Laboratory instrument	0.48 sec.	0.58	0.88	2.70	8.42	21.73
Fiber length	1.25 mm.					

referred to as the "Specific Surface Measurement" was developed by Clark (47) and later examined by McEwen (48).

In this method fibers are uniformly coated with silver and the area of this coating measured by virtue of the fact that hydrogen peroxide is catalytically decomposed by a silvered surface. The measurement of the rate of this reaction is used to indicate the total silvered area. The rate of this reaction with known areas of silvered cellophane was used to prepare a calibration chart with which to determine the size of an unknown area from the amount of undecomposed hydrogen peroxide and the average temperature of the reaction. The development of the method and the determination of the calibration chart are well described by Clark (47).

The modified procedure as given by McEwen (48) was followed in this determination. Fifteen to 20 mg. of fiber were silvered in 100 cc. of a boiling one per cent silver nitrate solution which had been precipitated with ammonia, after which enough excess ammonia added to just redissolve the precipitate. The silvering is carried on twice as long as necessary to make the fibers opaque. The silvered fibers are well washed with distilled water and transferred to the reaction flask with 95 cc. of distilled water and 5 cc. of Boyd's borate buffer solution.

The fibers are kept in suspension by moderate stirring with an electric stirrer, and 25 cc. of 0.5 N hydrogen peroxide rapidly introduced. After 50 seconds, the temperature is taken, and after 100 seconds the reaction is stopped by the addition of 15 cc. of 2 N sulfuric acid. The excess hydrogen peroxide is titrated with 0.5 N potassium permanganate solution and the area of the fiber sample read from the calibration report.

Bleached sulfite pulp had been beaten with all the available laboratory beating equipment in the study of the effect of refining treatment on relative compressibility. "Specific Surface Measurements" and drainage times were determined for this pulp at each interval in an attempt to show the relation between the two. The refining treatments used in this study include beating in a sharpened and in a dull beater, pebble-milling, and refining in the Morden Stockmaker and the Lampén mill. The data are given in Table XXV. The specific surface value is plotted in Figure 13 against drainage time. The adapted drainage time procedure using a three-inch suction head was used. Both the drainage times and the specific surfaces recorded are the average of three determinations.

Figure 13 shows that the drainage time does not appear to be a definite function of specific surface although, in general, with any one method of refining the higher the specific surface the greater the drainage time. The two pieces of refining apparatus, the Lampen mill and the pebble mill, which are believed to cut the fiber the least and to show the most fibrillating action, gave the highest increase in specific surface with increased drainage time. The refiners thought to have the highest cutting action—that is, the sharpened Valley beater and the Morden—showed a smaller increase of specific surface with drainage time. Thus, the specific surface determination agrees qualitatively with the accepted ideas concerning the relative severity of

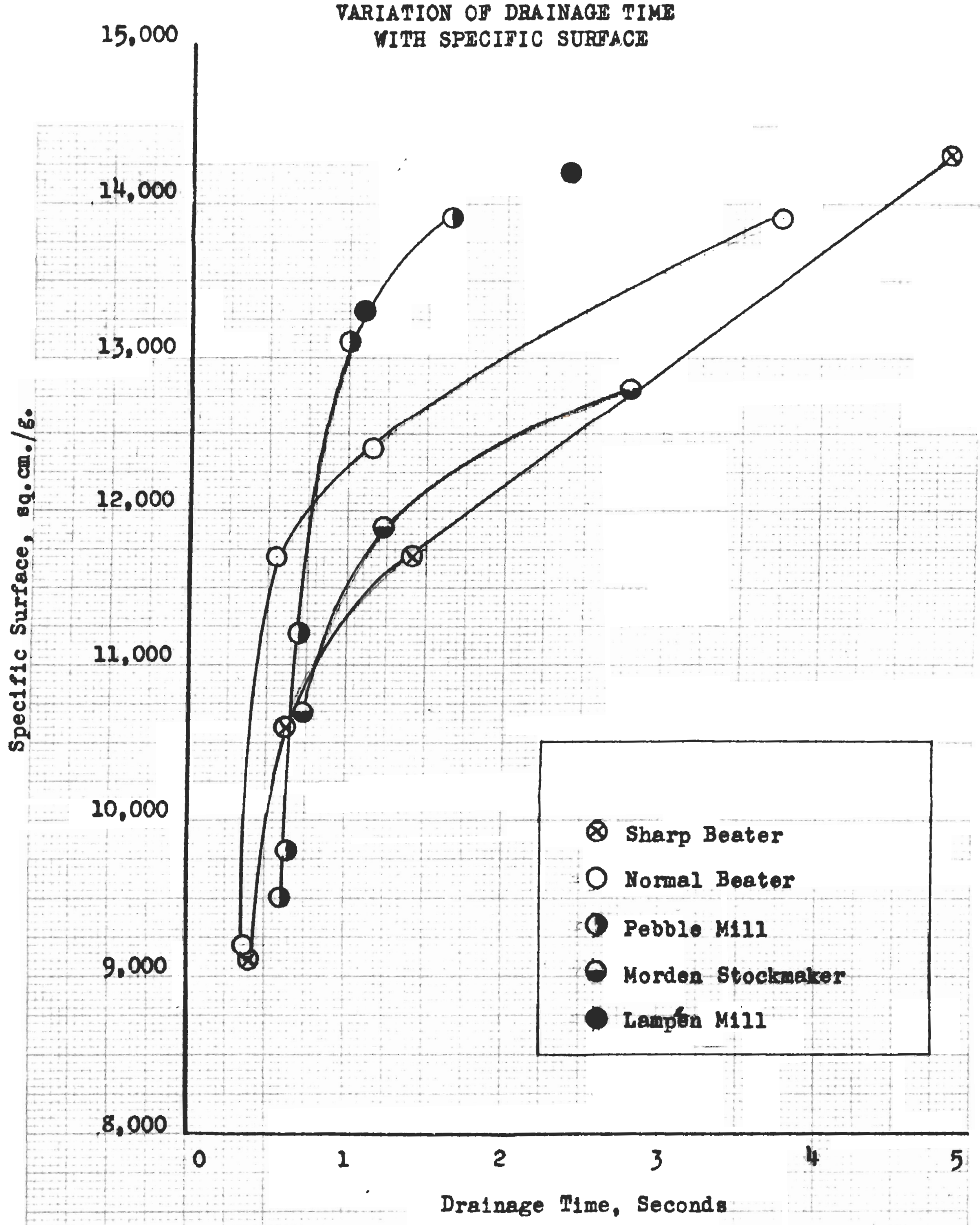
TABLE XXV

EFFECT OF SPECIFIC SURFACE

Time of Refining min.	Drainage Time sec.	Specific Surface sq.cm./g.
	Sharpened Valley Beater	
0	0.39	9,100
10	0.63	10,600
25	1.41	11,700
45	4.83	14,300
60	15.18	17,500
	Normal Valley Beater	
0	0.37	9,200
10	0.55	11,700
25	1.14	12,400
45	3.76	13,900
60	11.00	15,900
	Pebble Mill	
10	0.59	9,500
30	0.65	9,800
45	0.69	11,200
60	0.99	13,100
90	1.65	13,900
	Marden Stockmaker	
1/2	0.72	10,700
1	0.91	11,200
2	1.22	11,900
4	2.57	12,800
	Lampén Mill	
30	1.09	13,300
60	2.41	14,200
90	5.28	15,800

FIGURE 13

VARIATION OF DRAINAGE TIME
WITH SPECIFIC SURFACE



treatment with the different laboratory refining equipment.

It is felt, however, that this method of area determination while an indication of the change of area is not truly a relative measurement of the degree of fibrillation or of increased specific surface. McEwen (48) has shown that with cellophane a higher area measurement is obtained if the cellophane is cut into smaller pieces. Thus it appears that, as would be expected, the catalytic decomposition takes place at a more rapid rate the more bends, corners, and irregularities there are. Since the regularity of the fiber surface is far from that of cellophane, the calibration chart will not give the true surface value. Furthermore, since the surface regularity of the fibers would be expected to change on fibrillation and, in fact, with any refining action, the change in the measured specific surface area on beating would not be proportional to the actual change in surface although relative to the change in area.

Effect of Added Materials. Known amounts of electrolytes of different valences were added to samples of beaten pulp and allowed to stand for a period of one hour. The drainage times were then run on the samples. On account of lack of time, only one determination was made on each. These data are presented in Table XXVI and are illustrated in Figure 14.

At first glance the curves of the effect of the various ions seems to be rather confused. However, when one realizes that any addition of an ion effects both the hydration of the fibers and the charge upon the fibers, the effects produced can be more logically interpreted.

TABLE XXVI

EFFECT OF ION CONCENTRATION

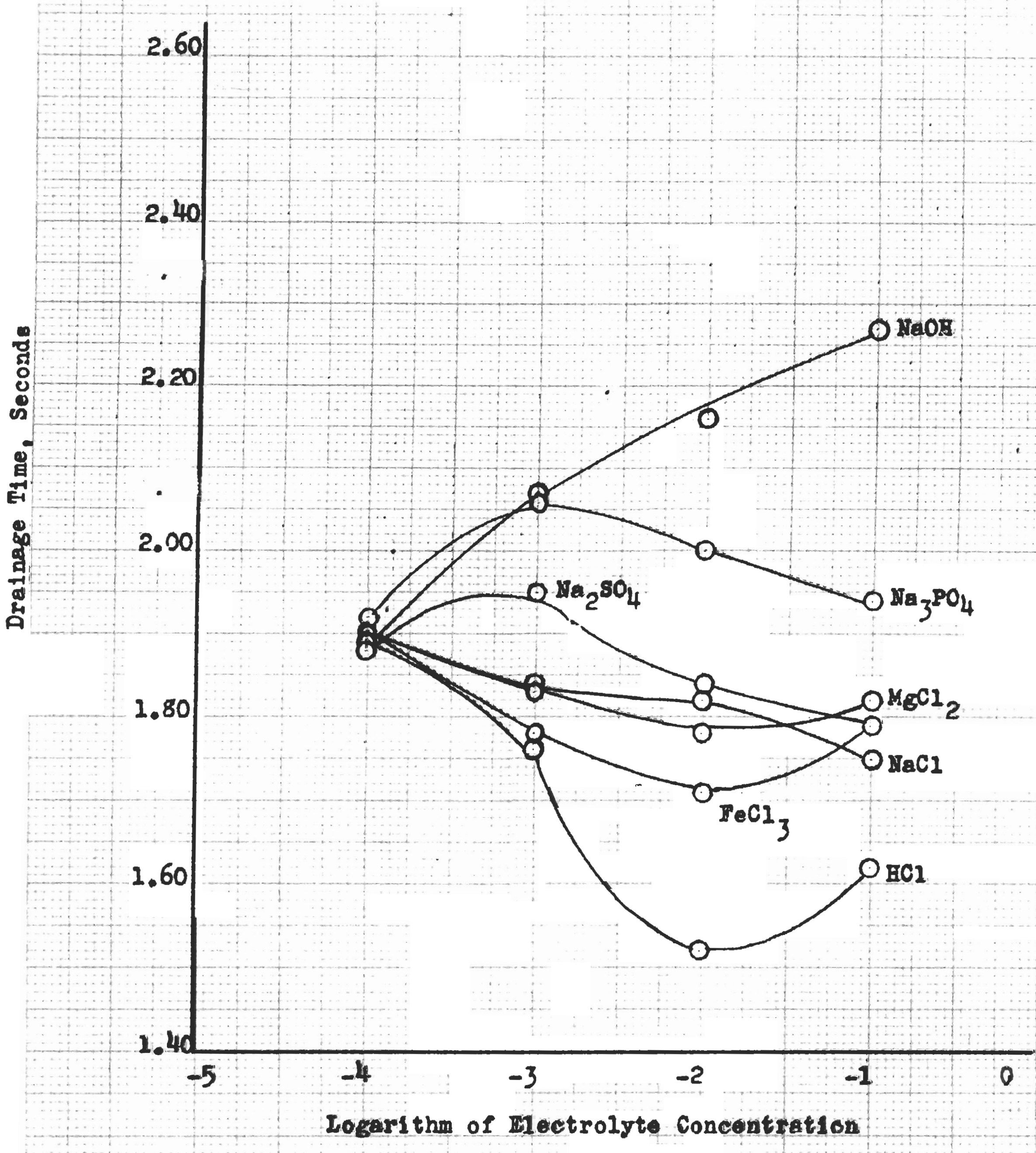
	Drainage Time, seconds Normality			
Material	0.0001	0.0010	0.0100	0.1000
NaCl	1.90	1.83	1.82	1.75
$MgCl_2$	1.89	1.84	1.78	1.82
$FeCl_3$	1.90	1.78	1.71	1.79
HCl	1.90	1.76	1.52	1.62
NaCl	1.90	1.83	1.82	1.75
Na_2SO_4	1.88	1.95	1.84	1.79
Na_3PO_4	1.92	2.06	2.00	1.94
NaOH	1.89	2.07	2.16	2.27

(Hydration as discussed in this section refers to colloidal hydration. This term is used to indicate water held by the forces of adsorption.) An increase in the hydration of the fiber would be expected to result in an increased drainage time owing to the effective closing of the capillaries, whereas an increase in the electrostatic charge on the fibers would tend to cause a mutual repulsion between fibers and hence a shorter drainage time.

The effect of sodium chloride is readily explained. The hydration of the fibers is increased by the addition of the highly hydrated chloride ion. However, since the drainage time decreases with concentration, it can be assumed that the chloride ion is preferentially absorbed and the effect of this on the charge of the fiber is much more

FIGURE 14

VARIATION OF DRAINAGE TIME WITH
LOGARITHM OF ELECTROLYTE CONCENTRATION



than the effect on hydration, causing a net decrease in drainage time.

The magnesium and the ferric chlorides produce the same general trend. In both cases, however, the combination of the positive ions with the hydroxyl ions present to form insoluble hydroxides complicates the picture. In both cases the initial effect appears to be due to the net effect of a decrease of the electrostatic charge caused by the greater effect of the polyvalent cations over the monovalent chloride ion and the evidently more important decrease in hydration because of the introduction of the less hydrated magnesium and ferric cations. At the higher concentration the hydrated layer is evidently practically at its minimum and the effect of a further decrease in charge tends to increase the drainage time. The increased effect of the trivalent ferric ion over the divalent magnesium ion is evident from the curves.

Hydrochloric acid shows a net effect of decreased hydration. The hydrogen ion is known to be a highly hydrated ion owing to its high mobility and also a strongly active positive ion. Since the effect of HCl decreases the drainage time the net effect appears to the result of the decreased hydration. Again, after the hydrate layer has reached a minimum, it may be presumed that the decrease of the charge takes effect and increases the final drainage time.

The negatively charged anions follow the same reasoning. The chloride ion has already been discussed. Sodium sulfate and phosphate show a net effect of an increased hydration because of absorbed sodium cations and a charge increase due to the polyvalent negative ions. The increased effect of the trivalent anion over the divalent is again noticed. Sodium hydroxide gives an increased drainage time with concentration which can be most logically attributed to the gelatinization of the cellulose by caustic.

The effect of dyes on drainage time was studied and the data are given in Table XXVII. As can be seen, a basic dye frees the stock, and a substantive dye slows the stock. An acid dye, on the other hand, has little effect on the drainage time.

TABLE XXVII

EFFECT OF DYES

Dye	Drainage Time, seconds Concentration of Dye, lb./1000 lb. 0.01	0.1	1	10
Methyl violet	1.95	1.89	1.88	1.82
Methylene blue	1.96	1.90	1.87	1.83
Crocein scarlet conc.	1.92	1.94	1.90	1.93
Pontamine yellow GH conc.	1.89	1.93	1.98	2.05

Hydration of the Fibers. As was discussed in the previous section, colloidal hydration of the fibers is believed to be an important consideration in the drainage behavior of a pulp. To test this, a strong dehydrating agent, tannic acid, was added to the fiber in various concentrations. The effect of this dehydrating agent upon the drainage time is shown in Table XXVIII.

Thus it appears that the colloidal hydration of the fibers has a decided effect upon the drainage time. Colloid chemists feel that a

TABLE XXVIII

EFFECT OF TANNIC ACID

Concn. of Solution %	Drainage Time sec.
0.000	2.20
0.001	2.18
0.010	1.79
0.100	1.63
1.000	1.10

one per cent solution of tannic acid is sufficient to dehydrate a gel. Since the drainage time of the samples treated with one per cent tannic acid is still appreciable, it appears that the increase of drainage with refining is not caused by hydration alone.

Since hydration of the cellulose might produce a solvation of the more readily dissolved cellulose or a colloidal solution of parts of the fiber, the viscosity change of the water used for beating was investigated. The viscosity as measured by an Ostwald viscosimeter showed no change. However, when the time of drainage through a very fine capillary filter was determined (A Jena 1G-4 crucible was used with a water leg beneath it to prevent surface tension effects), the apparent viscosity of the water decanted from the beaten fibers was higher than that for the original water sample, which indicated the presence of some colloidal material in the water after beating. The increase was not enough to account for a decided change in drainage time.

Boiling is known to decrease the colloidal hydration of a gel. This decrease is known to be irreversible in the case of cellulose. Therefore, an investigation was made of the decrease in drainage time caused by boiling a sample for 30 minutes, cooling to 20^{0} C., and determining the drainage time. This was done on the samples refined with all the laboratory refining apparatus in the investigation of the effect of different refining treatment on the relative compressibility.

The decrease in drainage time obtained by treating a sample in this way agreed roughly with the effect of refining treatment on specific surface. That is, the pebble mill and the ball mill showed the greatest decrease in drainage time with boiling, and the Morden and the sharpened Valley beater the least. This is in agreement with the theory, since a crushing and brushing action would be expected to make more surface available for hydration than would a cutting action.

SUMMARY AND CONCLUSIONS

1. An instrument and a testing technique for the determination of drainage time have been developed which more closely simulate drainage on the paper machine. This technique gives a much closer indication of freeness, which is defined in this thesis as the property of a pulp which controls the drainage of water from the pulp on the wire of a Fourdrinier paper machine.

Using the developed technique for determining drainage time, the different testing variables can be kept in the papermaking range. A low head, light sample weight, suction head beneath the wire, and a short time of drainage are all conditions of this method of testing. The short time of drainage is automatically recorded by photoelectric means by use of the sudden drop in specular reflection from the suspension surface as the sheet goes "dry."

This method was found to give a good degree of reproducibility between samples in spite of the very short drainage time. The ratio of the drainage values between two pulps obtained on the instrument agreed very well with the ratio of the machine drainage behavior for these pulps. The ratio of drainage on the machine was obtained by comparing the distances from the apron to the point where the sheet went "dry." The two pulps were run on the machine at the same sheet weight, machine speed, and headbox consistency.

2. Numerous examples of an inversion of the relative freeness between two pulps were found between existing testers. This phenomenon

was investigated thoroughly and found to be due to the difference in the head used to cause drainage on the different instruments. The fact that pulps differ in their relative behavior under different heads may indicate that they are actually compressed to different degrees or that the higher velocity of water discharge at the higher head has a different frictional effect with different pulps.

3. The fact that different pulps do not show the same relative change in drainage time under different heads is very important. First, any conversion chart between the different freeness scales applies only to the pulp with which the chart was prepared. Moreover, any tester which differs from the paper machine in respect to the head causing drainage will not give an absolute indication of how different pulps will behave on the machine. It is indicated that the true ratio between drainage times on the machine for different pulps can only be determined with an instrument similar to the one developed in this investigation and using the same conditions of head that are present on the machine.

4. A method was developed for estimating the effective suction on the paper machine. Two pulps which show different effects when different heads are applied were run on the machine and the ratio of the drainage times determined. The suction leg on the instrument was varied until the ratio of the instrumentally measured drainage times was equal to the ratio obtained on the machine. The effective suction leg obtained in this manner was far too large to be accounted for by the actual suction leg alone and is undoubtedly also influenced by other factors, such as the shake and the high head behind the slice.

5. It was shown that the change of drainage time with head has a definite ratio for any one pulp regardless of the degree or type of refining treatment. Therefore, for the same furnish, any tester will give an indication of the relative drainage behavior on the machine.

6. Although interconversion charts for freeness scales have been shown to have little value between different pulps, a comparison was made of the relative freeness values obtained on all of the existing testers and on the laboratory instrument for a bleached sulfite pulp. This gives a general comparison of the values obtained on the laboratory instrument and on all the other testers.

7. Temperature change was shown to have an effect on drainage time proportional to the change in the viscosity of water.

8. Drainage time was shown to be proportional to the weight of the sample minus a constant rather than to the sample weight alone. This was felt to be caused by the fact that capillary forces do not set up until a certain definite pulp thickness is obtained.

9. Wire size had very little effect upon instrumental drainage time. However, on the paper machine, a much larger proportion of the fibers pass through the wire and the wire size is of greater importance.

10. Fiber length variation produced only a small effect on drainage time. The shorter the fiber, the longer the drainage time became, but the change was not large enough to be of papermaking importance.

11. The effect of the addition of ions to pulp was studied in the light of the change of drainage time. An interpretation of the data through commonly accepted colloidal theory indicates that both the charge on the fiber and the effective hydration of the fiber are of importance in drainage behavior. The addition of tannic acid, a strong dehydrating agent, and the boiling of pulp, which is felt to irreversibly dehydrate cellulose fibers, both led to the conclusion that, although the hydration of the fiber is important, it is not the only cause of an increase of drainage time with beating.

12. An investigation of the relative fibrillation by the use of a measurement of the surface area indicated that fibrillation of a fiber also produced an increase in the drainage time. The data indicate that fibrillation also does not account for the total increase of drainage time with beating.

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