

J. A. Van den Akker

The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The Flocculation of Papermaking Fibers

by John G. Wollwage

June, 1938

THE FLOCCULATION OF PAPERMAKING FIBERS

A thesis submitted by

John C. Vollwage

B. S., 1934, Northwestern University

M. S., 1936, Lawrence College

**in partial fulfillment of the requirements of
The Institute of Paper Chemistry
for the degree of Doctor of Philosophy,
from Lawrence College,
Appleton, Wisconsin.**

June, 1936.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.....	1
II. LITERATURE REVIEW	
A. Factors Influencing Fiber Flocculation and Sheet Formation	4
B. Fiber Flocculation in White Water and Fiber Recovery	18
C. Patent Review	24
D. Summary of the Literature	25
III. PRESENTATION OF THE PROBLEM	26
IV. DEVELOPMENT OF EQUIPMENT AND THE EXPERIMENTAL METHOD	
A. Preliminary Experiments and Considerations .	30
B. Construction of the Flocculation Tester	35
C. Experimental Procedures for Flocculation Experiments	
1. Detailed Routine Procedure	44
2. Specific Procedures	
a. pH Determinations	45
b. Consistency Measurements ..	48
c. Photographic Techniques ...	49
3. Treatment of Data. Concept and Calculation of the Flocculation Index	50
4. Factors Influencing Flocculation Measurements	56

Table of Contents

Page

D. Development of a Torsion Balance and Techniques for the Measurement of Fiber-Fiber Adhesion Forces

1. Construction of the Balance 60
2. Procedures and Calibration of the Torsion Balance
 - a. Detailed Procedure 69
 - b. Calibration of the Balance 72

E. Pulps Used in the Experimental Work 76

V. RESULTS AND DISCUSSION

A. Results Using the Flocculation Tester

1. Reproducibility of Results. Flocculation Tendencies of the Standard Unbleached Spruce Sulphite Stock Dispersed in Tap Water 78
2. The Effect of Alum on Fiber Flocculation
 - a. Various Percentages of Alum in Tap Water 86
 - b. Effect of Alum With Distilled Water 92
 - c. Initial Alum Effect 99
 - d. Reversion of Fiber Dispersion Produced with Alum 102
3. The Effect of Bentonite Clay on Fiber Flocculation 111
4. The Effect of Temperature on Fiber Flocculation 115
5. The Use of a Deflocculating Gun to Aid Fiber Dispersion 122

Table of Contents	Page
6. The Effect of a Wetting Agent on Fiber Flocculation	132
7. The Effect of Beating on Fiber Flocculation	135
8. The Effect of Consistency on Fiber Flocculation	145
9. The Flocculation Characteristics of Air-Dried Pulp	150
10. The Flocculation of Douglas Fir and Birch Sulphite Fibers Relative to that of Spruce Sulphite Fibers	152
B. Results Using the Torsion Balance for Measurements of Fiber to Fiber Adhesion Forces	156
VI. SUMMARY AND CONCLUSIONS	169
VII. LITERATURE CITED.....	176

TABLE OF CONTENTS

Figure No.	Title	Page
1.	Diagrammatic Sketch of Flocculation Tester	36
2.	Photograph of Flocculation Tester	37
3.	Return Flow System of Flocculation Tester	39
4.	Light Arrangement - Flocculation Tester (in text)	42
5.	Graph of $\log F$ - $\log Y$ Relation for Flocculation Run #11, Unbleached Spruce Sulphite, Tap Water	55
6.	Diagrammatic Sketch of Torsion Suspension Mounting	61
7.	General View of Torsion Balance for Fiber- Fiber Adhesion Measurements	63
8.	Close-up of Fibers Mounted in Torsion Balance .	65
9.	Diagrammatic Sketch of Optical Lever Used on Torsion Balance	68
10.	Graph of $\log F$ - $\log Y$ Relation Showing Re- producibility of Flocculation Runs	82
11.	Flocculation of Unbleached Sulphite Stock in Tap Water	83
12.	Graph of $\log F$ - $\log Y$ Relation Showing the Effect of Alum on the Dispersion of Unbleached Sulphite Fibers in Tap Water	88
13.	Alum Effects	90
14.	Graph of $\log F$ - $\log Y$ Relation Showing Alum and Distilled Water Effects	93
15.	Alum and Distilled Water Effects	94
16.	Initial Alum Effect	100
17.	Reflocculation of Fiber Suspension Originally Dispersed With Alum - 1	104

Table of Figures

Page

18.	Reflocculation of Fiber Suspension Originally Dispersed with Alum - 2	105
19.	Reflocculation Effect of Caustic	106
20.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Effect of 25% Bentonite Clay on Fiber Flocculation	113
21.	Effect of Bentonite Clay	114
22.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Effect of Temperature on Fiber Flocculation ...	117
23.	Temperature Effects - 1	119
24.	Temperature Effects - 2	123
25.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Fiber Dispersing Action of Deacetylated Karaya Gum	126
26.	Viscosity Effect of Karaya Gum Deflocculant ...	130
27.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Effect of a Wetting Agent on Fiber Flocculation	134
28.	Effect of a Wetting Agent on Fiber Flocculation	136
29.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Effect of Beating on Fiber Flocculation	138
30.	Effects of Beating	141
31.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Effect of Consistency on Fiber Flocculation ..	147
32.	Effect of Consistency	148
33.	Dispersing Effect of Alum at 0.0047% and 0.0195% Fiber Consistencies	151
34.	Graph of $\log \bar{Y}$ - $\log Y$ Relation Showing the Flocculation Characteristics of Douglas Fir and Birch Sulphite Fibers	154

LIST OF TABLES

Table No.	Title	Page
I.	Flocculation Run No. 11, Detailed Data	51
II.	Reproducibility of Flocculation Runs.....	79
III.	Effect of Alum on the Dispersion of Standard Unbleached Sulphite Stock in Tap Water	87
IV.	The Effects of Distilled Water, Alum, and Sodium Hydroxide on the Flocculation of Standard Unbleached Sulphite Pulp	95
V.	Reversion Effects. Reflocculation of Fibers Originally Dispersed with Alum	103
VI.	Effect of Circulation in Flocculation Tester on the Viscosity of White Water Containing 0.02% of Karaya Gum Reflocculant	129
VII.	Effect of Consistency on Fiber Flocculation	146
VIII.	Flocculation Characteristics of Douglas Fir and Birch Sulphite Fibers Relative to that of Spruce Sulphite Fibers	155
IX.	Fiber - Fiber Adhesion Measurements, Unbleached Spruce Sulphite Fibers, Tap Water - 22° C.	158-59
X.	Fiber - Fiber Adhesion Measurements, Unbleached Spruce Sulphite Fibers, Distilled Water	159-60
XI.	Fiber - Fiber Adhesion Measurements, Unbleached Spruce Sulphite Fibers, Tap Water - 38° C.	166

I. INTRODUCTION

The necessity of determining and isolating the various factors which influence the basic structure of a sheet of paper or, more specifically, give rise to the orientation of papermaking fibers in flowing suspensions is obvious when it is desired to solve the many problems concerned with paper formation, curling of paper, and anisotropic swelling and strength characteristics of the sheet. With the advent of greater machine speeds and increased tonnage in recent years, such problems have mounted proportionally and have stimulated a considerable amount of thought and research along these lines, as indicated by the vast increase in literature dealing with the problems involved and published in the last 5 to 10 years.

Optimum fiber dispersion in the head-box of the paper machine and maintenance of this condition until the sheet is completely formed, minimum orientation or alignment of fibers as the stock passes through the slice, and proper introduction of the stock stream onto the wire are desired to give a randomly orientated but uniform fiber web. The use of practical experience, together with the application of fundamental hydraulic principles, has done much to effect some of the desired improvements in head-box, slice, and inlet construction, and the most recent hydrodynamical research by Moss and Bryant (1) on the motion of fibers in a flowing suspension has given an insight into the important features of head-box and slice design which create marked fiber orientation effects. All such work will ultimately assist in the design of wet-end paper machine equipment according to tested and proved

hydraulic principles, but before this can be gained it seems likely that several other facts should be known about the behavior of fibers in suspension, among which is the phenomenon of fiber flocculation, or the tendency of papermaking fibers to flock after they have once been individually dispersed. Such fiber bunching may occur in the head-box of the paper machine, because of improper design of the equipment, or it may take place on the wire after the stock has left the slice. In this latter case, even proper design of head-box and slice would not be the answer to improvement of formation, and the flocculation effect must become of first order importance.

The agglomeration of fibers and its deleterious effects on formation, occurring under various conditions, are well known to the papermaker. To overcome such difficulties, in some instances specific conditions for minimum flocculation have been defined by trial and error procedures. However, in general, the fundamental cause or causes of the phenomenon are not known. Sometimes the effects are attributed purely to physical conditions, such as the degree of beating to which the stock has been subjected, to the degree of agitation, or to the fiber dimensions themselves. At other times, however, there may be reason to believe that surface forces involving colloiddally active materials present in stock suspensions come into play and produce fiber flocculation. Obviously, too, the relative magnitude of chemically and colloiddally active forces, such as electrokinetic effects, compared with physical conditions such as fiber length, degree of fibrillation, etc., as they are involved, are not known.

Accordingly, it is the purpose of this investigation to follow, in a comprehensive manner, the various causes of papermaking fiber flocculation and to evaluate relatively the importance of such causes to the total phenomenon. The practical value of such a study is, perhaps, first concerned with the formation of the sheet on the machine as regards uniformity of structure and isotropic strength and swelling characteristics. Formation of paper as it relates to "look-through," to printing characteristics, and to the finish of the sheet, is an important property, in at least one of these respects, of any of the great variety of papers made. In addition to being of interest to the paper manufacturer, formation, and therefore fiber flocculation, is important to the producer of pulp laps and sheets which are subsequently to be used in a conversion operation, such as the manufacture of viscose. Here, uniform formation of the lap is necessary to give a uniform penetration of chemicals in the subsequent processing. Fiber flocculation is also a problem to the pulp mill in the process of riffing and fractionating dirt and resin from the stock, since this can be effectively accomplished only when the fibers are well dispersed. Finally, it is obvious that in white water recovery, in contrast to all other cases, maximum agglomeration of fibers is desired for the most efficient system.

All these problems would seem to justify an investigation of the fiber flocculation phenomenon.

II. LITERATURE REVIEW

The fact that the mechanism and specific causes of fiber flocculation are not clearly understood is directly reflected in the rather meager published literature concerning any observed effects. With the exception of several articles which discuss general causes of fiber agglomeration as observed in the paper mill and which give some of the conditions which may be controlled to prevent such flocculation, there have been no reports to indicate that any great amount of investigation has been carried out along these lines. There has been a realization that flocculation of fibers may have a bearing on sheet formation, but practically no measurements or evaluation of the effects have been made. References which are indirectly concerned with flocculation of stock, in that they may deal with the effects rather than the causes, are, of course, more numerous and include such topics as sheet structure, flow properties of pulp suspensions, and white water recovery systems.

In the following review of the published work, the articles directly concerned with fiber flocculation will be considered first and then the related work will be described. The patent literature which covers the use of deflocculants as well as flocculating agents, for use in white water recovery systems, etc., will be reviewed at the conclusion.

Factors Influencing Fiber Flocculation and Sheet Formation

One of the earlier papers which discussed sheet formation

in the light of the orientation of the fibers as they flowed onto the wire with subsequent matting was published in 1934 by McNeill (2). The mechanical operation of the paper machine as it affected orientation of the fibers was of chief concern, but the following statements were made concerning flocculation. (a) For the same amount of beating, comparative flocculating tendencies of pulps in decreasing order may be given as: sulphites > krafts > bleached sulphites > soda pulps. (b) An excess of alum decreases flocculation. (c) Resin size and gelatinous loadings prevent dispersion in proportion to the amount added. (d) Nongelatinous loadings up to 1 per cent per pound dmy (printing paper ream size, 22 1/2 x 17 1/2) help dispersion. (e) Increased temperature gives less flocculation, but this effect is considered to be due to the dilution effect on the wire of the machine. (f) The lower the consistency, the less the flocculation and, as a practical result, the author advocated the flooding of a relatively free stock onto the wire. (g) It was stated that no constant relation existed between the degree of dispersion and the degree of beating, although under actual operating conditions, beating seemed to increase the dispersion as measured by formation until a freeness around 35° S.R. (650 cc.) was reached. Slower stock gave much poorer dispersion, but this was undoubtedly due to the necessity of running less water on the wire with the stock so that proper drainage could be obtained. Finally, according to the author, optimum dispersion of stock can best be obtained by dilution. It should be noted that McNeill has reported on the factors affecting flocculation of fibers as they may be observed under actual operation of the paper machine.

All conditions, obviously, could not be held constant, and so apparent results may not give a true picture of flocculation effects.

Strachan (3) has likewise reported on observations made in the mill concerning the effects of fiber flocculation. He said both settling and filtration are speeded up by flocculation, and the prevention of the latter is essential in the formation of a uniform sheet. He listed the following conditions as favoring flocculation: (a) high consistencies, (b) very long stock, or even very wet fine stock, (c) excess neutral rosin size, (d) low pH values of the white water, (e) high temperatures, and (f) the presence of air in the stock. It is apparent that there is disagreement here with some of McNeill's conclusions on the effect of temperature on flocculation and, to some extent, with his conclusions on the effect of rosin. Strachan says ordinary neutral rosin size favors flocculation, but this does not hold when a high free rosin size is used. He suggests then that the flocculation in the former case may be due to the larger amounts of alum used, but this does not correlate well with McNeill's conclusion that excess alum increases fiber dispersion. In agreement with McNeill, however, china clay is said to have a marked action in restraining flocculation and it is postulated that this may be due to the introduction of additional negatively charged colloidal particles. Further, clay is flocculated under acid conditions and this is said to restrain fiber flocculation.

In other papers (4, 5), Strachan further suggested (g) that to close a sheet of long free stock it is necessary to operate at the

lowest possible consistencies, presumably to prevent flocculation, and (h) in the purification of white water, optimum conditions are obtained by adjusting the pH to 7.5 with lime and allowing flocculated fibers to settle in a conical shaped settling tank.

In a subjective discussion of sheet formation on the Four-drainer wire, Rubin (6) stressed the importance of the drainage characteristics of the stock as they relate to formation of the sheet. However, he also considered the necessity of maximum fiber dispersion as the stock goes on the wire and, at head-box consistencies with equivalent beaten stocks, listed the following order for the degree of stock dispersion in water: asparto > soda > bleached sulphite > kraft > unbleached sulphite > cotton > linden. With regard to the rate of stock drainage, a specific instance was cited of the operation of high speed news machines on which it was necessary to add a little clay to the furnish when the wood had been ground too free. Presumably, the effect of the clay was to slow up the drainage and thus improve the formation, but there would seem to be the unmentioned possibility that the clay may have exerted a direct effect on the flocculation characteristics of the fibers themselves. It is said, in general, that properly prepared clays and starches, being plastic colloids in nature, assist in fiber dispersion and closer sheet formation, but it will be noted that this is not in complete agreement with some of the previously reviewed discussions (2, 3). Rubin stated further that fiber dispersion is also related to the rate of fiber swelling and to hydration or fibrillation obtained during beating, and that it has been shown to be dependent on

such fiber constituents as pentosan or mannan, presence of acid or alkaline pulp lignins, and the temperature of the water used as a processing or conveying vehicle. This statement seems ambiguous, however, since the presence of pentosans, mannans, and acid or alkaline pulp lignins should only affect the fiber dispersion as they alter the beating characteristics of the stock and are necessarily only secondary factors in altering any degree of fiber dispersion. Also, apparently, the above mentioned temperature effect is only indirectly concerned with fiber flocculation as it affects the rate of beating. Further mention is made, however, of the effect of the temperature of the fiber furnish flowing on the wire and the resulting formation. It is proposed that colder water reduces drainage rates, enhances the effect of the shake and thus improves formation, but no mention is made of the possibility of a direct effect of temperature on fiber flocculation which might be due to alteration of fiber-fiber adhesion forces, or to an increase in the viscosity of the dispersing medium. Finally, it is said that stock dispersion decreases with increased consistencies, and that with fast, free-running stocks a better sheet is formed by slightly flooding the stock suspension onto the wire.

With regard to flooding relatively free stock onto the wire to improve formation as proposed by Rubin, it will be recalled that this was also suggested by McNeill (2) because of decreased flocculation tendencies at lower consistencies. This effect has also been observed elsewhere in actual practice, machine operators claiming that such operation was always necessary in the manufacture of book papers from relatively free stock. It is possible that the effect is

one of consistency, but turbulence in the stock pond on the wire, resulting from the flooding action, could conceivably play a more important role. In general, it is not possible to flood a highly beaten stock onto the paper machine wire without seriously affecting the sheet formation (7, 8). The beaten stock seems to ball up on the wire which may be due to fibrillation and enhanced flocculation tendencies.

Specht (9) investigated factors influencing drainage through Fourdrinier wires and, among other results concerning the effect of fiber mesh on drainage rates, etc., he found that, at a pH of approximately 5.3, stock drainage through a number of different weaves of wires for a news furnish was at a maximum. Fiber flocculation might very well influence the drainage properties of a stock, but whether the effect observed by Specht is due to flocculation or to some other factor, such as a surface tension decrease in the white water, cannot be concluded from the data presented. In addition, no mention is made of whether the pH variable was adjusted with acid or with alum.

In a more recent paper (10), Specht and Connor have reported on a continuation of this work in which they used various furnishes and investigated further the drainage factors of various types of weaves in wires. They also studied the effect of pH, obtained both with alum and with acid, on the drainage characteristics of a newsprint furnish through a typical wire weave. No data are presented but some of the conclusions given include: (a) "the use of sulphuric acid to acidify the stock results in a slower drainage rate for the same pH"; (b) "regardless of the initial pH changes without the addition of alkali,

the drainage is characteristic of the pH at which the drainage tests are run and not of the initial pH"; (g) "the presence of alkaline salts in stock or in the water varies the pH at which the stock has the highest drainage rate"; (h) "there appears to be a decrease in the measurable acidity as the time of contact of alum and stock is increased"; and (i) there is one pH value for maximum drainage which, however, changes for various stock or water conditions. Obviously, again, it is impossible to draw any conclusions concerning the mechanism affecting the drainage, but fiber flocculation effects could have a bearing on this. In the light of further work some of these results may be of interest.

The pH of the white water in a papermaking furnish, as well as that of alumina adsorption, and the anions in the solution, etc., conceivably may have an appreciable effect on the degree of fiber dispersion. It has been stated, in work already reviewed, that low pH values as well as pH values above the neutral point (obtained with lime) increase fiber flocculation, but the evidence presented is much too meager for any general conclusions. Some of the complexities of the papermaking furnish from a colloidal viewpoint have been described by Rowland (11), although not particularly with reference to fiber flocculation effects. He has pointed out that cellulose bears a negative electrostatic charge in aqueous solution and that, specifically in the sizing of the fiber, the positively charged alumina floc may serve as a mordanting agent for the negatively charged rosin particles. It is likewise conceivable that the alumina could alter markedly any flocculation characteristics of the electronegative fibers. Rowland stated

further, though, that the intensity of the negative condition at the fiber surfaces may be greatly reduced by hydrogen ions and may even become positive in the presence of aluminum ions. Meanwhile adsorption of hydrogen and possibly aluminum ions by the alumina would tend to intensify the positive nature of the latter. Again, these effects may have a bearing on flocculating tendencies. The possibility is mentioned that an isoelectric point as applied to cellulose may not exist, at least with reference to pH, unless it occurs under conditions of extreme acidity. The combined action of hydrogen and aluminum ions would seem to bring about a charge reversal on the fiber surface within the range of conditions in the papermaking system, but, opposed to these influences, the action of sulphate ions in keeping the fibers negative is pointed out, as well as their action in reducing the intensity of the positive nature of alumina. The complexity of colloidal factors which may alter fiber flocculation tendencies is thus obvious, and may well account for the lack of a positive knowledge of the effects.

Studies on filler retentions have also indirectly brought to light effects which could involve fiber agglomeration. Willets (12) found, among other results, that an increase in temperature in the sheet mold resulted in marked increases in filler retention of hand-sheets. Such an effect could be due to the actual flocculation of filler particles, fiber-filler flocculations, or conceivably to an improved fiber dispersion, since if a decrease in dispersion occurred (flocculation) the filtering action of the fiber mat on the filler particles would be expected to decrease. Again, however, these observations in themselves are insufficient for the drawing of any

conclusions.

Of interest with regard to filler retention and to possible effects on fiber flocculation, is the recently proposed Sreen method for increasing the retention of fillers and fibers described by Loddengard (13). A weak solution of bone or hide or some other animal glue, which has matured at a low temperature for about 24 hours, is added to suspensions of fibers and/ or fillers in which a small amount of alum is present, and as such is claimed to be a powerful flocculating agent. When this is added to the stock suspension some 30 to 60 seconds before the latter arrives at the apron of the paper machine, it is claimed that a very considerable improvement in retention on the wire is effected, resulting in a reduction of the solids in the white water of about 50 per cent. This improvement in retention presumably includes resin size, pigments, and dyestuffs. Further, the glue is claimed to have a corresponding flocculating effect on the remaining solids in the white water, facilitating recovery in save-alls, particularly those of the flotation and sedimentation types. The amount of dry glue used amounts to 0.05 to 0.1 per cent on the oven-dry weight of the stock. Nothing is mentioned regarding the effect of the glue on the actual fiber dispersion in the head-box and on the wire and the resulting sheet formation, but the fact that the glue is claimed to aid fiber recovery in the white water suggests that it would affect flocculation of fibers on the machine wire. An effect, however, producing opposite results is also possible. If the addition of the glue increased the viscosity of the white water to any extent, which is possible even with the addition of very small amounts of large

colloidally active molecules, an improvement in fiber dispersion might be expected due either to enhanced shearing forces within the dispersing liquid itself, or to decreased velocity of fiber rotations resulting in less fiber-fiber collisions.

Precht and Rausch (29), in investigating methods for increasing filler retention, found that optimum results were obtained with the Sween method and further noted that no injurious effects on sheet formation could be observed.

A condition of interest, for comparison with the use of Sween glue for improvement of retention, is that attained by the addition of very small amounts of a colloidal gum to the papermaking furnish to effect dispersion of the fiber constituents. A more detailed description of the deflocculant and its use will be given in the patent review; suffice it to say here that the material acting as a deflocculating agent is a deacetylated karaya gum obtained from the Cochlospermum gossypium tree indigenous to the northwest Himalayas and central table lands of India (14). The gum resembles tragacanth, a strongly hydrophylic gum, but the natural product does not dissolve or disperse in water to any extent; on partial deacetylation, however, the gum becomes extremely hydrophylic and when small portions of this deacetylated material are added to the papermaking furnish, fiber dispersion and the resulting sheet formation are very much improved. The effect of the gum on the viscosity of the white water, in concentrations as low as 0.02 per cent, is quite marked, but whether this accounts for the improved fiber dispersion or whether there is a colloidal effect altering

energy forces on the fiber surfaces does not seem to be known.

The use of wetting agents in the papermaking furnish has received considerable attention in recent years, but no effects on fiber flocculation and sheet formation have been reported, although it is conceivable that such effects might occur. These surface active materials have been used on the wire and impregnated in suction box covers (15) to increase drainage rates, but apparently no observations have been made on possible relations between drainage rate, surface tension effects, and fiber flocculation.

With regard to the wetting action of liquids on fibers, Bialkowsky and Kress (16), in studying the relation between the swellability of a liquid and its ability to hydrate cellulose, found that fibers were very hard to separate when beating was done in fuel oils and other non-wetting mediums. Whether this was a flocculation effect or was due more to the condition of the pulp furnished to the beater and the nonswelling character of the dispersing media was not evident.

Wetting agents have been shown to inhibit hydration (17), which at first thought would seem contradictory to general conceptions of hydration. However, it may be possible that the wetting agent markedly lowers the surface tension of "bound" or "associated" water and might exert a dehydrating effect. This, however, is of interest in a study of fiber flocculation only insofar as hydration influences the former.

From the work already reviewed it is difficult to say how

important a relation beating bears to fiber flocculation. In the first place it would seem necessary actually to speak of two variables, first, hydration and fibrillation without any essential reduction in fiber lengths, and, second, a direct fiber cutting action. Further, as already mentioned, the papers which have dealt with the effect of beating on fiber dispersion have done so only on the basis of actual mill observations, which would likely mean that other variables, such as consistency and temperature, contributed to the end result, since the effects were evaluated only in terms of the formation of the resulting paper. Considering that beating as a hydration effect increases the specific surface of the fibers (18), it is possible that such treatment would enhance flocculation characteristics both because of mechanical entanglement of the fibrillated stock and because of increased surface contact between the fibers. If beating were principally concerned with reducing fiber length, then a decrease in flocculation characteristics could be expected.

Thus far the literature reviewed has been more or less directly concerned with fiber flocculation or sheet formation as it is affected by such flocculation, and has been written as a result of practical mill observations. A few laboratory observations, however, have been made on fiber agglomeration effects. Campbell and Yortson (19) found that very dilute suspensions of beaten cotton linters, passing a 200 mesh screen, rapidly formed flocks a few millimeters in diameter in distilled water as well as in dilute solutions of acid, alkali, or alum. Similar flocculation of groundwood, screened to pass 200 mesh, dried

with methyl alcohol, and suspended in a solution of ethyl alcohol and chloroform, which had about the same density as the fibers, was observed. The authors suggested the possibility of obtaining measurements of these flocculation effects in an apparatus in which pulp is disintegrated in a jar, and at the same time circulated slowly through a wide tube outside the jar, but reported no further work along this line.

These investigators also made some measurements on the compactness of flocculated fibers by allowing stock of known low consistencies to settle in graduated cylinders, but the data obtained were not suitable for extrapolation to give any indication of the consistency of individual flocks. They further found that univalent electrolytes in moderate concentration, $M/100$ HCl, NaOH, and KCl, brought about practically complete retention of groundwood fines when a suspension of unscreened groundwood was allowed to settle in water. Without the presence of the electrolytes or a pretreatment by boiling the pulp suspension, it was stated that the dispersed fiber left a cloudy suspension of very fine material which settled with much difficulty. Microscopic evidence seemed to be in agreement with the conclusion that the very dilute electrolytes or boiling caused precipitation of the fines on the larger fibers. Experiments were also reported in which the flow of electrolyte solutions through preformed sheets was found to be greater than that of distilled water.

The flow of solutions through pulp pads is not necessarily related to the agglomeration of fibers in suspension, but in relation

to the effects of electrolytes and boiling on the flocculation of pulp suspensions just discussed, it may also be of interest to briefly review such analogous work.

Bell (20), in investigating the effects of beating on fibrous cellulose, developed several techniques which may have been dependent to some extent on fiber flocculation effects. By defining a flow constant for any pulp as the quotient of the flow time for 250 cc. of water under steady static conditions at 20.2° C. and the weight of the pulp used, he established that electrolytes and the effect of boiling hydrated pulp markedly decreased such flow constants, as did the dehydrating effect of alcohol. It was concluded that the ionic coagulation phenomena in the case of beaten fibers may indicate the occurrence of any or all of three effects: alteration of pore size, change of electric charge on the fiber, and dehydration. The first two of these effects may be the result of fiber flocculation or coagulation. Along with the coagulation effect of electrolytes, it was also found that the flow constant in water for a given pulp increased with time, although this was by no means constant. It was postulated as a phenomenon related to electrokinetic potential. A second experimental technique developed by Bell (20) presumably measured the development of a colloidal surface film on cellulose fibers during beating by determining the contraction on drying of a standard pressed fiber cake. Much of the work done by this author along these lines is not of interest here, but it was observed that dilute solutions of electrolytes, the boiling of pulp in water, or prolonged steeping had no effect on this colloidal surface film as measured by contraction of

the pressed pulp cake. The difference between these results and those observed in the determination of flow constants may indicate fiber flocculation rather than a dehydration effect as a factor involved.

A portion of Bell's work was checked at the Forest Products Laboratory of Canada (21); the interpretation given was that the effect involved a probable reduction in negative charge on the pulp surface which would allow surfaces already close together to approach nearer. Additional work from the same Laboratory (22) also indicated that the effects of electrolytes in hard water on the freeness of ground-wood pulps were negligible.

Thus it is apparent that electrolytes, boiling and steeping of fibers, etc., have an appreciable effect on the matting characteristics of the pulp, particularly when hydrated, and that flocculation of fibers may be a factor involved in such changes.

Fiber Flocculation in White Water and Fiber Recovery

Up to the present point, the literature reviewed has been chiefly concerned with fiber flocculation as it is involved in the problems of obtaining maximum fiber dispersion. It should also be of interest to examine briefly the published work on the use of save-alls in fiber recovery and on conditions known to effect the maximum fiber flocculation desired in this operation.

Save-alls are essentially classified into three types: filtration, sedimentation, and flotation types. The first is of little

interest here, however, because its performance is not much concerned with flocculation effects. With the second and third types, only those installations using chemical treatment to aid in the flocculation are of concern. Sedimentation alone involves only a mechanical flocculation of suspended material under quiescent conditions of flow, and the less the agitation and turbulence, the greater the flocculation.

The initial developments in flotation save-alls used only the introduction of small air bubbles into a tank of untreated white water, or pumped air under pressure into a portion of the white water which was then pumped back into a batch tank and the air, on being released, formed bubbles which carried the fibers to the surface (23). Chemicals were not added to aid the flotation, and the condition necessary for the adherence of the fibers to the bubble interfaces was simply that the contact angle of the white water on the fibers be finite.

Some of the earlier references to the use of chemical coagulants in aiding white water recovery (24, 25) suggested the use of large alum dosages to the settling tanks. The alum then, presumably formed large alumina flocks which coagulated the fiber mechanically.

More recent experiments performed by Bechtel (26) have indicated that the adjustment of the pH of white water with alkalies markedly reduced the solids content of the supernatant liquid. For different white waters the best recovery did not always occur at the same pH, the optimum value of the latter depending upon their aluminum content. It is probable that at the optimum pH the maximum

amount of alum flock was formed, effecting maximum clarification.

Graef (27) has discussed phases of white water sedimentation as they affect the velocity of fall of solid particles. He defined three phases: (a) free settling, expressing the velocity of fall by Stoke's law, (b) hindered settling, using an experimentally determined relation to obtain the rate of settling, and (c) concentration of settled particles, the rate of which is expressed by a differential form of Stoke's law. He stated further that, for the sedimentation of most white waters, an acid electrolyte is required because the solid particles carry adsorbed negative ions and, hence, require positive ions for their precipitation. Therefore, if an acid alum were to be used in the beaters instead of the usual basic alum, it is claimed improved sedimentation would be effected. This statement, however, is none too clear, since the basic papermakers' alum contains only an excess of aluminum oxide in addition to the sulphate of aluminum, and this excess aluminum oxide flocculated in aqueous solution would be positively charged. Graef also considered that the formation of flocks by the addition of electrolytes, such as alum, is a reversible process, involving an isoelectric point, and, hence, care must be taken not to overdose. The effect of temperature on the sedimentation of white water is said to increase the rate of settling of the particles and, accordingly, to improve the process. This increase is attributed to a reduction in the viscosity of the water with increased temperature and the more rapid reaction of the flocculating electrolytes in waters of higher temperature.

To increase retention, improve formation, and to make white water more suitable for reuse, Booth (28) has advocated the application of a lime solution. He has suggested applying 5 to 20 lbs. of calcium hydroxide per ton of paper to the fan pump on the machine, thus utilizing the excess of alum in a sized stock solution in producing a coagulating precipitate. Although not mentioned, it would seem that such use of lime would have to be governed by the hardness of the mill water. Booth also proposed that the formation of an alumina flock close to the point of sheet formation was an effective method for slowing up the drainage, an aid, for example, in improving the formation with long-fibered stock. Lime was said to free the drainage from stock that contains no alum. It was further suggested that the water for ideal sheet formation, for rosin-sized paper, is somewhere close to neutral, with as little titratable acidity as possible, compatible with the pH desired. For paper where high bulk is wanted, it was recommended that the water carrying the stock have a pH above 7. Presumably Booth considered that less flocculation and hence a less compact sheet is formed under these conditions. As is evident, however, from some of the previous suggestions made, pH itself should not be the only factor involved in the flocculation, and consideration would have to be given to the amount of alumina, anions, etc., present in the white water. Also, if lime itself aided the drainage, the effect might be attributed to a flocculation of the stock.

Investigating the effects of chemical treatment of white water on the fiber recovery from an Adka type flotation save-all, Brecht, Eberstadt, and Kilpper (30) reported the following results.

The influence of rosin additions to the white water as a pretreatment was most marked as compared with the influence of alum and caustic. In the case of rosin, if the amount added exceeded that necessary for optimum yield on the save-all, there was very little adverse effect on the latter, but if a limited amount of alum or caustic was exceeded, there was a marked decrease in yield. A highly saponified rosin soap was much more effective in producing good fiber recovery yields than a high free rosin size. In most all cases, it was observed that the fiber yield was markedly dependent on the stuff content of the white water. If the percentage of filler ran much above 15 per cent, the amount of solids recovered by the save-all decreased markedly. The effect of the saponified rosin in increasing fiber yields was assumed to result from its action in reducing the surface tension of the suspension and from its action as a flocculant. The latter was said to be due to the fact that it is adsorbed by the fiber and filler and in this way the association of the suspended particles with the air bubbles, likewise surrounded with a thin layer of rosin molecules, was favored. Why the flotation effect was slightly impaired by the addition of too much size was not stated. With regard to the effect of alum and caustic the authors pointed out that other investigators have proposed that the gelatinous alumina formed aids in the flotation process because of an agglomeration action. Accordingly, caustic and alum should be added, depending upon the pH value of the white water, so that a sufficient amount of alumina relative to the solids content of the water is present. Brecht, Eberstadt, and Kilpner, however, believed the situation to be more complicated,

involving an isoelectric point and charge reversal of the fibers.

Anypash (31) has described results obtained with a flotation save-all and the use of a chemical dosage of rosin and alum to aid in the flocculation. A pH value of 5.5 to 7 in the clarified water is said to be most desirable, and it is considered that flocculation is aided by the gelatinous alumina which bind the particles together. Temperature is said to have no influence on flotation.

Other results which indicate that the amount of chemical dosage affects the efficiency of flotation save-alls were given by Lindovsky (32). Too much, as well as too little, size and alum added to the save-all impaired its operation.

According to Bucksdorff (33), who described the use of Sween animal glue in a flotation save-all, cellulose fibers are easy to recover while recovery of the largest and finest fractions of mechanical pulp is more difficult. Ordinary clay did not offer any problem, contrary to observations made on other flotation save-alls not using the Sween glue.

To sum up, it is apparent that the factors affecting fiber flocculation in a save-all recovery system are not always the same. Large dosages of alum have been effective in aiding flocculation and sedimentation in some cases, while in others a reversible process, involving an isoelectric point, has been observed and care has had to be taken not to overdose. Lime has been added to the white water to form all the alumina possible from the available aluminum present,

and this has aided in fiber recovery. Lime alone has been said to free the drainage from the stock, but whether this was a flocculation effect could not be deduced. In flotation type save-alls, all chemical dosage of rosin size, alum, and caustic aided in flocculation and general efficiency of the system, but in general care had to be taken to prevent overdosing. Fillers were observed to interfere with fiber recovery, except when a flocculating glue was used in the white water. High temperature was said to favor flocculation and fiber recovery in a sedimentation save-all while the effect was not observed in a save-all of the flotation type.

Patent Review

A complete survey of the patent literature concerned with the development of mechanical apparatus used in head-box and slice design to introduce a well-dispersed stock suspension on to the paper machine wire has been given by Ness and Bryant (1). Other patents of interest are concerned principally with the use of dispersing agents in fiber suspensions.

Le Compte (34) has described the use of a deacetylated karaya gum to secure good formation in various types of paper. The necessity of deacetylating the gum is explained, and it is suggested that the physical character of the deacetylated product is due to a marked polarity of the molecule. The maximum amount of the gum to disperse wood fibers is given as 2 per cent on the dry fiber weight. Violent agitation or mechanical attrition of the dilute gum dispersion is said to markedly reduce its effect. In another patent (35), the

method of making the deacetylated gum has been described.

A process of effecting agglomeration in pulp suspensions by the addition of a small amount of matured animal glue has been discussed in the experimental literature. More complete details are given in the patent granted to K. Sveen (36). Claims are made for improved retention and white water recovery. The materials proposed to be effective coagulants in the presence of alum are animal glues, such as gelatine, joiner's glue, glue from leather waste, and fish glue, as well as albuminous substances such as casein. The storing of the glue for several days at ordinary temperature is said to improve its coagulating properties. It is also apparently important that the active substance be rapidly distributed into the diluted pulp and not be subjected to any violent agitation.

Summary of the Literature

From observations made chiefly in actual mill operation, investigators have postulated that the following factors increase fiber flocculation, or adversely affect sheet formation: rosin sizing, gelatinous loadings, long fiber stocks, appreciable hydration, low pH values of white water or pH values above the neutral point (obtained with lime), and the presence of air. Bleaching, the presence of non-gelatinous loadings, low consistency, and agitation in general, are said to decrease flocculation. There were conflicting reports as to the effect of temperature on flocculation, and, to some extent, on the effect of the addition of alum and the effects of beating.

Drainage rates from pulps have been shown to be optimum at rather definite pH values which fact may involve fiber flocculation. The use of sulphuric acid rather than alum to acidify the stock in such experiments resulted in a slower drainage rate at the same pH. Also, making the white water alkaline with lime in the absence of alum was said to free up the stock drainage.

The use of a deacetylated colloidal gum, even in concentration as low as 0.02 per cent, has been proposed to aid in obtaining fiber dispersion. Whether its action was due to an increase in the viscosity of the suspending fluid, or to a colloidal effect altering energy forces on the fiber surfaces, did not seem to be known. Matured animal glue was reported to have very favorable effects on increasing retention on the wire and effecting flocculation of fines and solids in white water, but no detrimental effects on sheet formation on the wire, due to fiber flocculation at that point, were observed.

Wetting agents have not been observed to affect fiber flocculation and sheet formation.

Laboratory observations have been made on the flocculation of ground wood fines and also on beaten cotton linters by the addition of univalent electrolytes in very small concentration or by the boiling of the fiber suspension. Other work on the flow of solutions through pulp pads further indicated that electrolytes, boiling and steeping of fibers, etc., may have an appreciable effect on the matting characteristics of pulp, and that flocculation effects may be involved in such changes.

In white water treatment, where maximum fiber flocculation is desired, large dosages of alum, obtained by introducing considerable amounts of alumina into the system, seemed to flocculate fibers mechanically in sedimentation type save-alls. In flotation save-alls, the dosage of alum, as well as rosin size and caustic, appeared to be more critical, too much of the chemicals being as harmful as too little. The effects of temperature and pH were again in question.

III. PRESENTATION OF THE PROBLEM

To understand the phenomenon of fiber flocculation and to be able to predict its effect in problems of sheet dispersion and sheet formation on the wet-end of the paper machine, in problems of fiber dispersion in the pulp mill, and in problems of fiber agglomeration in white water recovery, it appeared necessary to isolate and evaluate the individual factors which produce this effect. Many of these have been discussed in the literature, but it is evident that the investigators in this field have not reached the same conclusions as to the relation and importance of each factor to the phenomenon as a whole. Therefore, it logically followed that equipment and techniques would first have to be developed which would allow control of all the variables involved, and at the same time would permit a qualitative or, preferably, quantitative measurement to be made of the degree and rate of fiber flocculation.

One of the first requirements in the development of equipment which had to be considered was that constant reproducible conditions of stock agitation had to be obtained, so that this important factor in flocculation could be held constant. Two possibilities suggested themselves: (a) the use of a specifically designed mixing tank which would allow complete dispersion of the fibers, possibly with the use of stirrers, and then permit measurements to be made on the degree and rate of flocculation; or (b) the use of a large vertical glass standpipe in which fiber flocculation of a suspension could be observed during its laminar flow through the tube.

In both of these methods the measure of the degree and rate of flocculation might conceivably be made (a) visually, (b) photographically, (c) photoelectrically, or (d) by a combination of photographic and photoelectric techniques, involving measurements of the film density of a photographic negative using a scanning light source. Other techniques which could possibly be developed to advantage in this work included the formation of handcasts under standardized conditions with subsequent determination of formation, the use of sedimentation rate or sedimentation velocity determinations on fibrous suspensions, and "compactness" measurements of flocculated suspensions.

Finally, it seemed plausible also to investigate, at least in an exploratory manner, the role which the possible existence of fiber-fiber adhesion forces play in the phenomenon of fiber flocculation. From previous work it seemed likely that in addition to mechanical factors involved in flocculation, such as the condition of fibrillation of the fibers, etc., there was also the possibility that surface energy forces act on the fibers. There was no indication as to what the order of magnitude of such forces might be, but if they exist, their measurement could best be carried out on a sensitive torsion balance.

IV. DEVELOPMENT OF EQUIPMENT AND THE EXPERIMENTAL METHOD

Preliminary Considerations and Experiments

When the problem of the development of equipment for use in evaluating fiber flocculation effects was first considered, two types of apparatus immediately suggested themselves. The possibilities, already mentioned, included: (a) the use of a glass tank and motor-driven stirrers to effect dispersion of the stock, or (b) the use of a large vertical glass standpipe in which fiber flocculation of a suspension could be observed during its laminar flow through the tube.

The first of these, which would have been the more simple in design and construction, was never investigated, however, because of the possible difficulties in reproducing constant degrees of agitation. The proposed equipment was to include only a glass tank in which fiber dispersion could be obtained by turbulent agitation with stirrers. After the pulp had been dispersed, the stirrers could be stopped, and the degree and rate of flocculation followed visually or photographically. The success of such apparatus would depend on how well equivalent degrees of dispersion could be obtained by the turbulent stirring action. In any turbulent fluid motion, fluid particles always move in an erratic and undetermined course, and as such would affect the dispersion of the suspended fibers. Reproducibility of dispersion can be expected only if the fluid motion producing it is reproducible. Further, in this type of "tank" measurement, which might be termed an evaluation of "static" flocculation, factors affecting the

fiber settling characteristics, such as their density, would have an influence on the results. A "dynamic" method of measurement which would allow the fibers to be acted upon by a continuous but constant and controlled agitation, and would permit the observation of flocculation under actual flow conditions, seemed much more desirable.

Attention was thus centered on the development of the type of equipment listed under (b) above which would permit investigation of "dynamic" flocculation as a stock suspension was allowed to flow through a vertical glass pipe. It will be recalled that somewhat similar apparatus had been proposed in the literature (19), but was never developed.

Preliminary consideration indicated that optimum results would most likely be obtained in a system in which controlled laminar flow of a well-dispersed stock suspension, free from eddy currents, could be observed in a vertical pipe. The initial dispersion could be accomplished by vigorous stirring in some type of head-box, the only limiting condition being that eddy currents from the head-box would have to be prevented from entering the observation flow tube.

After the stock dispersion entered the pipe its flow would have to be laminar, or so-called "stationary" flow, to prevent the formation of eddies within the tube, and to impose reproducible conditions of agitation. In the conception of laminar flow, fluid particles are considered to move along fixed paths, the velocity at any given point on any given path being constant. A closed surface of such paths,

usually referred to as streamlines, not as small imaginary tubes through which the portions of the liquid, comprising the total cross section of the pipe, move. The relative velocities of the streamlines vary, but in ordinary hydraulic problems, involving flow in pipes, the fluid velocity is regarded as the average of the individual streams. However, when rod-like particles, such as papermaking fibers, are suspended in a fluid, these relative velocities are of significance and, through viscous action on the fiber surface, cause the latter to rotate, the exact action imparted to the fiber depending on its orientation to the velocity gradient. It can be shown mathematically (37) that, for appreciable velocity gradients, fibers would turn end over end with the speed of rotation directly proportional to the velocity gradient. Further, two or more fibers in immediate contact and moving down the tube, would tend to be pulled apart, depending upon the relative shearing forces due to the velocity gradients which exist across the pipe, and the adhesive forces, mechanical or otherwise, which tend to keep the fibers together.

Accordingly, the conditions which may be postulated to exist in a dilute stock suspension flowing laminarily through the vertical glass observation tube of the proposed "flocculation tester" include: (a) the stock enters the top of the tube in a completely dispersed condition and with a minimum of eddy currents in the dispersing medium; (b) as the dispersion moves down the column, fibers are acted upon by viscous forces due to relative motions in the fluid, individual fibers being rotated, moved about and brought into contact,

and groups of two or more fibers which may be adhering together tending to be sheared apart; (g) at some point down the flow tube, the number of fibers colliding with each other and tending to adhere will exceed the number being sheared apart and separated by the fluid motion and, at this point, fiber bunching or flocculation should be observed; (d) since the shearing forces will vary with changes in fluid velocity in the tube, the flocculation point will depend on the flow rate.

To determine the feasibility of a vertical pipe apparatus of the nature just described, preliminary tests were made on a temporary, moderately small scale set-up. This consisted of a 7-liter glass bottle whose bottom had been removed, a 4-foot length of 1 1/2-inch diameter Pyrex glass tubing, a 3/8-inch gate valve, and two variable speed, motor-driven stirrers. The bottle was mounted in an inverted position in a wood frame and connected with large rubber tubing to the glass tubing which was mounted vertically in a wooden support stand. The gate valve was inserted in the bottom of the glass flow tube, using a one-hole rubber stopper. The stirrers were mounted above the inverted bottle, and three copper flow eveners were placed in the neck of the bottle and extended partially down into the glass tube. Their purpose was to eliminate cross eddy currents, arising from the stirring action, from moving down into the flow pipe with the suspension.

To determine the maximum flow rate permissible in the 1 1/2-inch glass pipe, so that the critical velocity would not be exceeded

and produce the undesired condition of turbulent flow, the following equation was evaluated:

$$V_c = R_c \cdot \eta / d \cdot \rho .$$

where V_c is the critical velocity, R_c , the Reynolds' number, η , the viscosity in poises, d , the pipe diameter in centimeters, and ρ , the fluid density. A Reynolds' number of 2100 was used (38), giving a critical velocity of 5.52 cm./sec., or a maximum flow rate of 3775 cc./min. The actual flow rate used in any of the preliminary experiments never exceeded 1500 cc./min., so that conditions for laminar flow always existed.

So-called flocculation tests were made with an unbleached wet-lap Mitscherlich pulp and involved the disintegration of an amount of pulp required to give the desired consistency in 8.5 liters of water (which was the calibrated volume of the apparatus), the dispersion of this stock in the glass bottle, and the adjustment of the desired flow rate with the gate valve. The discharge from this valve was caught in a container, and when approximately 1.5 liters had passed through the tube, this volume was returned to the glass bottle.

As the suspended stock flowed through the vertical stand-pipe at velocities less than the calculated critical rate of flow, flocculation of the individual fibers to form bunches was observed to take place at a definite height in the glass tube, depending upon the rate of flow, the stock consistency, the presence of alum in the dispersion, and the effect of beating. Because of the crudeness of

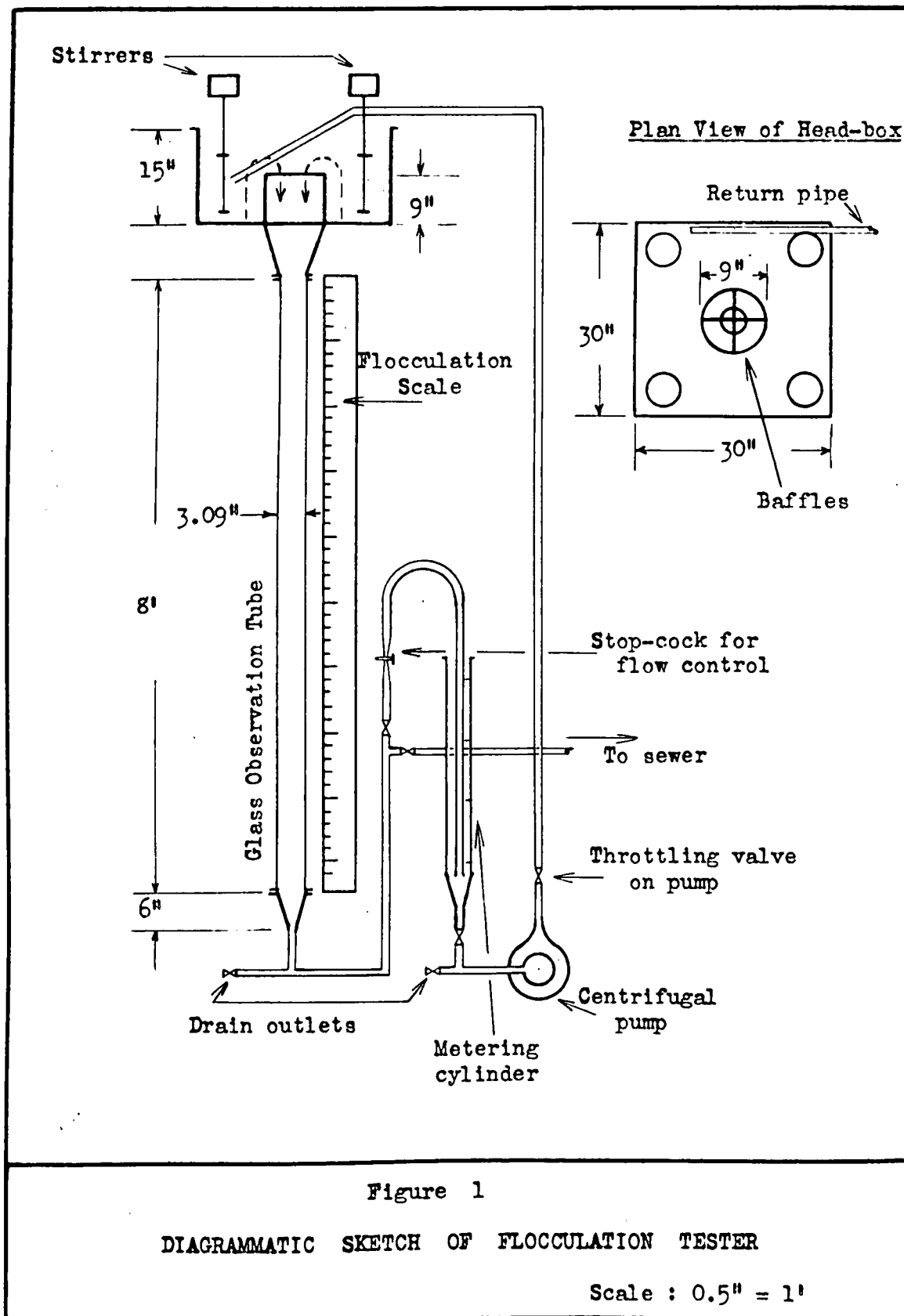
controlling flow rate, the baffling, etc., some difficulty was experienced in obtaining check runs on identical conditions, but marked differences in flocculation characteristics of the stock appeared with the use of alum and on changing the consistency, so that the technique seemed worthy of refinement and application to a larger scale apparatus.

Construction of the Flocculation Tester

A description of the equipment which was finally developed can best be given by the aid of a diagrammatic sketch (Figure 1), and an actual photograph of the completed apparatus (Figure 2).

The flocculation pipe, perhaps better referred to as the observation tube, was an 8-foot length of 3-inch nominal size Pyrex glass pipe, obtained from Corning Glass Works, Corning, New York. It was selected specially for visual work, and was free of internal strains or imperfections which would impair visibility.

The head-box mounted above the observation tube was constructed of 16-gauge sheet copper, being 30 inches square and 15 inches deep. A 9-inch diameter hole centered in the bottom of the tank served as an outlet. Soldered to this outlet was a 9-inch to 3-inch flanged copper reducer, also made from 16-gauge sheet copper. The 9-inch to 3-inch reduction was accomplished in an 8-inch length. Connection of the flanged copper reducer to the glass observation tube was made with a flanged pipe joint furnished by the Corning Glass Works and described in their Bulletin (39). In this type of joint a separate cast iron flange with an inside diameter slightly larger than the outside diameter of the end of the flanged pipe is mounted on the latter



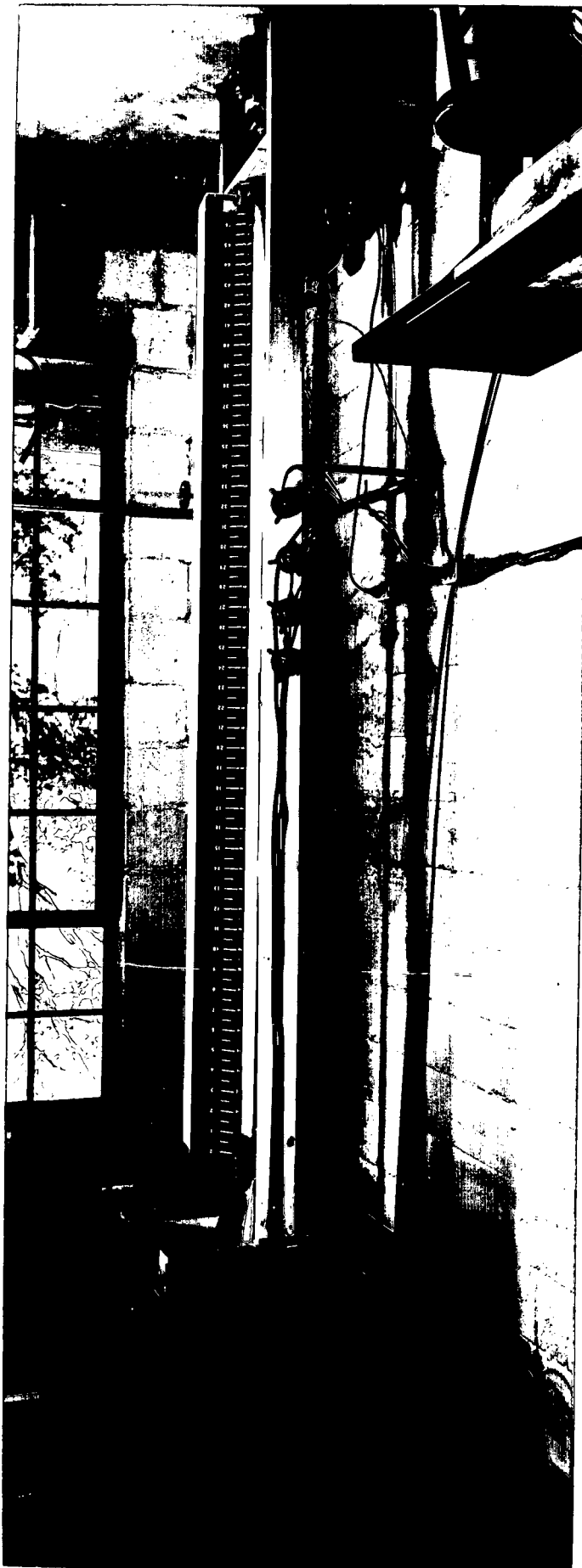


Figure 2

FLOCCULATION
TESTER

- A - Copper head-box
- B - Copper reducer
(9" to 3")
- C - Observation tube
- D - Flocculation
scale and illum-
inant box
- E - Rheostat controls
for variable
speed stirrers
- F - Rubber piping out-
let for spent steam
from indirect heat-
ing coil
- G - Electrical outlets
- H-H' - Drainage pipe
to sewer
- I - Centrifugal pump
and motor
- J-J' - Drainage outlets
- K - Return flow pipe
to head-box
- L - Wooden support
frame

by means of an asbestos insert. A blue fiber asbestos gasket was used at the interface of the flanged glass pipe and the copper flange of the head-box reducer. The two flanges were pulled together with three 5/16 x 1 3/4 inch machine bolts.

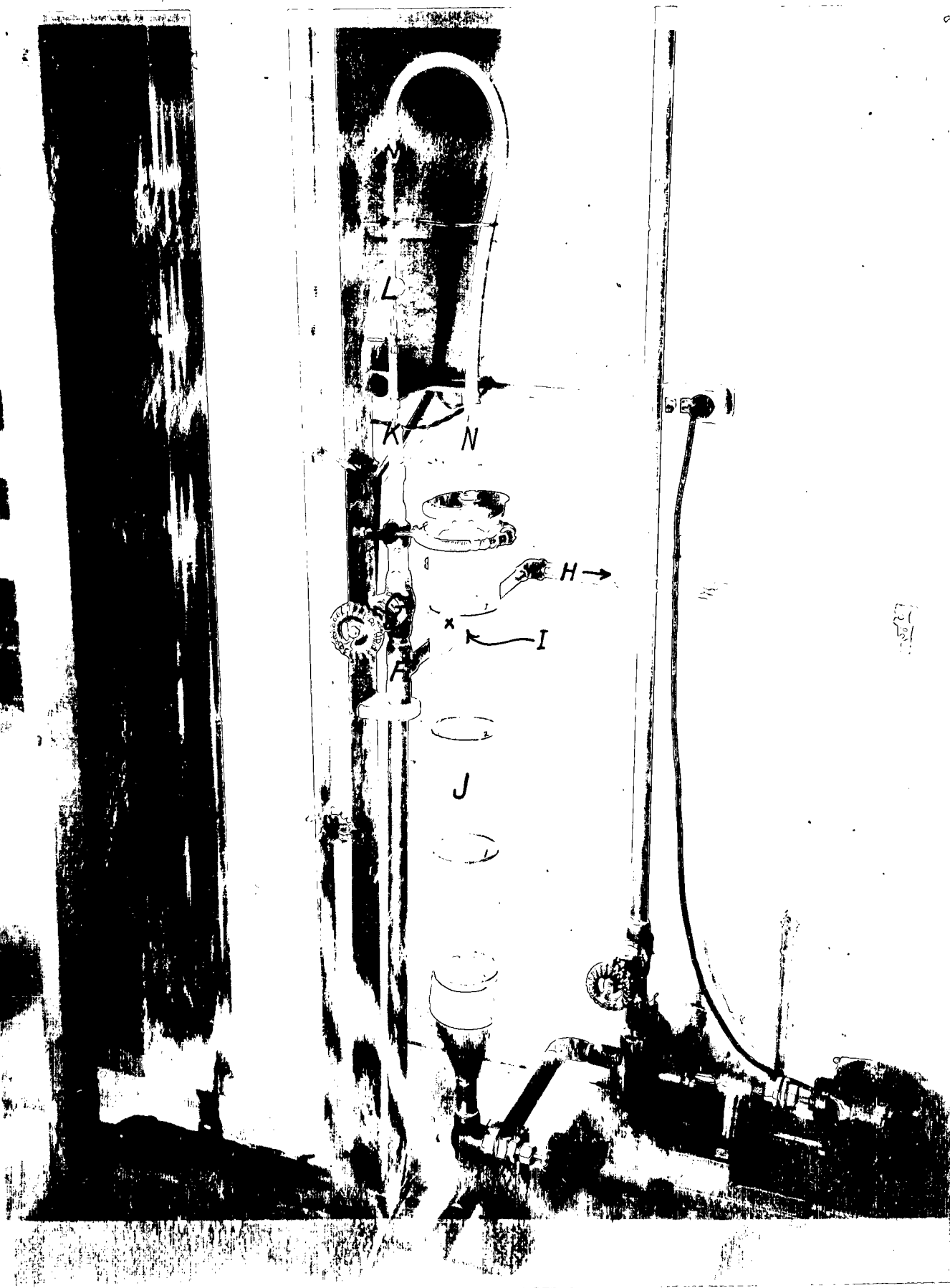
The lower end of the flocculation tube was connected to a second flanged copper reducer, 3 inches to 1 inch in 6 inches, with the same type of flanged pipe joint. This was the start of the return flow piping system, which included flow valves for the regulation of the flow rate through the observation tube, a calibrated glass cylinder for directly measuring flow rates, and a small centrifugal pump. The details of the system are shown in Figure 3.

Here the lower section of the observation tube is shown at (A), the flanged glass to copper joint at (B), and immediately below this the small copper reducer. The piping (C) carrying the flow from the reducer is 1-inch copper pipe connected with Mueller streamline brass fittings. These fittings are machined with an inside shoulder to match the pipe diameter and wall thickness, and when the solder seal is completed, the interior of the pipe and fitting is of uniform size. This was of advantage in preventing stock from "hanging up" and accumulating in tees and elbows, and permitted very rapid cleaning of the equipment. The use of copper pipe and fittings, as well as a copper head-box, was necessary to prevent corrosion and the introduction of extraneous metallic ions into the system.

Continuing with reference to Figure 3, at the bottom of the observation tube and small copper reducer, not readily visible because

Figure 3

RETURN FLOW SYSTEM OF FLOCCULATION TESTER



of its mounting in the wood support frame, the piping system was branched with a tee leading to a drain pet-cock (D) and the main flow line (E). The latter was then carried up 3 feet vertically to a second tee (F) and a 1-inch bronze gate valve (G). The tee permitted the main flow line to be tapped with an intercepting discharge pipe (H) leading to the sewer. This discharge line was of 3/4-inch pipe and had a shut-off valve located at (I), not readily seen on the photograph because of its position behind the glass measuring cylinder (J). With this sewer valve closed, the main return flow from the observation tube proceeded up through gate valve (G), used only for complete shut-off purposes, and into a bronze reducing fitting, 1-inch to 1/2-inch. This fitting was connected to a glass reducer (K), 1/2-inch to approximately 1/4-inch, by means of rubber tubing. Flow from the reducer then passed through a specially ground glass stop-cock (L) used to control the flow rate. The inside diameter of the stop-cock was 3/16 inch. From the stop-cock, the flow passed through a second glass reducer (M), 1/4-inch to 1/2-inch, and at this point its direction was reversed with 1/2-inch rubber tubing connected to the glass reducer (M) and led into the glass flow measuring cylinder (J). It is to be noted here that the 1/2-inch glass tubing (N) which was used to lead the flow into the bottom of the calibrated glass cylinder, was open at its lower end (not quite visible on Figure 3). Hence, a free fluid surface always existed in the glass cylinder, and the column of the fluid served to impress a head on the suction end of the small centrifugal pump (O). The latter was an all bronze cast, open impeller type pump, with a Monel metal shaft. It was rated at 5 gallons per minute against

a 24-foot working head, and was driven with a 1/4 horse power motor on a direct connected shaft at 1725 revolutions per minute. The discharge from the pump was piped directly up to the head-box. In this return line there was a shut-off gate valve (B) to throttle the discharge rate of the pump.

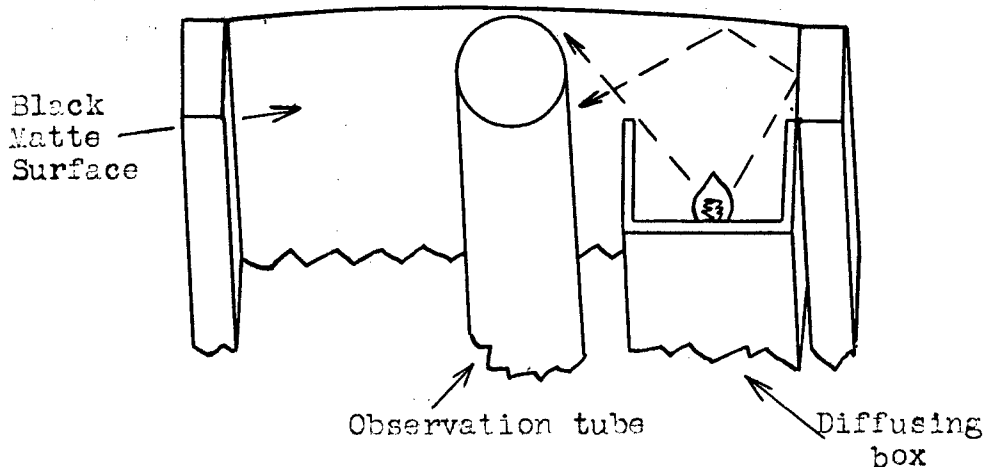
The fact that both visual and photographic determinations of the flocculated conditions of the fibers was to be made necessitated uniform lighting of the entire 8-foot glass observation tube. This was accomplished by using a battery of 8 lights, mounted in a diffusing box which was placed along-side and to the right of the observation tube (see Figure 2). The lights in the diffusing box were mounted sufficiently well back in the box so that any direct illumination did not reach the glass tube. Direct illumination was undesirable because of the marked refraction of the images of the light source by the circular glass tube. A black matte, diffusing surface was mounted directly behind the observation tube, and gave good contrast to the fibers viewed by reflected light. A diagrammatic, cross-sectional sketch of the lighting arrangement is shown in sharp perspective in Figure 4.

For visual purposes, eight 100-watt frosted glass bulbs were used in the diffusing box. When photographs were taken, the middle six of these bulbs were replaced with 500-watt photoflood lamps. Additional illumination of the flocculation scale was not necessary when visual evaluations of the flocculation condition were being made, but for the photographs, one 500-watt photoflood light was placed on the floor, directly below the glass column with its light reflected

vertically upwards. This eliminated any serious reflections of the light source from the circular glass pipe.

Figure 4

Lighting Arrangement - Flocculation Tester



Calibration of the Flocculation Equipment

The total volume of water contained in the flocculation tester was 55.6 gallons at 15° C., or 464 ± 1 pounds. This amount included 12.7 inches of depth in the head-box, the entire volume of the rednoor on the head-box, the observation tube volume, and the volume of the return flow system, inclusive of the 3 liters of the metering cylinder. The volume calibration was carried out with tap water at 5° C.

The metering cylinder, (J) in Figure 3, was calibrated with distilled water at 25° C. to contain 3 liters, exclusive of the volume of the glass inlet tube. The cylinder was used to measure the mean

velocity of flow in the observation tube. After the stop-cock in the return flow system had been adjusted to give approximately the desired flow rate, the gate valve below the calibrated glass cylinder was closed. The complete volume of flow through the observation tube was then retained in the cylinder, and timing the flow of 3 liters permitted subsequent calculation of flow velocity. Immediately after the fluid level passed the 3-liter graduation mark, the lower gate valve was reopened and adjusted to "bleed" just sufficient of the stock suspension into the suction end of pump as was necessary to maintain the fluid level at approximately the 1 1/2-liter mark in the cylinder.

The necessity of maintaining laminar flow in the vertical observation tube has already been discussed. Laminar flow in pipes is limited hydraulically by the critical velocity. If the latter is not exceeded, flow through any particular system, for which the critical value has been calculated, will be non-turbulent, or laminar. As already given, the relation expressing critical velocity in circular pipes in terms of the Reynolds' criterion, R_0 , absolute viscosity, η , diameter of the tube, d , and the fluid density, ρ , is:

$$V_c = R_0 \cdot \eta / d \cdot \rho$$

Values for the Reynolds' criterion depend on the particular system and circumstances in question. However, the value of 2100 for circular pipes has been given as an absolute minimum (32) and, in the absence of actual flow tests on the system, a lower critical velocity can be safely calculated, using this value. For the 3-inch diameter glass tube of the flocculation apparatus, the critical velocity is then

0.0903 ft./sec. which corresponds to a maximum flow volume of 7.56 liters/min., or a flow time of 24 seconds for 3 liters. Only in a few exceptional cases in the experimental work was this flow rate exceeded, assuring viscous or laminar flow for all conditions.

Experimental Procedures for Flocculation Experiments

Detailed Routine Procedure

The standard procedure adopted for making a flocculation run consisted of the following steps:

(a) The flocculation apparatus was filled with $46\frac{1}{2}$ ± 1 pounds of water (a relatively hard tap water from the City of Appleton mains unless otherwise specified) to the calibrated level in the head-box.

(b) The temperature of the tap water was between 5 and 10° C. as it was removed from the mains, and for runs made at the standard temperature of 25° C., it was necessary to warm the water. This was done indirectly by using a steam coil in the head-box. The water was circulated in the apparatus while being brought up to standard temperature, as this aided in the elimination of dissolved air liberated during the warming operation. Variations in actual temperatures from the values specified in any experiment were generally within ± 1° C., with occasional maximum variations of ± 2° C.

(c) The amount of pulp to give the desired consistency in the apparatus was weighed out, and stirred in two liters of water for 7500 revolutions in the standard British disintegrator, described in

the TAPPI Standard Method, T 205 m-36. The disintegrated stock was then dispersed in the head-box after a sample of water from the latter had been removed for a pH determination. The standard consistency which was used, as the effect of other variables on flocculation was investigated, was 0.01 per cent. This value was indicated by preliminary experiments as optimum for the purposes of the visual observation.

(d) The 4 high-speed stirrers in the head-box were then adjusted as well as possible to a constant speed by setting the rheostat controls so that a constant fixed resistance was always in series with each motor. The actual speed of the stirrers was such that they set up appreciably strong turbulence, effecting absolute fiber dispersion in the head-box.

(e) Chemicals, if required in the white water for a particular run, were added at this point.

(f) The complete furnish was then allowed to circulate for at least 15 minutes, and a second sample of white water withdrawn by pipette for pH determination, if the addition of chemicals was expected to change this latter value. A 70-mesh wire screen, formed into a thimble, was used to screen out fibers from the pH samples.

(g) The temperature in the head-box was checked and recorded, the stirrer speeds checked, and the determination of the flocculation end-points then begun.

(h) Evaluations of the flocculation end-points were made at specific flow rates in the observation tube. This end-point may be defined as the position down the observation tube where definite fiber bunches could be seen, as well as small portions of the dispersing

medium which were devoid of fibers. Above this point there existed a relatively complete degree of dispersion of the fibers, while below the condition was one of definite flocculation. Visual observation was made with the observer standing approximately 10 feet from the glass tube, under optimum conditions of illumination.

(1) As previously given, the flow rate through the observation tube was adjusted with the stop-cock control. Further, for any given conditions, only that range of flow rates was used which gave flocculation end-points between 10 and 35 units on the arbitrary flocculation scale mounted alongside of the observation tube (see Figure 2). The mean velocity of flow through the latter was determined by measuring the time for the flow of 3 liters of the stock suspension into the calibrated measuring cylinder, and using the equation:

$$\bar{V} = 3000/\pi \cdot r^2 \cdot T = 64.93/T ,$$

where \bar{V} is the mean velocity of stock through the observation tube in centimeters per second, r is the radius of the observation tube, and T , subsequently referred to as the flow time, is the time in seconds, for the flow of 3 liters of suspension.

(1) Two determinations of the flow time for any given stop-cock setting were always obtained before any flocculation observations were made. A third determination of the flow time was made after the flocculation end-point had been evaluated. This latter step was advisable, since occasionally a small fiber bunch would catch in the stop-cock, particularly at the very low velocities, thus changing the flow value and the flocculation end-point. If all three values of the flow

time agreed to within ± 0.5 second, they were averaged to give a value of T , used to calculate V , the flow velocity, in the equation given above.

(k) After a definite and constant flow rate had been carefully set and determined, at least seven separate estimations of the flocculation end-point, described in (h) above, were made during a period of approximately five minutes duration. These seven values, necessarily somewhat subjective in nature, always agreed to within a maximum range of five units on the flocculation scale; usually the agreement was better than this. Five units correspond to 10 inches on the 8-foot scale. The seven readings were averaged and recorded as the flocculation value for the specific flow time.

(l) At least ten such flocculation end-points, varying between 10 and 35 units on the scale, were determined for each of ten specific flow rates. These data then permitted calculation of a mathematical relation between the flocculation value and the flow velocity, the details of which will be described in a following section.

(m) Photographs of the observation tube for a permanent visual record of specific flocculation conditions were usually taken after the visual observations had been made. The photographic details are given in the following section describing specific procedures.

(n) After necessary evaluations of the degree of flocculation had been made both visually and photographically, a final sample of the white water was withdrawn for pH measurement, and the temperature in the head-box recorded. Also, two 1-liter samples of the fiber suspension were removed from the head-box, each sample from a different

position, and were filtered through tared Jena 1-G-1, fritted glass bottom crucibles. The filtered samples were dried to constant weight at 105° C., giving a check on the consistency of the stock suspension used for the particular run.

(2) Unless a time factor was being investigated and it was necessary to leave the stock in the head-box, the equipment was drained to the sewer after each run, and thoroughly cleaned by flushing with several charges of water. To prevent any hard water scum from drying on the interior of the glass tube, the latter was always finally rinsed down with distilled water.

Specific Procedures

pH Determinations. All pH determinations run on white water samples were made with the glass electrode calibrated against M/20 potassium acid phthalate buffer solution. Measurements were always made at room temperature and were accurate to within 0.05 pH units.

Consistency Measurements. As already described, consistencies of the individual runs were checked by filtering two 1-liter samples of the dispersion and determining the oven-dry weights of the fiber contained therein. The standard consistency, at which the majority of the flocculation runs were made, was originally selected as 0.01 per cent. However, the average consistency of these runs, determined from the samples removed from the head-box, was slightly lower than this value. This is accounted for by the following facts.

The standard pulp, an unbleached spruce sulphite, was stored in a wet pressed condition in an air-tight, 5-gallon glass jar. Three

successive monthly moisture tests on this stock gave 24.7, 25.4, and 24.7 per cent oven-dry pulp, indicating very little change in moisture content during this period. On the basis of the calibrated volume of the flocculation tester which contained 464 pounds of water, and the 25.4 per cent oven-dry pulp figure, 83.5 grams of wet stock was used for each run made at the standard consistency. The 25.4 per cent oven-dry value was used because the majority of runs were made within the month following this particular moisture determination. However, the total of two consistency samples made for each of 29 runs, all at, presumably, the same stock density, gave the average consistency value of 0.0097 per cent. This would indicate that the moisture content of 75.3 per cent, obtained both before and after these runs were made, was the more accurate value, and accounts for the 3 per cent variation of the average consistency from the intended value of 0.01 for all 29 runs. This slight discrepancy is of no significance as far as the results of the flocculation runs are concerned, except that the standard consistency is to be regarded as 0.0097 per cent with the average per cent deviation from the mean being ± 1.4 per cent. The maximum per cent deviation from the mean of any two consistency samples for an individual run was ± 1.3 per cent.

Photographic Techniques. All photographs of the observation tube were taken with an 8 x 10 inch wide angle protar lens with the aperture set at f.12.5. Supersensitive panchromatic film, 8 x 10 inches, and an exposure time of 1/25 second were used. It was necessary to employ this rather short exposure to "stop" the fiber flow and prevent

blurring of the image. With the "dark field" illumination that was necessarily used (see previous section on description of equipment) and this camera speed, the entire negative, except for the portion showing the observation tube, was much too thin. However, since all that was required was good definition of the fibers in the tube, the negatives served their purpose. Developing of the latter was done in the 3-solution pyro developer, D-1, for 5 minutes. Prints were made on number 2 Aso paper, the general procedure being to over-expose and under-develop to overcome undesirable contrast.

Treatment of Data. Concept and Calculation of the Flocculation Index

The method of securing the data giving the variation of the flocculation value with flow rate through the observation tube has already been described on pages 44-5 which gave detailed procedures. The variables measured directly are (g), the flow time for three liters of the fiber suspension, T , and (h), the flocculation value or arbitrary scale reading connoting distance down the observation tube at which fiber flocks were definitely formed. From the flow time, T , the flow rate or the velocity of the suspension through the observation tube, can be calculated, using the equation:

$$V = 64.93 / T .$$

To show how a mathematical relation between V , the flocculation value, and T , the flow velocity, was obtained, Table I, which gives the basic and calculated data used in the procedure, is presented. The data is for flocculation run no. 11, giving the flocculation

characteristics of an unbleached spruce sulphite stock dispersed in tap water at a pH of 7.12, 0.0101 per cent consistency, and at a temperature of 25° C.

Table I

FLOCCULATION RUN NO. 11

Unbleached Spruce Sulphite Stock Consistency 0.0101%
Tap Water, pH 7.1 pH at end of run 8.2
Temperature 25° C.

\bar{X} (sec.)	\bar{F} (arb. units)	$\frac{\bar{V}}{\text{cm.}}sec.$	$\log_{10} \bar{F}$	$\log_{10} \bar{V}$	$(\log_{10} \bar{V})^2$	$\log_{10} \bar{V} \cdot \log_{10} \bar{F}$
65.6	19.	.990	1.2788	-.0045	.0000	-.0058
52.	25.2	1.249	1.4014	0.0965	.0093	0.1352
40.3	31.4	1.612	1.4969	0.2073	.0430	0.2103
137.4	10.8	.472	1.0334	-.3261	.1063	-.3370
50.8	23.	1.279	1.3617	0.1069	.0114	0.1456
84.5	14.6	.768	1.1644	-.1143	.0131	-.1331
43.2	27.8	1.503	1.4440	0.1769	.0313	0.2554
106.2	12.9	.612	1.1106	-.2136	.0456	-.2372
57.6	21.6	1.127	1.3345	0.0518	.0027	0.0631
88.1	14.6	.736	1.1644	-.1328	.0176	-.1546
117.4	10.4	.553	1.0170	-.2573	.0662	-.2617
46.6	26.6	1.393	1.4249	0.1440	.0207	0.2052
68.5	19.7	.948	1.2945	-.0232	.0005	-.0300
95.5	14.4	.680	1.1584	-.1675	.0280	-.1940
77.	16.6	.844	1.2201	-.0793	.0063	-.0968
			18.905	-.5352	.4020	-.3294

Points of flocculation were visually estimated for fifteen different flow velocities in the range of 0.5 to 1.5 centimeters per

second. Column 1 gives the actual flow time in seconds for a 3-liter volume of the fiber suspension; column 2 is the flocculation scale reading; column 3 gives the velocities of flow calculated from the values in column 1. The remainder of the column headings are self explanatory, and are tabulated since they are used in subsequent calculations. Summations of the last 4 columns are given at the bottom of the table.

Plotting the flocculation values, F , as ordinates against the actual flow time, T , gave a series of points which appeared to vary as a power function of the type:

$$F = K_1 \cdot T^{K_2} \quad (1)$$

K_1 and K_2 being constants with the latter having a negative value.

It is interesting to note that plotting the flocculation values directly against V , the velocity, rather than the flow time, T , would at first appear to give a linear relation between F and V . If equation (1) expresses the relation of F and T , then since

$$T = 64.93/V \quad (2)$$

the following equation results:

$$F = K_1 \cdot 64.93^{K_2} / V^{K_2} \quad (3)$$

With this latter relation, if the power constant, K_2 , is a negative number between 0 and 1, it is possible that F and V would appear to vary linearly within a limited range of values.

The adequacy of using the power function given in equations (1) and (3) was checked by plotting \bar{I} against both \bar{I} and \bar{Y} on log-arithmetic coordinate paper. Since straight lines were obtained in both cases, the relation was deemed suitable.

The values of \bar{I} and \bar{Y} were fitted to a curve by the method of least squares. Taking the logarithm of both sides of equation (3) results in:

$$\log \bar{I} = \log K_1 + K_2 \cdot \log 64.93 - K_2 \cdot \log \bar{Y} \quad (4)$$

$$\text{or} \quad \log \bar{I} = K_3 - K_2 \cdot \log \bar{Y} \quad (5)$$

This gives a direct linear relation between the logarithms of \bar{I} and \bar{Y} . Since \bar{I} , \bar{Y} , and K_3 are necessarily positive numbers, the usual method of fitting a line of the type, $Z = a + b \cdot X$, by least squares can be used. This entails solving the normal equations to obtain the constants K_2 and K_3 . These equations are:

$$K_3 \cdot \sum 1 - K_2 \cdot \sum \log \bar{Y} - \sum \log \bar{I} = 0 \quad , \quad \text{and} \quad (6)$$

$$K_3 \cdot \sum \log \bar{Y} - K_2 \cdot \sum (\log \bar{Y})^2 - \sum \log \bar{Y} \cdot \log \bar{I} = 0. \quad (7)$$

Referring specifically to Table I, giving the data for run no. 11, the normal equations become:

$$15 K_3 + 0.5352 K_2 - 18.905 = 0 \quad , \quad \text{and} \quad (8)$$

$$-0.5352 K_3 - 0.402 K_2 + 0.3294 = 0 \quad . \quad (9)$$

Solving (8) and (9) simultaneously gives:

$$K_2 = -0.901 \quad , \quad \text{and}$$

$$K_3 = 1.29 \quad ,$$

and the relation between $\log F$ and $\log V$ is expressed in the equation:

$$\log F = 1.29 + 0.901 \log V \quad . \quad (10)$$

The data of Table I is plotted in Figure 5, and the curve defined by equation (10) fitted to the points.

If the relations between the flocculation values and the flow velocities are established for various conditions, it seemed plausible from results obtained on preliminary experiments to expect that the degree of flocculation in each case could be characterized numerically by the parameter of the system, K_3 . Whether the first derivative of the log-log relation, or the slope constant, K_2 , would be constant for all conditions was somewhat a matter of conjecture. It was obvious not to expect it to approach zero or one, but it also seemed probable that smaller variations, greater than might be attributed to experimental error, could have some significance with regard to the mechanism of fiber flocculation. More of this point will be mentioned when the results warrant it.

The parameter, K_3 , of the power function relating F and V has been termed the dispersion index. It is a pure number, inversely proportional to the degree of flocculation observed under given conditions in the flocculation tester. In the discussion of results, the

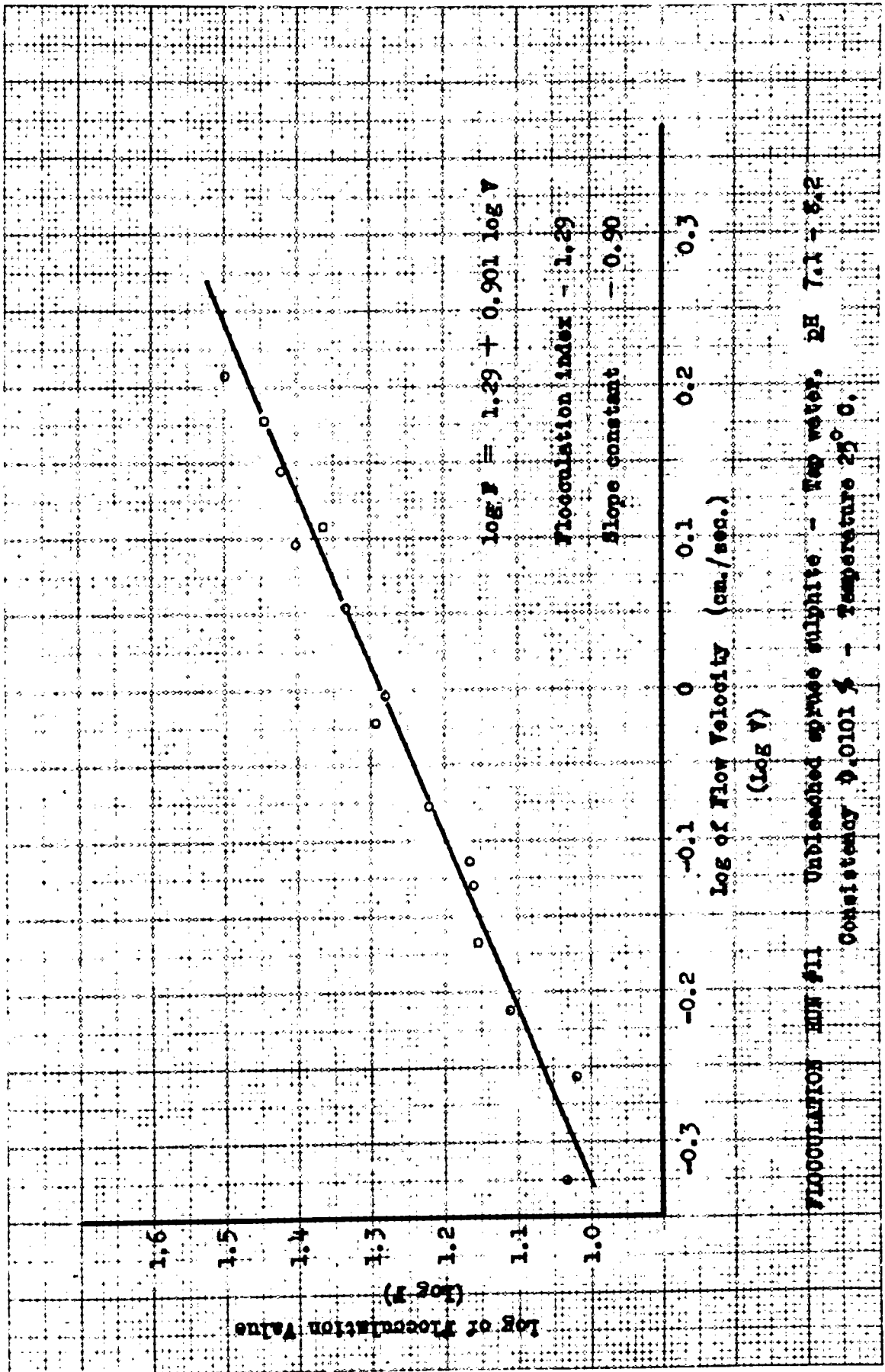


Figure 5

data of all the experimental work will be presented graphically by plotting the log-log relation between \bar{Y} and \bar{Y} giving the constants of the equation.

Photographs of specific flocculation conditions will also be presented in the discussion of results. When obtainable, the flocculation value for the specific flow rate at which the picture was taken will be given, but it should be remembered that this value, as well as the photograph, are not as representative of the average flocculation condition as is the dispersion index.

Factors Influencing Flocculation Measurements

Before completing the discussion of the flocculation tester and methods of procedure, it may be well to consider briefly the subjective nature of the visual end-point, as well as the effect of the baffles in the head-box on the flocculation, the effect of stirrer speeds, and the effect of a small change in static pressure head occurring during measurements of the flow rate.

The visual end-point of flocculation, as it was observed in the glass tube, has already been described. Careful standardisation of this part of the procedure was required to eliminate as much subjective error in the measurement as possible. It was found necessary to view the flocculation tube from at least a distance of 10 feet, so that the entire tube could be seen in perspective. To assist further in obtaining this latter condition, it was desirable to have the observer turn his head through 90°, and make the observations

with both eyes in the same vertical line. The end-point was then judged as the position above which the fibers appeared reasonably well dispersed, and below which definite flocculation occurred. This made it necessary to limit the range of flow velocities so that the end-point did not occur above 10 or below 35 units on the flocculation scale, since at these values there was both dispersed and flocculated stock above and below each of the limiting end-points. In some of the first runs made, flocculation values in the region of 40 were obtained, but they showed much poorer correlation with the average data than did values above 30. Therefore, the limits of 10 to 30 or 35 scale units were imposed.

Care also had to be exercised in judging the flocculation end-point in different runs exhibiting widely different degrees of dispersion. When very marked dispersion existed, such as that obtained with the addition of a small amount of alum, the largest fiber flocks that formed were very much smaller than those obtained, for example, in the case of a fiber and water dispersion alone. In the latter case the flocks may have been of the order of several centimeters in diameter, while in the former case they were only one-fifth to one-third this size. The flocculation end-point, however, was always judged, not by the size of the fiber bunches formed, but as that point above which the fibers appeared dispersed relative to a flocculated condition existing below the end-point. Thus, in the case of the marked dispersion obtained with alum, the degree of flocculation at any given end-point would not have been as harmful to the formation of a sheet as that

amount of flocculation occurring at an end-point observed in the case of a fiber-water dispersion. This may make for some inconsistency in relative values of the flocculation indices, but it was the optimum procedure with regard to obtaining reproducibility of results.

The baffles in the head-box had to be carefully arranged to give the optimum condition. Obviously, two conflicting operations were performed by first dispersing the fibers as completely as possible with a maximum amount of agitation in the head-box, and, second, attempting to baffle the stock flow such that no eddy currents followed down into the observation tube. The optimum condition desired was the introduction of a completely dispersed fiber suspension, flowing without eddy currents, into the glass tube. The first attempt to obtain this condition was quite unsuccessful. The reducer, connecting the head-box with the observation tube, (see Figure 1) was completely divided by vanes into 6 flow compartments, the latter extending partially down into the glass tube. Rather than eliminate cross-eddy currents, however, as they were intended to do, the vanes preferentially directed large streaming eddies from the stirrers directly down into the observation tube, causing very nonuniform flow at this point. In addition, because of a correspondingly slower flow in other compartments, stock tended to flocculate between these vanes and then later was moved down into the observation tube, causing very nonuniform conditions. This type of baffling was finally discarded, and a circular baffle was used; this was placed in the head-box completely above the reducer, as already described. Although very small eddy currents occasionally

moved down into the observation tube with this arrangement, they completely died out in the first 10 inches of the tube and did not appear to affect flocculation readings.

Since the baffles had to be carefully adjusted to eliminate eddy currents in the observation tube, it is seen that the stirrer speeds also required careful attention. As already described, the rheostat controls in series with the motors were always set at the same value at the start of each run. Further, the stirrers were always allowed to run for about 1/2 hour to warm up bearings, etc., so that they would be operating at sensibly constant speeds during any run. However, much was to be desired of this control. Occasionally spurious results would arise, which could well have been attributed to variations in stirrer speeds bringing about greater or less turbulence in the head-box and thus affecting the degree of dispersion of the fibers entering the observation tube. A desirable improvement in the present apparatus, in this respect, would be the use of small induction motors to drive the stirrers.

Finally, mention might be made of small variations which occurred during the measurement of flow rates in the observation tube. It will be remembered that the latter was accomplished by introducing the entire discharge of the observation tube into the bottom of an auxiliary, calibrated measuring cylinder. As the cylinder filled up a small percentage change occurred in the effective hydrostatic head producing the flow. For example, at a flow rate of 0.676 centimeters per second through the observation tube, the total average time for

3 liters flow was 94.6 seconds. The first liter was delivered in 30.8 seconds, the second in 31.5 seconds, and the third in 32.3 seconds. These differences would account for about a 5 per cent maximum variation in the mean flow velocity in the observation tube. However, this variation in itself was of no significance in altering the flocculation end-point, since, as will subsequently be seen, the latter could not be reproduced within a smaller limit of error. Further, any possibility of error was essentially eliminated by setting the liquid level in the measuring cylinder at the 1 1/2 liter mark during the time flocculation observations were actually being made.

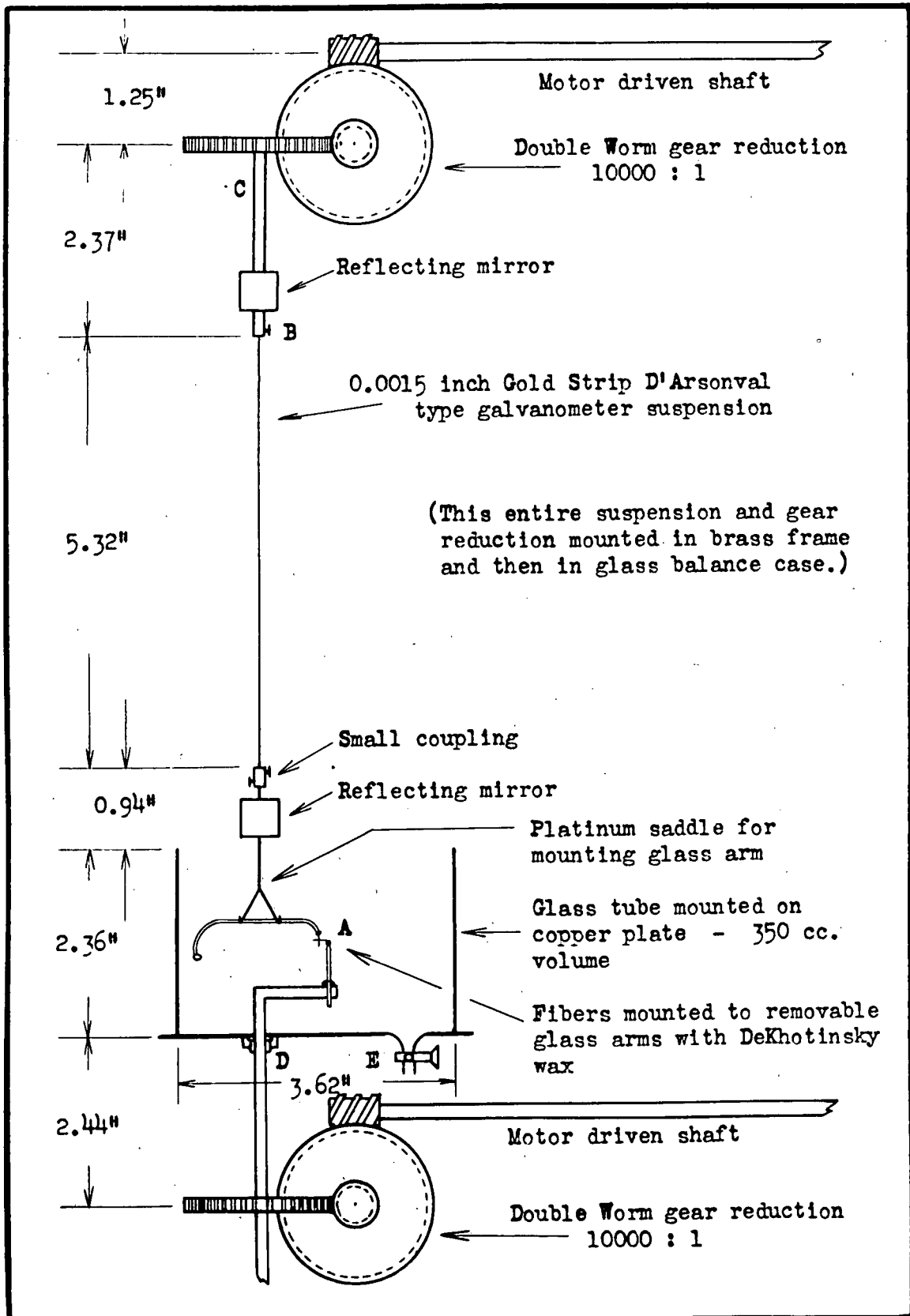
Construction of a Torsion Balance for the Measurement of Fiber-Fiber Adhesion Forces

Because of the possibility that adhesion forces may play a role in the phenomenon of fiber flocculation, a torsion balance was constructed to permit their measurement. A diagrammatic sketch of the balance is shown in Figure 6, and Figure 7 gives a general view of the equipment.

The balance consisted of a gold strip torsion ribbon, similar to those used in D'Arsonval type galvanometers, which had been rolled into a flat strip from 0.0015 inch diameter wire. This gold suspension, approximately 13.5 centimeters in length, was connected to an upper suspension mounting by means of a small socket and set-screw, shown at B, Figure 6. The upper suspension rod, O, was capable of being slowly rotated about its own axis by a motor-driven

Figure 6

DIAGRAMMATIC SKETCH OF TORSION SUSPENSION MOUNTING
For Measurement of Fiber-Fiber Adhesion Forces



shaft, connected to the rod through a double worm gear reduction of 10,000 to 1. As will be described later, the procedure finally developed for making adhesion force measurements did not require movement of this upper suspension, but the equipment was designed in this manner for flexibility of operation. A small reflecting mirror was mounted on the upper suspension rod, and, when necessary, allowed the angle of rotation of the latter to be measured using an optical lever.

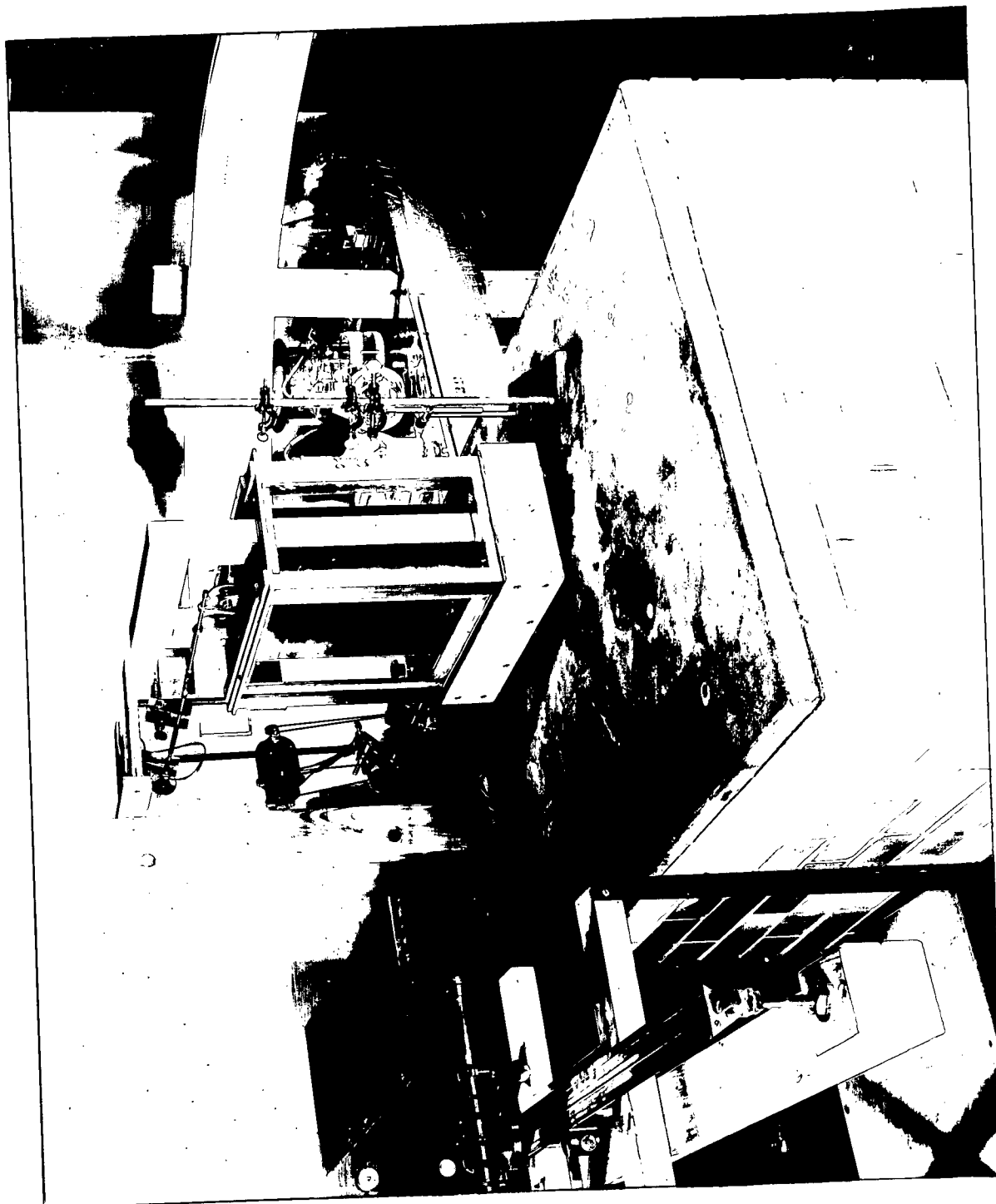
At the lower end of the gold strip torsion wire, a platinum wire saddle was connected by means of a very small brass coupling. The saddle, when in position, held the upper glass arm (see Figures 6 and 8) on the end of which was mounted one of the individual fibers used in the measurement. The upper glass arm was simply laid in position in the saddle, this giving ample rigidity for making the necessary measurements.

The platinum saddle, after being mounted on the end of the gold torsion wire, hung down into a glass-copper cell so that, when the latter was filled with a liquid, the entire glass arm and most of the saddle were submerged with only the top vertical portion of the latter breaking the liquid surface. On the saddle, above the point at which it projected from the liquid, a small reflecting mirror was mounted which permitted the angle of twist of the torsion wire to be measured with the aid of an optical lever.

The glass-copper cell of approximately 350 cc. volume was used to contain the liquids under which the fiber-fiber adhesion forces

Figure 7

GENERAL VIEW OF TORSION BALANCE FOR FIBER-FIBER ADHESION MEASUREMENTS



were measured. It consisted of a 2.36-inch section of a 3.5-inch diameter glass tube mounted on a flat, 0.062-inch thick, copper plate with Vinylite resin. Only a very small amount of the latter material served as an excellent, waterproof, water-insoluble cementing agent.

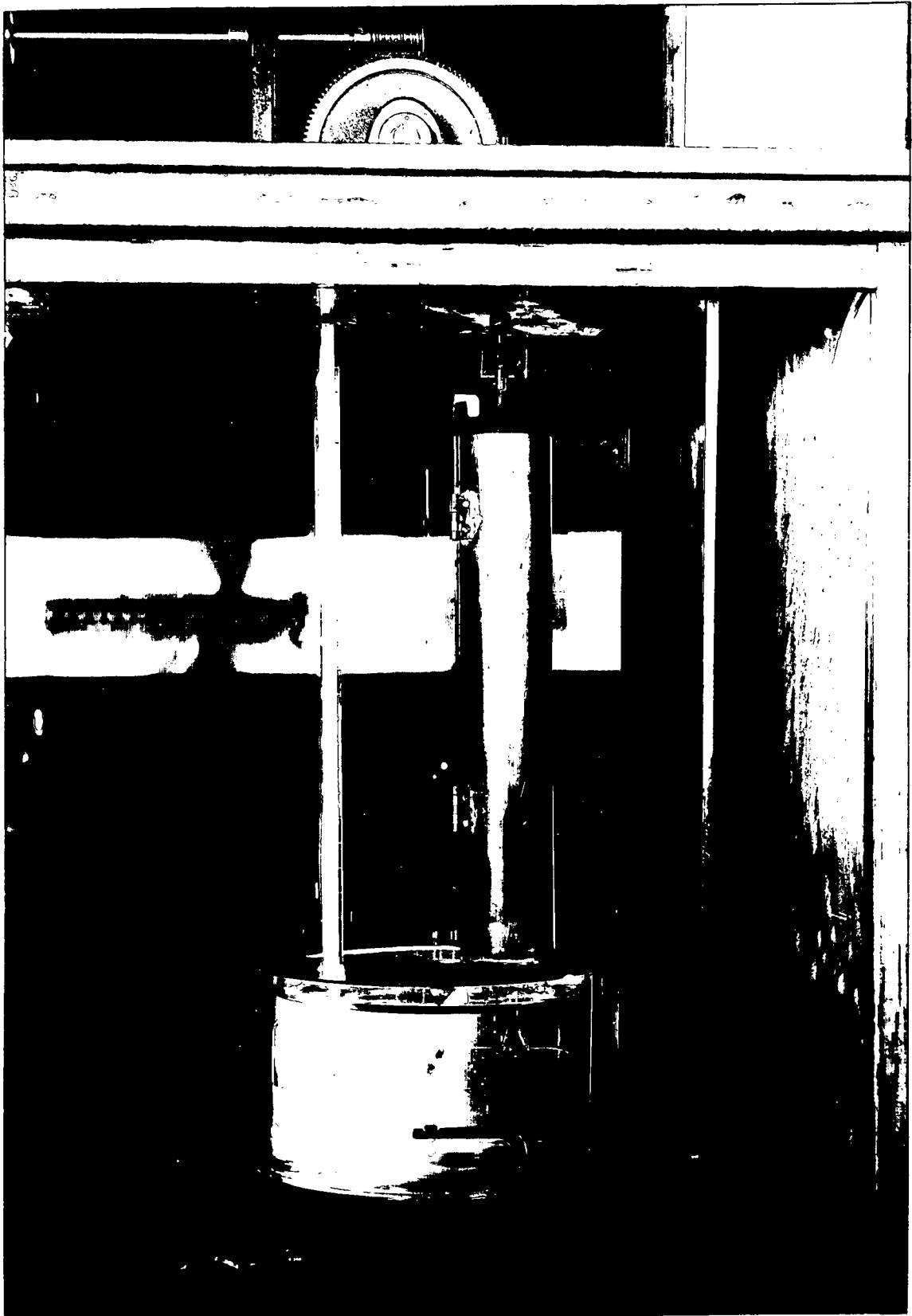
Through the bottom of the copper plate of the cell, a small 0.125-inch diameter brass rod was extended, the end of which was bent through a 90° angle. A small 0.062-inch diameter hole was drilled through this end of the brass arm, serving as a socket in which the lower vertical glass arm was mounted. At the upper tip of this glass arm, the second of the individual fibers used in the force measurements was attached with DeKhotinsky wax. To prevent leakage from the cell at the point where the brass rod extended through the copper bottom, a small stuffing box was used. This is shown at D in Figure 6. A drain pet-cock, E, was also mounted on the copper bottom, and permitted rapid drainage and cleaning of the cell.

The brass arm in which the lower vertical glass rod and fiber were mounted could be rotated by the same type of driving mechanism used in the upper movable suspension. The speed reduction of 10,000 to 1 from the motor-driven shaft was also accomplished with a double set of worm gears.

A general view of the balance equipment is shown in Figure 7. The balance, itself, was set on an optical pier to eliminate vibration. The pier (constructed of cement and brick) had been built free of the building foundation and was practically vibration-free, as a flat dish

Figure 8

CLOSE-UP OF FIBERS MOUNTED IN TORSION BALANCE



of mercury placed on the pier showed no distortion of reflected images. Behind the optical pier, as seen in Figure 7, a small motor, used to drive the movable suspension and arms of the balance, was mounted on a table entirely separate from the pier. The motor was series wound, turning over at approximately 3600 revolutions per minute at no load. There was a permanently built-in gear reduction of $8 \frac{1}{2}$ to 1 on one end of the motor shaft, and this reduction was used to drive the balance shafts through a belt and pulley arrangement. The procedure finally adopted for making adhesion measurements required that only the lower shaft and balance arm be moved. However, the motor was mounted midway between the upper and lower shafts, and could be connected to either one by merely changing the belt and pulley.

In actual operation the motor speed was very appreciably slowed down by means of a pulley brake connected to the high speed end of the motor shaft (see Figure 7). This merely consisted of a pulley mounted on the free end of the motor shaft which was braked by a raw-hide thong connected to a screw and spring arrangement for applying tension to the thong. Before the pulley brake was designed, it was attempted to use a rheostat shunt control across the armature of the motor, but this appreciably reduced the motor torque, which was not desirable. The motor was connected to a 110-volt circuit through a reversing switch, allowing it to be run in either direction.

The drive shafts to the balance were split into three sections and were connected at two points with rubber tubing. This aided materially in eliminating any transference of motor vibration

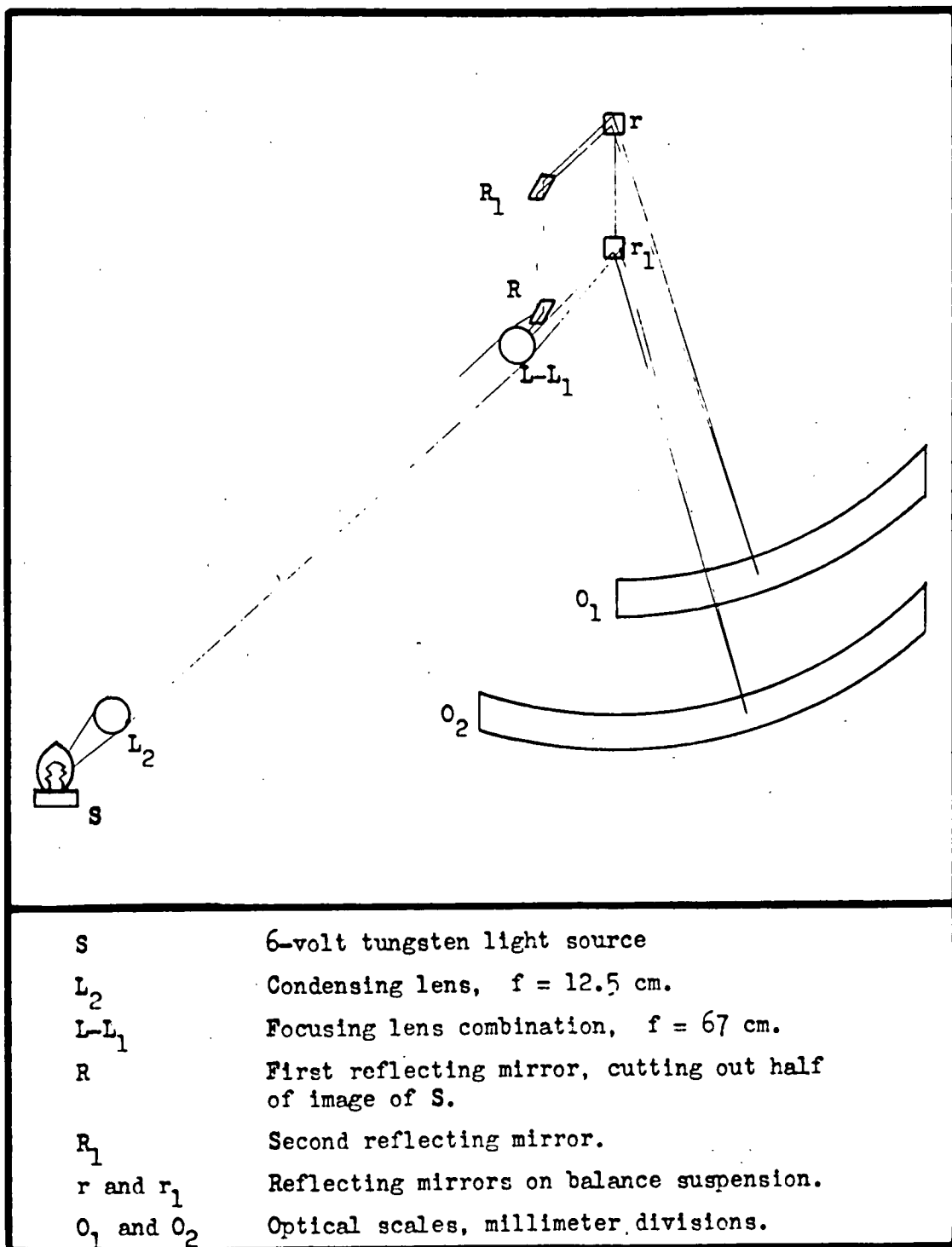
through the drive shafts to the balance.

In Figure 7 there is also shown the optical scale used to measure the angle of twist of the torsion wire, and, immediately to the right of the balance case, the system of lenses and reflecting mirrors used to focus the optical lever. The light source used in the latter arrangement was located at the extreme right of the balance and pier and is not shown in Figure 7.

A diagrammatic sketch of the set-up used for the optical lever is given in Figure 9. The light source, S , was a 6-volt, double filament tungsten lamp. A collimating lens, L_2 , and a hair-line were placed in front of the source which was located at the focal plane of the lens. The beam of essentially parallel light was directed upon the focusing lens combination, $L-L_1$, 130 centimeters distance from the collimating lens. The focusing lens combination consisted of a positive and a negative lens of +50 centimeters and -200 centimeters focal lengths, giving an effective focal length of +67 centimeters to the combination. Behind the focusing lens combination, a small narrow reflecting mirror, R , was mounted, sending the beam of one of the light filaments up to mirror R_1 which then reflected the filament image to R , the small mirror mounted on the upper suspension rod of the torsion balance. Each of the mirrors, R and R_1 , of the torsion balance reflected half of the light of the source to the optical scales, Q_1 and Q_2 . The focusing lenses, $L-L_1$, were approximately 25 centimeters in front of the mirror R_1 , or the axis of the torsion wire, and the optical scales Q_2 and Q_1 were 107 and 95

DIAGRAMMATIC SKETCH OF OPTICAL LEVER USED ON TORSION BALANCE

Figure 9



centimeters distance from x_1 and x , respectively. Images of the hair-line were focused upon the scales Q_1 and Q_2 , enabling precise measurements of the deflections of the beams reflected from x and x_1 .

Procedures and Calibration of the Torsion Balance

Detailed Procedure

The adhesion force measurements were made by bringing two fibers mounted on the ends of glass arms into intimate contact and then measuring the angle through which the torsion wire was twisted as the fibers were pulled apart. The detailed procedure used in making these measurements is given in the following paragraphs.

(a) After the torsion wire and platinum saddle were properly mounted, the glass-copper cell was filled with the sample of water under which the adhesion measurements were to be made.

(b) Individual fibers were mounted on the ends of the removable glass arms with a very small portion of DeKhotinsky wax (see Figure 5). This was accomplished by first isolating the individual fiber from a small wad of wet pulp, using forceps. The wax on the tip of either of the small glass arms was then softened by warming next to a very low flame, and one end of the fiber was then stuck into the soft wax, being held in position until the latter hardened. Care was always taken to handle the glass arms and fiber bunches with forceps to prevent contamination, and to keep them in ground-glass stoppered containers when they were not mounted in the balance.

(c) DeKhotinsky wax, which became very soft at 50° C., was

used for mounting the fibers. There was some question as to the effect of the heat required in the mounting procedure and the possible desiccation of the fiber, but no other suitable mounting media could be found. Attempts were made to use a resin which was soft and tacky at room temperature, but this did not hold the fibers firmly enough.

(d) After the fibers were mounted, the glass arms were submerged in the cell of the balance and placed in position, the top arm laid horizontally in the platinum saddle, and the lower arm placed vertically in the socket of the brass rod which extended up into the cell through the copper bottom.

(e) A copper shield, shown in Figure 5, was then placed around the torsion wire to prevent any disturbance arising from small eddy currents in the air of the balance case. A thermometer was also placed in the water contained in the glass cell.

(f) The glass balance case was closed and the torsion suspension was then allowed to come to rest. The position of the light beam reflected by the top mirror of the balance onto the top optical scale, θ_1 , was noted and this position retained throughout the measurements.

(g) When the torsion suspension sensibly came to rest, as indicated by no oscillatory motion of the light beam reflected by the lower mirror mounted on the platinum saddle, the position of the hair-line image on the lower scale, θ_2 , was noted.

(h) The lower fiber mounted on the vertical glass arm was then brought into contact with the top fiber, using the motor to drive the balance shaft. The speed at which the lower fiber was moved was approximately 0.007 centimeters per second. After the initial contact

of the fibers was made, as observed by a sudden movement of the lower hairline image, the motion of the lower fiber was allowed to continue until the deflection of the light beam was 5 centimeters on the scale. This corresponded to a displacement of 0.04 centimeters of the upper fiber from its initial position.

(j) By using the reversing switch on the motor, the direction of rotation of the drive shaft was then reversed and the lower fiber moved forward, thus pulling it away from the upper fiber. The lower fiber speed maintained during this procedure was again approximately 0.007 centimeters per second, corresponding to a speed a little less than 1 centimeter per second for the travel of the light beam across the lower scale.

(k) The maximum displacement on this scale of the light beam was then noted, and the displacement value, x , was obtained by subtracting the rest point reading from the displacement reading.

(l) After the fibers were separated and the maximum displacement of the light beam noted, the movement of the lower fiber was continued forward while its rate of motion was checked with a stop watch. This was done by measuring the time interval for 10 revolutions of the belt connecting the motor and the drive shaft. Knowing that the diameter of the drive shaft pulley was 0.875 inches, the belt length 20 inches, and the length of the lower brass arm 1.75 centimeters, the rate of fiber movement was calculated from the relation:

$$\text{Rate of fiber motion} = 0.0805 / \bar{t} \text{ (cm. / sec.)} ,$$

where \bar{t} was the time in seconds for 10 revolutions of the belt. The value of \bar{t} was kept within the limits of 10 to 16 seconds, giving

maximum and minimum values of 0.008 and 0.005 centimeters per second, respectively, for the rate of fiber motion.

(1) When the fiber movement rate had been checked, the motor was stopped and the upper suspension allowed to come to equilibrium. The rest point was then rechecked and the force measurements repeated. Five such individual measurements were made on a single pair of fibers, and displacement values averaged.

(2) The temperature of the liquid in which the measurements were made was then checked, and finally the horizontal distance of the point of contact of the two fibers from the axis of the torsion wire was measured. This latter value was required in the calculations of the adhesion force, and was measured with a cathetometer. The latter is shown in the horizontal position in which it was used (Figure 7, at the extreme left of the photograph).

Calibration of the Balance

To calculate the adhesion forces from the data obtained by the procedure described above, it was necessary to know the torsion constant of the gold strip torsion wire, and also the relative value of the fluid friction on the balance arms that might exist at the speed at which the fibers were moved when being separated.

The torsion constant of the gold strip, defined as the torque per unit angle of twist, was obtained by measuring the changes in the periods of simple harmonic oscillations, imposed by various known moments of inertia suspended by the torsion wire. These measurements were made in air with no liquid in the glass cell. The torsion wire

and platinum saddle which had an unknown moment of inertia were suspended in their regular positions. This system was then set in rotational vibration and the period of simple harmonic motion measured by timing three complete oscillations. Five such measurements were taken and the time values averaged. Then a mass having a known moment of inertia (either a copper or platinum wire) was suspended in a platinum wire saddle, this system set in oscillation and the new period measured. With the aid of the following equations, the torsion constant of the wire was then calculated. Let

I_0 = unknown moment of inertia of platinum saddle and mirror;

T_0 = period of oscillation of this system in seconds;

I_1 = known moment of inertia (either platinum or copper wire);

T_1 = period of oscillation of the system; platinum saddle, mirror and known moment of inertia;

k = torsion constant of the wire;

then, with only the saddle and mirror suspended and the system vibrating in simple harmonic oscillation, the period T_0 is given by the relation:

$$T_0 = 2\pi \sqrt{\frac{I_0}{k}} \quad \text{or} \quad (1)$$

$$k = 4\pi^2 \cdot \frac{I_0}{T_0^2} \quad (2)$$

With the moment of inertia of the system changed by the addition of a known moment of inertia:

$$T_1 = 2\pi \sqrt{\frac{I_0 + I_1}{k}} \quad , \quad \text{or} \quad (3)$$

$$k = 4\pi^2 \frac{(I_0 + I_1)}{T_1^2} \quad . \quad (4)$$

Solving (2) and (4) gives

$$I_0 = \frac{T_0^2 \cdot I_1}{T_1^2 - T_0^2} \quad . \quad (5)$$

The moments of inertia of the thin platinum and copper wires used for calibration are given by the relation:

$$I_1 = 1/12 m \cdot b^2 \quad , \quad (6)$$

where m is the mass of the wire in grams and b the length in centimeters.

Therefore, from equations (2) and (5) we have:

$$k = \frac{K}{T_1^2 - T_0^2} \quad . \quad (7)$$

where $K = (1/3) \cdot \pi^2 \cdot m \cdot b^2$ for each known moment of inertia. The platinum wire used for calibration purposes weighed 0.2106 grams and had a length of 3.115 centimeters, giving a value of 6.73 gm.-cm.² for K in equation (7). The 24-gauge copper wire had a K value of 4.36.

The value of the torsion constant, for the type of gold strip suspension used, was approximately 0.08 dyne-centimeters per radian twist. Agreement between the values obtained using both platinum and copper wires

for the known moments of inertia was within 0.5 per cent.

If there was no fluid frictional drag on the upper horizontal glass arm, the adhesion force between two fibers, as measured with the torsion balance, could be obtained using the equation:

$$F = \frac{t \cdot x}{2 \cdot y \cdot q} \quad (8)$$

where F is the adhesion force in dynes; t , the torsion constant of the suspension; x , average deflection of the light beam beyond the rest point in centimeters; y , the distance in centimeters from the point of contact of the fibers to the vertical axis of the torsion wire; and q , the length of the optical lever, or the distance from the torsion wire to the optical scale. Equation (8) was obtained from the fundamental expression of Hooke's law:

$$\text{Torque} = F \cdot y = t \cdot \theta \quad (9)$$

θ being the angular displacement of the torsion wire.

The effect of frictional drag on the upper glass arm during the force measurement would be to decrease the force measured by the displacement of the optical indicator on the scale. Since the same glass mounting arms were always used in the same position, and since the rate of motion of the fibers during the actual measurements was held reasonably constant, the drag effect was constant for all measurements in which the viscosity of the fluid did not markedly change. Accordingly, the only purpose in applying a constant correction factor for this effect to all the results was to give a more absolute value

to the latter. The correction factor was obtained by first removing the vertically mounted, lower glass arm and then connecting the motor to the upper drive shaft of the balance. The entire suspension was then rotated at approximately the same speed as that used during the fiber measurements. As the two optical indicators were passing from left to right, the exact position of the lower indicator (moving on optical scale Ω_2 in Figure 9) was noted as the upper indicator passed an arbitrary zero point. After continuing rotation of the suspension in this direction for several minutes, its direction was reversed so that the indicators travelled from right to left across the scales. Again the position of the lower indicator was noted at the time the upper indicator passed the zero point. The difference between the two scale readings obtained when the lower indicator was travelling in opposite directions was divided by two and this quotient in centimeters always added to all displacement values. In water the correction factor was approximately two centimeters. Any further application of the factor will be discussed in the section on results.

Pulps Used in the Experimental Work

The majority of experiments in this investigation were made on a single unbleached spruce sulphite pulp. This was done so that the factor of type of fiber used could be held constant while the effects of other variables, such as chemicals, temperature, etc., on flocculation were being observed.

The standard pulp was a Canadian spruce, unbleached, quick cook, sulphite stock obtained in wet laps from a neighboring pulp mill.

Approximately 25 pounds of pulp on the air dry basis (75 pounds of wet laps) were obtained to insure an adequate supply. As received from the mill, the stock possessed some residual odor of sulphur dioxide, so that it was deemed advisable to wash it before storing. This latter operation was done in three batches, the pulp being given two hot water washes for about one-half hour each at 3 per cent consistency. After draining, the pulp was pressed to approximately 25 per cent over dry, disintegrated by hand into large crumbs, and stored in batches in air tight 5-gallon glass jars.

A few flocculation experiments were also made on an unbleached Douglas fir sulphite stock and an unbleached birch sulphite pulp. Both of these pulps had been cooked in the laboratory, and also were air-dried, containing only 6 per cent moisture. The permanganate number of the Douglas fir stock was 11.3 and that of the birch sulphite, 10.

V. RESULTS AND DISCUSSION

The discussion of results will be given in two sections: (A) the results obtained using the flocculation tester, and (B) the measurement of fiber to fiber adhesion forces.

In the first section the data will be considered in the following order: (a) reproducibility of flocculation runs, (b) alum effects, (c) the effect of bentonite clay on fiber flocculation, (d) temperature effects, (e) the use of deflocculating gums, (f) the effect of wetting agents, (g) the action of heating on fiber flocculation, (h) the effect of consistency, (i) flocculation characteristics of air-dried pulp, and (j) the flocculation of Douglas fir and birch sulphite fibers relative to that of spruce sulphite pulp.

Reproducibility of Results. Flocculation Tendencies of the Standard Unbleached Spruce Sulphite Stock Dispersed in Tap Water

To establish the limits of experimental error within which flocculation runs could be duplicated, the results obtained for seven identical runs have been tabulated in Table II. These runs were made on the standard unbleached spruce sulphite pulp, dispersed in tap water at 0.0097 ± 0.0003 per cent consistency and $25 \pm 2^\circ \text{C}$. Columns 1, 2, and 3 in the Table give, respectively, the consistency, temperature limits, and the pH of white water samples taken both at the start and at the end of each run. The dispersion index values and the slope constants given in the last two columns are the constants K_1 and K_2 , respectively, in the equation:

$$\log Z = K_3 + K_2 \log Y$$

expressing the linear relation found to exist between $\log Z$ and $\log Y$. In all the runs at least 10 individual points have been used to establish the above equation.

Table II

REPRODUCIBILITY OF FLOCCULATION RUNS

Unbleached Spruce Sulphite

Run No.	Consistency %	Temperature Limits °C.	pH of White Water		Dispersion Index (K_3)	Slope Constant (K_2)
			Start	Finish		
8	0.0099	25.5-26.0	7.2	8.0	1.45	0.87
11	0.0101	25.0-25.7	7.1	8.2	1.29	0.90
12	0.0107	26.0-25.8	7.3	8.0	1.27	0.96
18	0.0097	24.0-24.5	7.4	7.9	1.23	0.93
21		24.			1.22	0.95
22	0.0093	26.2-28	7.2	8.0	1.23	0.95
35	0.0093	24.5-25.3	7.4	8.1	1.18	1.07

It is recognized that somewhat of a discrepancy exists between run 8 and the remaining six runs, which is believed to be of a subjective nature. After optimum baffling conditions and stirrer speeds for use in the head-box were developed, run 8 was the first test made to establish the flocculation tendencies of the unbleached spruce sulphite pulp in tap water alone. Following it, a series of runs were made, using alum in the stock and tap water suspension. As will be seen later, alum, when present in the form of alumina with the fibers,

is a good dispersing agent and, therefore, in these alum runs no large fiber flocks were ever formed. Accordingly, at the flocculation end-points observed in these alum runs, the sizes of the fiber bunches were appreciably smaller than those which existed at the end-points first established in run 8. When the alum experiments were completed and runs 11 and 12 were made to redetermine and check the flocculation tendencies of the pulp fibers alone, it seems probable that the observer's conception of the flocculation end-point had been changed and that, in this case, flocculation was considered to occur in the observation tube at the point where the fibers were just beginning to bunch, rather than a position slightly further down the tube, where flocks of appreciable size had already formed. This latter end-point was used in run 8 because, at that time, it was thought to be the one more easily seen. This difference in the conception of the flocculation end-point could readily account for the difference between the dispersion index values of run 8 and the other six runs.

Therefore, the results of run 8 have been discarded, and the average flocculation tendencies of the standard unbleached sulphite stock in tap water determined from the remaining six runs. The equation expressing this average result is:

$$\log Z = 1.24 + 0.96 \log Y \quad (1)$$

Comparing it with the individual data in the last two columns of Table II shows that in the case of the parameter constant K_7 , or the dispersion index, the per cent average deviation from the mean is ± 2.4 per cent, with a maximum per cent deviation of ± 4.5 . For the slope

constant (K_2) of the equation, the average per cent deviation from the mean is ± 4 per cent, with a maximum of + 11 per cent.

The data from runs 11 and 15, representing the maximum variation between the six check runs, have been plotted graphically in Figure 10. The dotted line on the graph represents equation (1) above, the average of the results of all six runs.

Photographs of runs 8, 11, and 22 were taken and are shown in Figure 11. The degrees of flocculation shown in each of the pictures are not directly comparable, because of differences in flow velocities, but a comparison of runs 8 and 11 will substantiate, to some extent, the remarks already made concerning the discrepancy between the dispersion index of run 8 and those of the other six runs. The pictures indicate a slightly greater flocculation in run 8, which may be accounted for by the somewhat lower flow velocity (0.86 cm./sec. compared to 1.01 cm./sec. for run 11). However, if the flocculation indices as given in Table II were directly comparable, the degree of dispersion in run 8 would have to be considerably greater than that shown.

A comparison of the photographs for runs 22 and 11 indicates a somewhat greater degree of dispersion for run 22. This, again, may be partially accounted for by differences in flow velocities at which the pictures were taken. However, the actual variation in the flow rate of 0.05 centimeters per second is too small to account solely for the dispersion difference shown photographically. This brings another point up for consideration with regard to interpretation of photographic

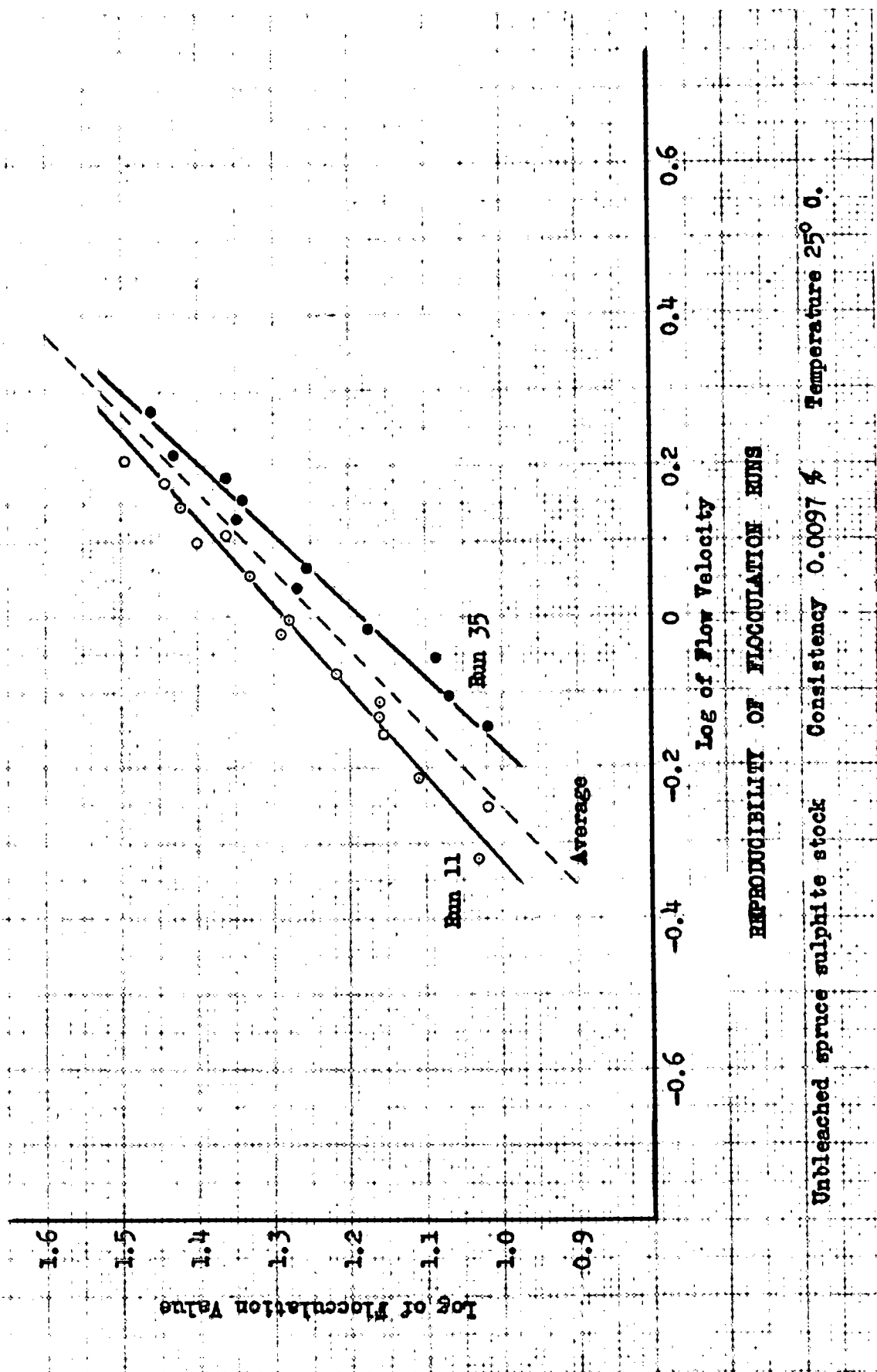


Figure 10



Run #8 Flow velocity 0.86 cm./sec.



Run #11 Flow velocity 1.01 cm./sec.



Run #22 Flow velocity 1.09 cm./sec.

FLOCCULATION OF UNBLEACHED SULPHITE STOCK IN TAP WATER

Consistency 0.0097 % Temperature 25° C. Tap water, pH 7.2-8.0

Figure 11

data; namely, the photographic record only represents a condition of flocculation occurring at a given instant. As already pointed out in a previous section, this end-point may vary by as much as ± 3 units of the flocculation scale shown on the photograph for run 8, Figure 11. Therefore, slight variations may occur in the photographic records which are not significant and do not show up in the average dispersion index values. Conclusions from photographic records are thus always made in conjunction with these latter results. The dispersion indices for runs 11 and 22 agree well within the limit of error of the method, and it may therefore be concluded that the differences in the degree of dispersion shown by the photographs of these runs may be attributed to some variation of the flocculation tendencies within the individual runs, as well as to a small difference in flow velocities at which the pictures were taken.

To conserve space in the mounting of subsequent photographic data, the image of the flocculation scale adjacent to the observation tube has been removed from the prints. Before cutting, however, the scale divisions of 15, 20, 25, and 30 were extended directly up to the image of the observation tube on the prints with black India ink. Also, just below the 15th scale division an arrow has been drawn on all photographs indicating the direction of flow of the stock in the glass observation tube. The flocculation scale was always photographed with the observation tube as shown in the picture for run 8, but has been removed from all other prints before mounting.

If the photographs are viewed with their long direction held

vertically before the reader and the arrow, giving the direction of flow, pointing down, they will give the condition seen by an observer standing some 5 feet in front of the flocculation tester. In run 22, at the particular flow velocity at which the photograph shown in Figure 11 was taken, the flocculation end-point was considered to be at 19.

Before completing a discussion of the data presented in Table II, mention should be made of changes in pH of the white water which occurred during the course of the runs. It will be observed from this table that the initial pH of the tap water averaged about 7.3, while at the completion of the runs the white water pH was approximately 8.0. This decrease in the hydrogen ion concentration of the white water was also noted in lower pH ranges obtained when alum was used in the water, as will be seen from data to be presented subsequently. Further, only when there was sufficient alum present to buffer the white water pH down to approximately 4.5, was this effect eliminated. If the increase in pH occurred only in the ranges below the neutral point and in the presence of alum, it might be attributed to a slow neutralization of the hardness of the water. However, since it occurs in this case with fiber and tap water alone, it would appear that the fiber played some role in the phenomenon, either through the introduction of alkaline lime salts into the water, or through some adsorption effect. An additional possibility is that the pH increase might be due in part to alkalinity from the glass observation tube. Other instances of this decrease in acidity of the white water during flocculation runs will be cited as the discussion

continues.

To sum up, data from six directly comparable runs made with the flocculation tester indicate that the constants in the relation:

$$\log I = K_1 + K_2 \log I \quad .$$

can be checked by means of the procedures developed to within the following errors: ± 5 per cent variation in the case of K_1 , the dispersion index, and ± 10 per cent for the slope constant, K_2 . It has also been shown that care must be taken to avoid subjective errors in judging the flocculation end-point, and that slight variations may occur in the degrees of dispersion recorded photographically which are not representative of average results. It is, therefore, desirable always to evaluate such photographic data in the light of average results expressed by the dispersion indices.

Effect of Alum on Fiber Flocculation

One of the first factors to be investigated in this study of fiber flocculation was the effect of various quantities of alum on the dispersion of fibers in tap water. The alum used in these experiments was a crystalline c.p. quality having the formula, $Al_2(SO_4)_3 \cdot 12 H_2O$. This product is not the same as a technical grade of basic papermakers' alum, the latter containing a slightly higher percentage of alumina and a little less water of crystallization, but the chemical purity of the hydrated aluminum sulphate was desired in this work.

The quantities of alum added to the head-box of the flocculation tester were based on the percentage of oven-dry weight of fiber in the suspension. Because of the low fiber consistency of approximately 0.01 per cent and the extreme hardness of the water used, an appreciable percentage of alum, based on this dry fiber weight, was required to bring about much change in the white water pH. One hundred per cent alum, or 0.0008 pounds per gallon of water, increased the acidity of the latter to just below the neutral point. Four times this amount was required to bring the pH down to 4.4.

The standard procedure for making a flocculation run was used to investigate the effects of adding 100, 300, 400, and 710 per cent alum separately to four fiber-tap water suspensions. The results obtained are shown in Table III and are presented graphically in Figure 12.

Table III

EFFECT OF ALUM ON THE DISPERSION OF STANDARD UNBLEACHED
SULPHITE STOCK IN TAP WATER

Fiber Consistency 0.0105% Temperature 26° C.

Run No.	Per cent Alum Added on Dry Fiber Weight	White Water pH		Dispersion Index (K_3)	Slope Constant (K_2)
		Start	Finish		
9	100	6.8	7.7	1.72	0.84
13	100	6.8	7.8	1.67	0.92
14	100	6.6	7.7	1.63	0.91
15	300	5.1	5.7	1.64	0.96
12A	400	4.4	4.5	1.58	0.77
10	710	4.3	4.3	1.69	1.06

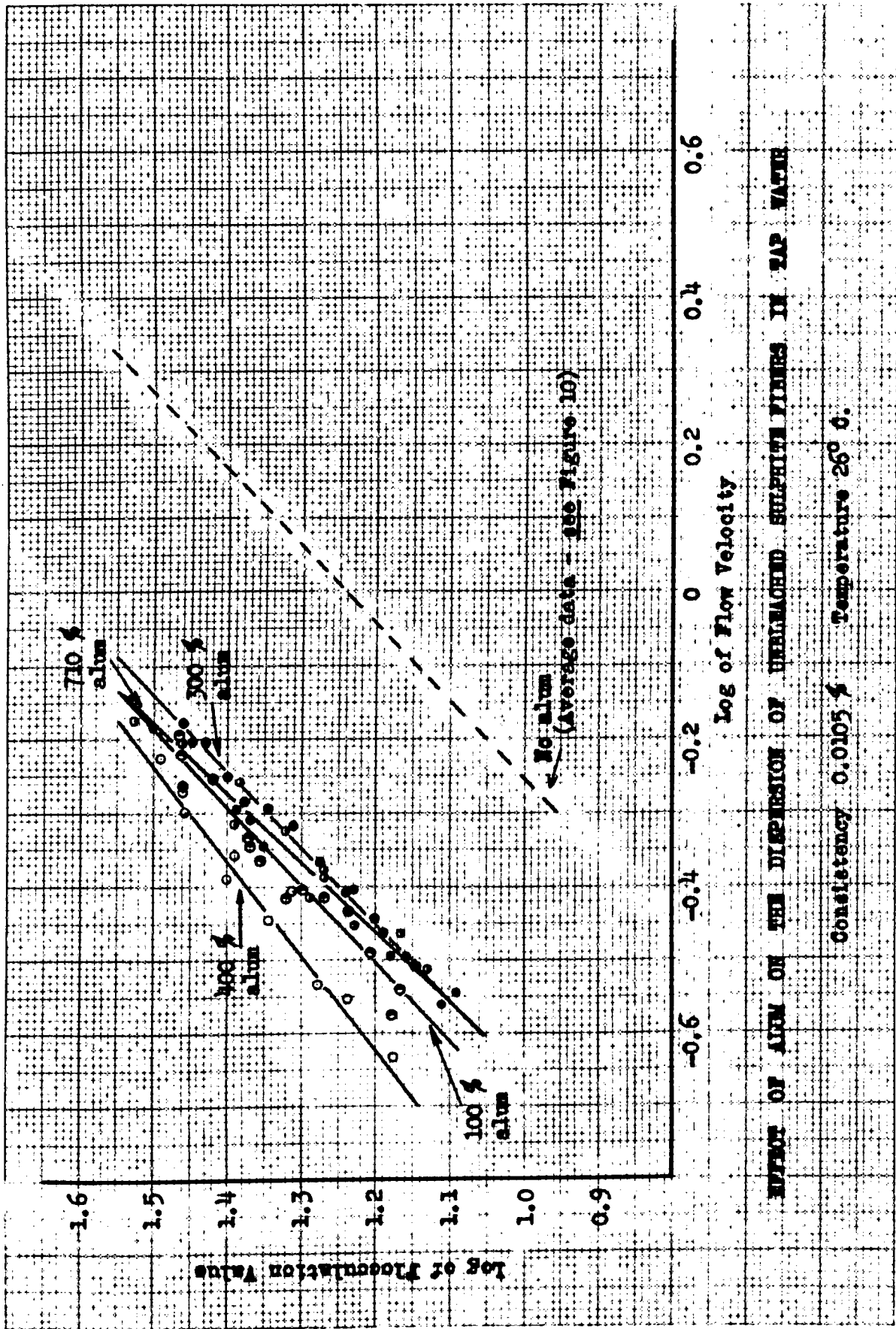


Figure 12

A comparison of the dispersion index values in Table III with the average value of 1.24, which was obtained as the dispersion index for fiber suspended in tap water alone, shows that the addition of 100 per cent or more of alum resulted in a marked improvement in fiber dispersion. The average of the dispersion index values for three runs made with 100 per cent alum was 1.67, with a maximum variation of ± 5 per cent, which was within the limits of error of the method. The addition of quantities of alum greater than 100 per cent, based on the fiber weight, had no significant effect on the dispersion index.

A visual evaluation of the marked increase in fiber dispersion, resulting from the addition of alum, can be made from Figure 13. Here, the top photograph shows the degree of dispersion of the standard unbleached sulphite stock in tap water at a flow rate of 0.47 centimeters per second. The following three pictures show the effects of 100, 300, and 710 per cent of alum, respectively, when added to individual tap water-fiber suspensions. All the photographs were taken under identical conditions of consistency, temperature, and flow velocity. The flocculation values given beneath the pictures are the scale readings at which flocculation was considered to occur under the given flow conditions. These values of 23, 20, and 22 for the 100, 300, and 710 per cent alum additions, respectively, indicate no significant difference in the degree of dispersion between the various conditions, which is in agreement with the dispersion index values in Table III.

Initial inspection of the photographs would suggest that a

Runs # 36x and 22 Tap water, pH 7.2 - 8.0 Flocculation - 8.3

Runs # 36xa and 13 Tap water plus 100 % Alum, pH 6.8 - 7.8 Flocculation 23

Run # 15 Tap water plus 300 % Alum, pH 5.1 - 5.7 Flocculation 20

Run # 10 Tap water plus 710 % Alum, pH 4.3 Flocculation 22

ALUM EFFECTS

Unbleached spruce sulphite stock Consistency 0.0100 ± 0.0010 %
Flow velocity 0.47 ± 0.01 cm./sec. Temperature $25.5 \pm 1^{\circ}$ C.

Figure 13

little less dispersion was obtained with only 100 per cent alum. This may actually have been the case for the specific instant at which the photograph was taken, but it is also quite probable that greater amounts of alumina floc, present in the stock suspension when 300 and 710 per cent alum were used, have aided in producing the photographic effect of increased dispersion in each of these cases. The light scattering effect of the small particles of the alumina floc might well have had less effect on the visual end-point, since the difference in shape between a fiber bunch and the alumina floc could be more readily detected in this case.

Referring again to Table III, it will be seen that the slope constants for the equations derived for each of the conditions agree within the accepted limits of error, with the exception of the case of run 12A, where the slope constant of 0.77 is almost 15 per cent less than the mean value for the six runs. The variation is not consistent, however, (see also Figure 12) and no significance has been attached to it.

Table III also shows the increase in the pH of the white water which occurs during the flocculation run, the increment being approximately 0.5 pH unit, which compares to the increase observed in the case of a fiber-tap water suspension alone. With sufficient alum present to buffer the pH of the white water to around 4.5, no decrease in acidity was observed. As previously mentioned, in these particular cases with alum present in the white water, the effect might be attributed to a slow neutralisation of the hardness of the water,

but this does not explain the fact that the condition occurs when no alum is present.

To sum up, 100 per cent of alum added to a suspension of fibers in hard water has been observed to markedly increase the degree of fiber dispersion. Quantities of alum greater than 100 per cent, based on the fiber weight, gave no further change in the degree of dispersion. Experimental data have not been given to show the effect of less than 100 per cent alum, but from preliminary tests it is known that 50 per cent alum did not produce as complete a fiber dispersion as that obtained with 100 per cent alum, while 10 per cent of the chemical exerted very little dispersing effect.

Effect of Alum With Distilled Water

To gain insight into the effect of alum as a dispersing agent, a series of flocculation runs were made with the standard unbleached sulphite pulp and distilled water in the flocculation tester. The flocculation tendencies of the dispersed fiber in distilled water were first evaluated. One hundred per cent alum on the fiber weight was then added to the suspension and the flocculation tendencies of the system redetermined. Finally, 12 per cent sodium hydroxide was added to the alum-fiber-distilled water system and its effect on the flocculation characteristics evaluated. The results obtained, as expressed by the dispersion indices, are given in Table IV, presented graphically in Figure 14, and shown photographically in Figure 15.

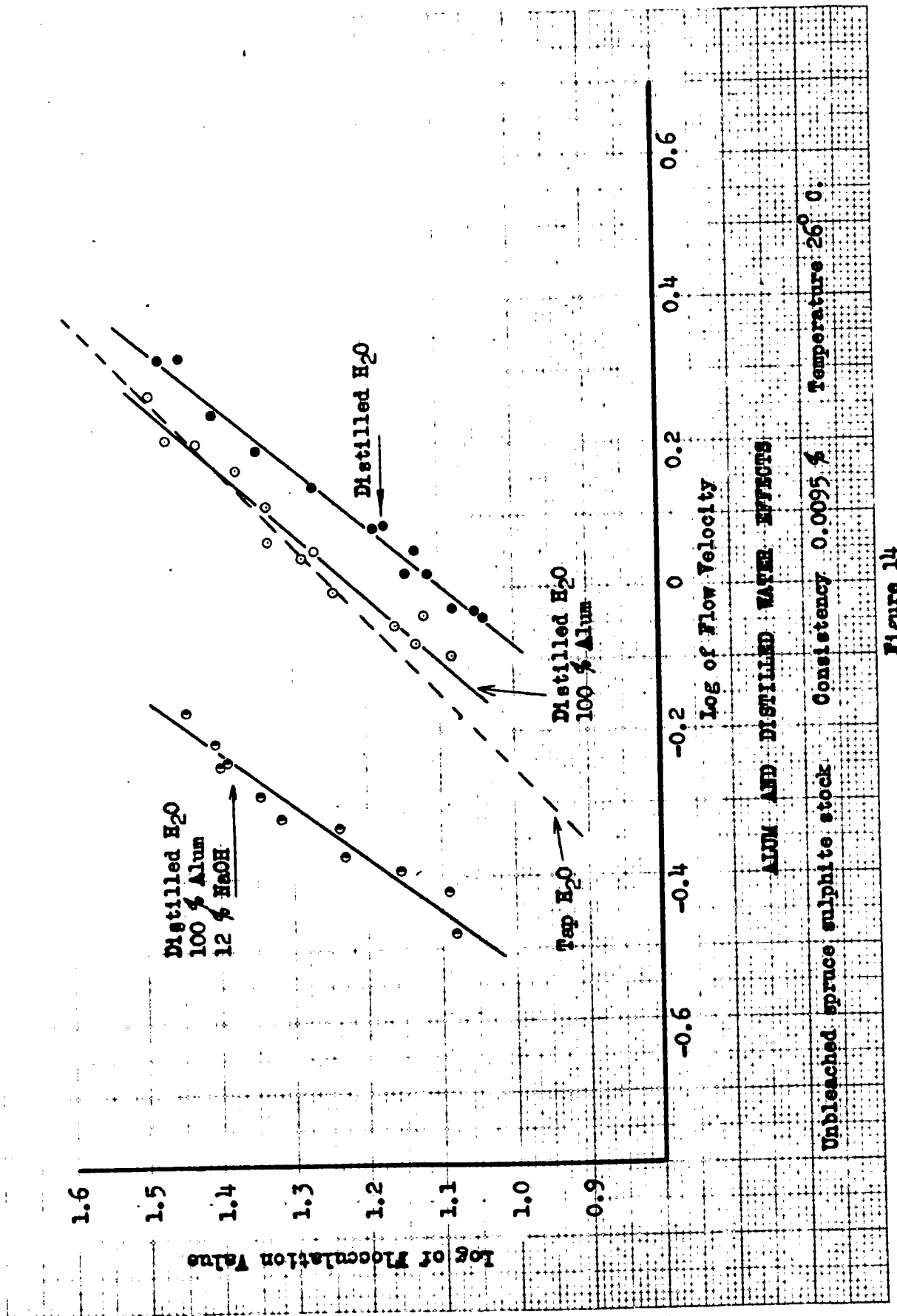


Figure 14

Run # 22 Tap water, pH 7.1 - 8.2 Flocculation - 17

Run # 16 Distilled water, pH 6.0 - 6.8 Flocculation - 14

Run # 16A Distilled water plus 100 % Alum, pH 4.5 Flocculation - 16.6

Run # 16ASC Distilled water plus 100 % Alum plus 12 % Caustic, pH 4.6 Flocculation - 51

ALUM AND DISTILLED WATER EFFECTS

Unbleached spruce sulphite stock Consistency 0.0095 \pm .0002 %

Flow velocity 1.03 \pm 0.02 cm./sec. Temperature 26° C. \pm 2°

Figure 15

Table IV

THE EFFECTS OF DISTILLED WATER, ALUM, AND SODIUM HYDROXIDE
ON THE FLOCCULATION OF STANDARD UNBLEACHED
SULPHITE PULP

		Consistency 0.0095%		Temperature 26° C.		
Run No.	Chemicals Added	White Water Start	Water pH Finish	Dispersion Index (E_1)	Slope Constant (E_2)	
16	No chemical	6.0	6.8	1.09	1.19	
16A	100% alum to run 16	4.5	4.5	1.21	1.13	
16ASC	12% NaOH to run 16A	4.6	4.6	1.70	1.33	

From these results the following conclusions may be drawn:

(a) a small but significant increase in fiber flocculation has occurred in distilled water as compared to the flocculation obtained under identical conditions in tap water; (b) 100 per cent alum added to a suspension of fibers in distilled water increased the flocculation tendencies only very slightly; and (c) the addition of a small amount of caustic to the alum-fiber-distilled water suspension markedly increased the fiber dispersion. Accordingly, it is indicated that the dispersing action of alum is due to the formation of aluminum hydroxide, or alumina, in the suspending medium. Alum itself, or the aluminum ion, seems to have very little effect.

The dispersing action of the alumina flock would not be expected if the effect were simply a mechanical one. If anything, in this respect, it would be postulated that the gelatinous alumina would tend to increase the fiber agglomeration. Therefore, an explanation

of the phenomenon seems more likely to be concerned with changes of energy on the fiber surfaces due to adsorption effects. It may be possible that, in the presence of the alumina floc, the cellulosic fibers become electropositive and, with an excess of the positively charged alumina floc present, the degree of dispersion is markedly increased over that which existed when the fibers were simply electro-negative and there were no additional charged bodies present in the suspension.

The enhanced flocculation occurring in distilled water as compared with that observed in tap water was not at all marked, but the difference as measured by the dispersion indices seems large enough to be significant. If not due to experimental error, however, this effect seems contrary to general conceptions. Any difference which might exist would be expected to occur in the opposite direction, since an increased flocculation in tap water might be accounted for by the flocculating action of bivalent cations on the electronegative fibers. More experimentation along these lines is necessary before any postulations can be made.

The slope constants of the equations expressing the relations between $\log \bar{X}$ and $\log \bar{Y}$ for the distilled water runs, as given in Table IV, are appreciably larger than the average slope constant previously obtained in the case of the tap water runs. The difference is shown graphically in Figure 14, where the $\log \bar{X} - \log \bar{Y}$ relations of the various runs in distilled water can be compared with the average $\log \bar{X} - \log \bar{Y}$ relation obtained for fiber dispersed in tap water alone

and shown as a dotted line on the graph. It has already been mentioned that an interpretation of any change in the slope of the $\log \bar{X} - \log \bar{Y}$ curves which concerns the fiber flocculation mechanism is not at once obvious. In the case of the data which have been presented thus far, and which involve only the flocculation of fibers in tap water, with and without the presence of various quantities of alum, the maximum variation of the slope constants has been from 0.77 to 1.07. For fibers dispersed in tap water alone, the average slope constant determined for six runs was 0.96, with the maximum deviation from the mean being about + 11 per cent. In the experiments in which various quantities of alum (100, 300, 400, and 710 per cent based on the fiber weight) were added to the tap water, an average slope constant of 0.91 was obtained from the equations giving the relations between $\log \bar{X}$ and $\log \bar{Y}$ for these various conditions. In this latter case the maximum variation was ± 15 per cent from the mean and was considered to be due to experimental error, since no consistent variation was observed. For the flocculation runs made in distilled water, with and without the presence of alum, or alum and caustic, the average slope constant for the $\log \bar{X} - \log \bar{Y}$ curves was 1.22, the maximum deviations from the mean being approximately ± 9 per cent. Thus, a significant difference would seem to exist between slope constants obtained in tap water experiments and those obtained for flocculation in distilled water.

Disregarding the specific data for a moment, and considering the two extreme changes in the slope constant which could conceivably take place, the following postulations may be made. If the slope constant approached zero, flocculation of fibers would occur in a rather

limited range on the flocculation scale, regardless of the flow velocity through the observation tube. This would indicate that, after the fibers made contact through random collision, they would tend to remain together; this would necessarily mean that the forces of adhesion were of a considerably greater order of magnitude than the shearing forces resulting from relative motion of the fluid particles through the flow tube and tending to pull the fibers apart. On the other hand, if the slope constant of the $\log \bar{F} - \log \bar{V}$ equation tended to approach infinity, very small changes in flow velocity would produce very large changes in the flocculation values, indicating the existence of very small or no adhesion forces between the fibers.

Accordingly, if changes in the slope constants (K_2) of the $\log \bar{F} - \log \bar{V}$ relations are greater than the limits of experimental error, their value, together with those of the dispersion indices (K_3), must be considered in evaluating the degree of flocculation for the given conditions. Hence, referring back to the specific data obtained for the flocculation effects observed in distilled water as compared to those observed in tap water, the following considerations may be made. Since the slope constants were greater for the equations evaluating the flocculation in distilled water, it is possible that fiber to fiber adhesion forces were smaller than those which may exist when the fibers were suspended in tap water. However, since the dispersion index was significantly smaller for the case of flocculation in distilled water, it is indicated that greater fiber agglomeration was observed in the flocculation tester for this condition, and that a factor, or

factors, other than fiber to fiber adhesion forces, were responsible for the flocculation.

Actually, how much significance can be placed on the slope constant of the $\log I - \log I$ equations remains to be seen from additional flocculation data. The above explanation is a plausible interpretation of the results which may occur, but before it is of any use in helping to explain the phenomenon of fiber flocculation, limits of error will have to be defined beyond which changes in slope constants become significant.

Initial Alum Effect

The previously discussed experiments showing the dispersing effect of alum, or more specifically of the alumina flock, were all made after fiber and alum had been well dispersed by circulation through the flocculation tester. The initial effect of the addition of alum to an aqueous fiber suspension is not to increase dispersion, but to produce a rather marked flocculation. The effect is best described with reference to Figure 16.

These pictures were taken during a special run made specifically to show this effect. In the top photograph the standard unbleached spruce sulphite stock at 0.01 per cent consistency, dispersed in tap water at 25° C., is shown flowing through the observation tube at a velocity of 2.07 centimeters per second. All conditions, including the flow velocity, were held constant and 21.2 grams of alum, dissolved in about 500 cc. of water, were added to the head-box of the flocculation

Run # 39xa Tap water, pH 7.2 - 8.0

Run # 39xb Tap water plus 100 % Alum. 30 seconds after addition of Alum

Run 39xc Tap water plus 100 % Alum 5 minutes after addition of Alum

INITIAL ALUM EFFECT

Unbleached spruce sulphite stock Consistency 0.01 %
Flow velocity 2.07 cm./sec. Temperature 25° C.

Figure 16

tester. In adding the alum solution, it was poured as uniformly as possible over the entire free surface of the liquid in the head-box to prevent local concentration. Within one minute after the alum had been added, the marked flocculation effect shown in the second photograph of Figure 15 could be seen in the glass observation tube. The flocculation of the fibers occurred simultaneously with the appearance of a slight turbidity in the fiber suspension. This condition of flocculation existed for only several minutes and, after this brief period, the stock flowing into the observation tube appeared as shown in the lower photograph of Figure 16.

Definite conclusions as to the causes of this initial effect of the alum cannot be drawn from the present results. It is possible that an isoelectric point with regard to alumina adsorption by the fibers occurred. A portion of the alum solution that was spread over the stock surface in the head-box may have passed down into the baffling system and thence into the observation tube without receiving much agitation from the stirrers in the head-box. If this be the case, it is conceivable that, through lack of vigorous dispersing action, just sufficient alumina was adsorbed by the fibers to render them electrically neutral, and in this manner enhanced their flocculation tendencies. After the fibers and alum had received sufficient agitation, more alumina may have been adsorbed by the fibers to render them completely electropositive and thus effect good dispersion. It is to be emphasized that this is simply a postulation to account for the results. Despite the fact that an exact mechanism cannot be given, however, the effect is

of marked interest, since it shows to what degree nonmechanical factors influence the phenomenon of fiber flocculation.

Reversion of Fiber Dispersion Produced With Alum

A reversion of the degree of fiber dispersion, or an increase in flocculation of stock which was originally dispersed with alum, was observed to occur after the fibers and alumina flock had been allowed to stand in the flocculation tester for some time. The time factor was not constant, since there were cases in which an increase in flocculation was observed after the stock had stood for only several hours, while in other cases the reversion effect was not noticed until the fibers and alumina had stood for more than 24 hours. The various runs in which this reflocculation was observed are listed in Table V, and photographs showing some of the effects are given in Figures 17, 18, and 19.

Table V

REVERSION EFFECTS. REFLUCCULATION OF FIBERS ORIGINALLY
DISPERSED WITH ALUM

Unbleached sulphite stock - Consistency 0.0105% - Temperature 25° C.

Run No.	Conditions of Run	White Water pH		Dispersion Constant (K_3)	Slope Constant (K_2)
		Start	Finish		
9	100% Alum	6.8	7.7	1.72	0.84
9S	Run 9 allowed to stand 20 hours	8.0	8.0	1.51	0.82
9SA	100% Alum added to run 9S	6.8	7.6	1.78	1.10
13	100% Alum	6.8	7.8	1.67	0.92
13S	Run 13 allowed to stand 20 hours	7.7	7.8	1.62	0.88
14	100% Alum	6.6	7.7	1.63	0.91
14S	Run 14 allowed to stand 20 hours	7.8	8.0	1.60	0.90
14S1	Run 14S allowed to stand 1 hour	8.0		1.55	1.10
14S2	Run 14S1 allowed to stand 20 hours	8.0	8.0	1.42	1.08
15	300% Alum	5.1	5.7	1.64	0.96
15S	Run 15 allowed to stand 14 hours	5.7	5.9	1.64	0.94
15S1	Run 15S allowed to stand 24 hours	6.0	6.1	1.65	1.02
15S1C	19% NaOH added to run 15S1	8.0	7.6	1.52	1.02
15S1C1	Run 15S1C allowed to stand 12 hours	7.7	7.4	1.52	1.00
16ASC	100% Alum, 12% NaOH added to distil- led H ₂ O and fibers	4.6	4.6	1.70	1.33
16ASC1	Run 16ASC allowed to stand 20 hours	4.8	4.9	1.37	1.01
16ASC1C	12% NaOH added to run 16ASC1	6.2	6.0	1.34	1.09
16ASC1CA	100% Alum added to run 16ASC1C	4.5	4.5	1.66	1.25
18	Fiber-tap water suspension	7.4	7.9	1.27	0.93
18S	Run 18 allowed to stand 24 hours	8.0	8.0	1.19	0.92
18S1	Run 18S allowed to stand 24 hours	8.2	8.2	1.12	0.99

Run # 38x and 9 Tap water plus 100 % alum, pH 6.8 - 7.7 Photograph taken approximately 1/2 hour after alum and fiber were mixed Flow velocity 0.467 cm./sec.

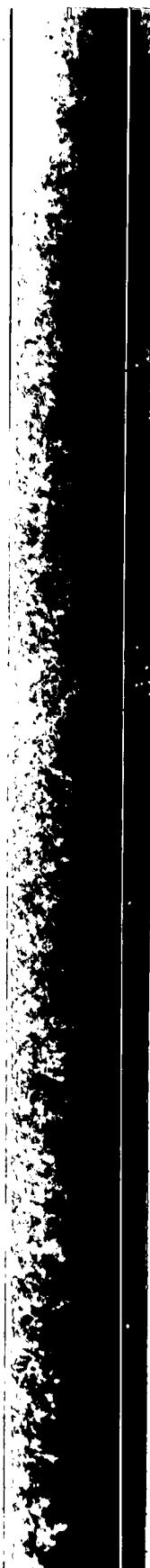
Run # 98 Tap water plus 100 % alum, pH 8.0 Photograph taken approximately 24 hours after alum and fiber were mixed - run not continuous Flow velocity 0.668 cm./sec.

Run # 98A 100 % alum added to run 98, pH 6.8 - 7.6 Flow velocity 0.312 cm./sec.

RETROCCULATION OF FIBER SUSPENSION ORIGINALLY DISPERSED WITH ALUM - 1

Unbleached spruce sulphite stock Consistency 0.0102 % Temperature 26° C. Tap water

Figure 17



Runs # 38x and 14 Tap water plus 100 % alum, pH 6.6 - 7.7 Photograph taken approximately $\frac{1}{2}$ hour after fiber and alum were mixed Flow velocity 0.467 cm./sec.



Run # 1492 Tap water plus 100 % alum, pH 8.0 Photograph taken 46 hours after fiber and alum were mixed - run not continuous Flow velocity 0.787 cm./sec.

REFLOCCULATION OF FIBER SUSPENSION ORIGINALLY DISPERSED WITH ALUM - 2

Unbleached spruce sulphite stock Consistency 0.0102 % Temperature 25° C.

Figure 18

Run # 15 Tap water plus 300 $\frac{1}{2}$ alum, pH 5.1 - 5.7 Photograph taken
approximately $\frac{1}{2}$ hour after fiber and alum were mixed Flow velocity 0.46 cm./sec.

Run # 15S1C Tap water plus 300 $\frac{1}{2}$ alum Allowed to stand in flocculation tester 38 hours
19 $\frac{1}{2}$ NaOH added, pH 8.0 - 7.6 Photograph taken after addition of NaOH Flow velocity 0.454 cm./sec.

REFLOCCULATION EFFECT OF CAUSTIC

Unbleached spruce sulphite stock Consistency 0.0111 $\frac{1}{2}$ Temperature 25° C.

Figure 19

The reversion effect was first observed in the case of run 9, which was originally made to show the dispersing effect of 100 per cent alum. The relation of $\log \bar{X} - \log \bar{Y}$ for the condition was established over a period of several hours (the usual length of time required to make a flocculation run), and the results showed a marked fiber dispersion due to the addition of the alum (see dispersion index given in Table V). The flocculation tester was then shut down for several hours and the fiber and alumina flock allowed to settle in the head-box. After several hours the equipment was again put into operation and the stock recirculated, principally to obtain a photograph of the degree of fiber dispersion observed several hours previous. It was immediately evident, however, that a marked decrease in the dispersion of the stock had occurred during the 2-hour period of standing. The stock was allowed to circulate for an additional hour at this time, but with no improvement in dispersion. Following this the equipment was shut down a second time, the stock allowed to stand for some 20 hours, and the degree of flocculation redetermined. The results showed a decrease in the dispersion indices from 1.72 to 1.51 (see Table V). A visual evaluation of the effect can be obtained from Figure 17. The top photograph shows the degree of dispersion obtained shortly after the addition of 100 per cent alum to a fiber suspension in tap water. The picture shown is not an original photograph of run 9 since a picture of this run was not taken until a reversion of the fiber dispersion had occurred. However, the conditions of the run were duplicated at a later date and rephotographed. The second picture in Figure 17 shows the increase in flocculation of run 9 after the latter had been standing

24 hours. It should be noted that, although the effect is quite apparent from the photographs, it would be even more marked if the latter had been taken at comparable flow velocities. Slowing down the flow rate of 0.883 centimeters per second, at which the photograph for run 9 was taken, to 0.467 centimeters per second would have produced an even greater degree of flocculation. The third print in Figure 17, although made from a poor negative, shows, to some extent, the redispersing effect of an additional 100 per cent alum added to run 98. Here again the effect would be greater than that shown photographically if comparable flow velocities had existed when both photographs were made.

To show that this increase in flocculation on standing was not spurious in the case of run 9, other series of runs showing similar effects are listed in Table V. Run series 14 shows the reversion, but over a considerably longer period of time. The difference in the dispersions of run 14 and 14S2 is partially shown in Figure 18. Again, the effect would be even more marked if the photographs had been taken at comparable flow velocities. The reduction in the dispersion index for the two runs of 1.63 to 1.42 agrees with the photographic evidence. It is of further interest to note that very little difference in flocculation was observed when run 14 was allowed to stand 20 hours (run 14S). However, after this fiber suspension was allowed to stand for only 1 hour more, a significant decrease in the dispersion index was noted.

In the case of runs 13 and 13S, the dispersion indices listed do not show a significant difference for a 20-hour standing period.

When 300 per cent alum was added to the fiber-tap water suspension (run series 15, Table V), no significant changes in the fiber dispersion were observed over a period of 38 hours. During this time the pH of the white water increased only from 5.1 to 6.1. The addition of 19 per cent sodium hydroxide, based on the dry fiber weight, however, produced a significant decrease in dispersion, as shown by the decrease in the dispersion index from 1.64 to 1.52. The effect is also shown photographically in Figure 19.

The flocculation run series 16, made with distilled water, shows a reduction in the dispersion index from 1.70 to 1.37 when the fiber-alumina-distilled water suspension was allowed to stand 20 hours. In this case the reversion occurred while the white water was definitely acidic (pH 4.9). Readdition of alum to the reverted system increased the dispersion again, as indicated by the dispersion index value of 1.66 for run 16ASC10A. A change in the slope constants of about 25 per cent also occurred for run series 16 during this cycle of dispersion, re-flocculation and redispersion. When the fiber was first effectively dispersed in distilled water by adding alum and caustic to produce an alumina flock (run 16SA) the slope constant obtained for the $\log \bar{Y} - \log Y$ relation was 1.33. After standing for a period of 20 hours, which brought about an increase in the flocculation tendencies of the system, this slope constant decreased to 1.01. When an increase in dispersion was finally brought about a second time by the addition of more alum and caustic, the slope constant increased again to a value of 1.25.

This variation in the slope constant following first a

decrease and then an increase in the fiber dispersion of run series 16 may be of some help in understanding all the reversion phenomena which have been observed. Recalling that a decrease in the slope constant may indicate an increase in fiber to fiber adhesion forces, reversion in the fiber dispersion may occur when a stock suspension is allowed to stand for some time in the flocculation tester, due to a more intimate association of the alumina flock with the fibers. Such an association may occur when both fibers and flock are allowed to settle in quiescent conditions. Further, the alumina flock particles themselves may agglomerate and, because of their gelatinous nature, these larger alumina flocks may enhance fiber flocculation by purely physical means. Any such agglomeration or association of alumina particles with each other or with fibers might be expected to be redispersed when the suspension was recirculated in the head-box of the flocculation tester, but conceivably this action need not occur to such an extent that the degree of dispersion obtained was the same as that which existed originally. The dispersing action observed when more alum was added after the first reflocculation may be explained by assuming that the introduction of more finely dispersed alumina flock counteracted the flocculation resulting from the agglomeration of the alumina particles originally present.

When a suspension of fibers and tap water alone was allowed to remain in the flocculation tester for a period of 48 hours, a small increase in the degree of flocculation was observed. This is shown in Table V, run series 13. The actual increase in flocculation in this case was not very great, but, assuming that it is significant, it cannot well

be accounted for on a physical basis. There was no gelatinous alumina flock present which might have agglomerated and, further, it is known that no hydration of the fibers occurred through repeated circulation in the flocculation tester, at least as indicated by a change in freeness of the stock. A slow adsorption of bivalent cations from the tap water, which conceivably might increase flocculation, is not in agreement with other results.

In conclusion, then, it is to be said that the increased flocculation tendencies of a dilute fiber suspension which occur when the latter has been allowed to stand for various periods in the flocculation tester, particularly in the presence of alumina flock, are not well understood. This actual increase in flocculation of a given fiber suspension, due to reversion effects, is much smaller than that which may be made to occur in the same fiber suspension by changing other variables. In this respect it is less important, particularly from a practical point of view. However, the observations which have been made have been reported in detail, since with further experimentation they may aid in explaining the phenomenon of fiber flocculation.

The Effect of Bentonite Clay on Fiber Flocculation

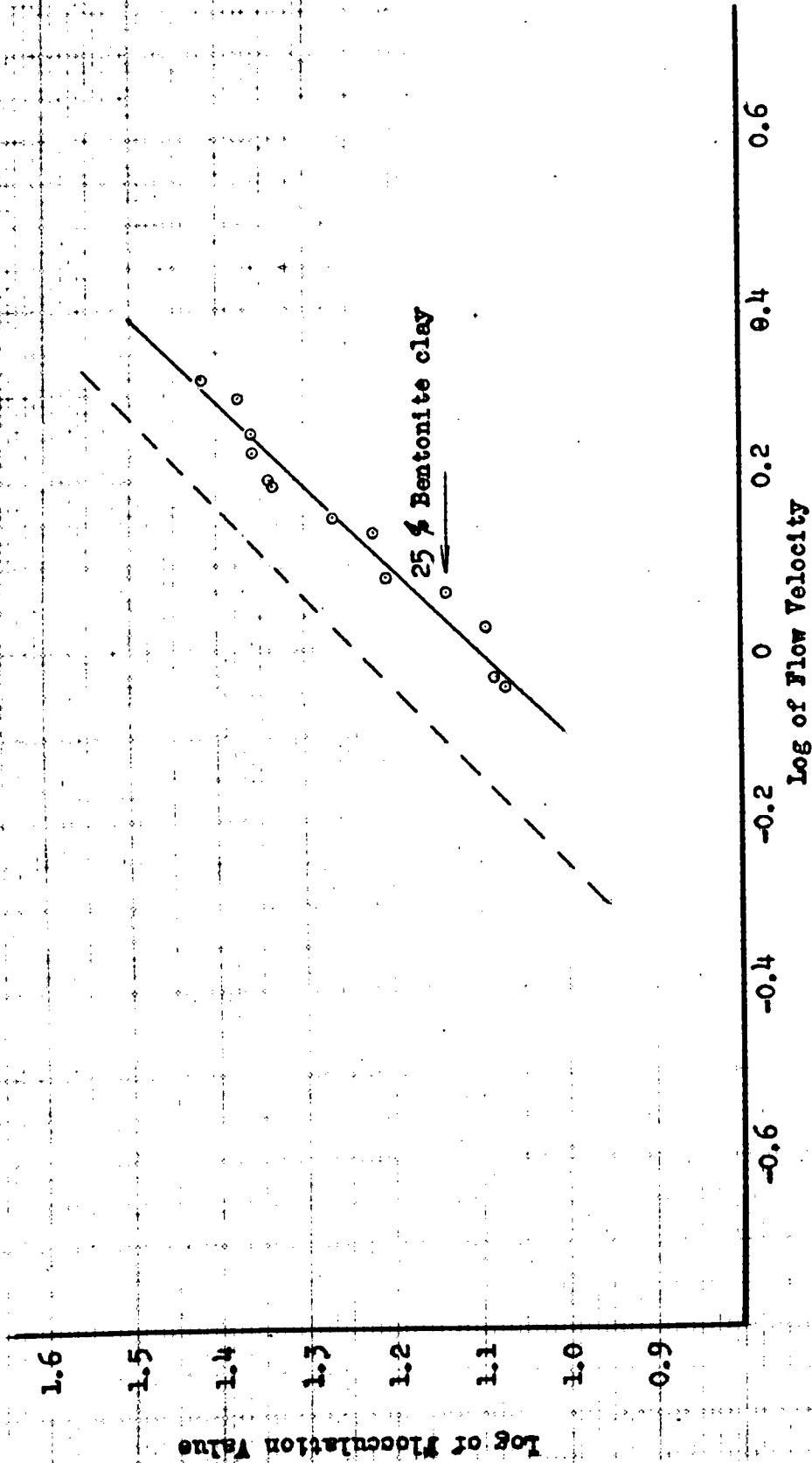
In the previous section the dispersion and flocculation effects observed when alum was added to a fiber suspension have been discussed. It was shown that the marked dispersing action of the alum was due to the formation of alumina flock with the alkalinity of ordinary tap water. Since this alumina flock is a positively charged gelatinous colloidal material, it seemed logical to investigate what effect, if

any, a negatively charged hydrophilic material would have on fiber dispersion. Bentonite clay, which is used under certain conditions in papermaking furnishes, is such a material.

Flocculation run 17, therefore, was made with 25 per cent bentonite clay, based on the dry fiber weight, added to a tap water suspension of the standard unbleached spruce sulphite stock. The fiber consistency was 0.0098 per cent and the temperature at which the run was made 23.5° C. The bentonite clay was dispersed with the stock in the standard British disintegrator, and the stock and clay then was added to the water in the head-box of the flocculation tester. The pH of the white water at the start of the run was 7.4 and increased to 7.9 during the course of the test.

The variation of the flocculation end-point with flow velocity through the observation tube was determined for thirteen different flow rates, the data being given in graphical form in Figure 20. The dotted line on the graph gives the average $\log \bar{I} - \log \bar{V}$ relation for fiber suspended in tap water alone. The dispersion index determined for the bentonite clay run was 1.10, and the slope constant, 1.03. A comparison of this dispersion index with the average value of 1.24, obtained for the fiber-tap water suspension, indicates that the bentonite clay has increased the flocculation of the suspended fiber. This result is substantiated photographically in Figure 21.

It might be postulated at first thought that the introduction of a negatively charged colloid into an aqueous suspension of



EFFECT OF 25 % BENTONITE CLAY ON FIBER FLOCCULATION

Unbleached spruce sulphite stock Consistency 0.0098 %

Tap water

Temperature 23.5° C.

Figure 20



Run # 22 Tap water, pH 7.2 - 8.0 Flocculation 18



Run # 17 Tap water and 25 % Bentonite clay, pH 7.4 - 7.9 Flocculation 13.5

EFFECT OF BENTONITE CLAY

Unbleached spruce sulphite stock Consistency 0.0095 %

Flow velocity 1.06 cm./sec. Temperature 25° C.

Figure 21

electronegative fibers would tend to increase the dispersion of the latter. The results show, however, that such is not the case. The actual increase in flocculation that was obtained suggests that the gelatinous nature of the clay resulted in poorer fiber dispersion simply because of a mechanical agglomerating action. This is in agreement with postulations made in the literature that gelatinous loadings increase flocculation and impair sheet formation.

Further experimentation on the effect of less hydrophilic clays, or actually nonhydrous fillers such as calcium carbonate, on fiber flocculation would be desirable.

The Effect of Temperature on Fiber Flocculation

Since there were differences reported in the literature as to the effect of temperature on sheet formation, it was of interest to investigate the effect of temperature on fiber dispersion as observed in the flocculation tester.

Two series of flocculation runs were made on the standard unbleached spruce sulphite stock suspended in tap water at 0.0095 per cent consistency. The first run (26-h) was made at a temperature of $55 \pm 0.5^{\circ} \text{C.}$, which was maintained in the fiber suspension throughout the run by "bleeding" the required amount of steam through the copper heating coil in the head-box. After flocculation values at fourteen different flow rates had been established, the fiber suspension was cooled down to $25 \pm 1^{\circ} \text{C.}$, and its flocculation tendencies re-determined (run 26-c).

The second run (27-c) was made at a temperature of $10.5 \pm 1.5^{\circ}$ C. In this case it was necessary to start the run at approximately 9° C. and then determine the flocculation end-points for only seven flow velocities through the observation tube. During this period the temperature of the stock suspension rose to 12° C. At the time the run was made the room temperature could not be lowered much below 20° C., with the result that it was difficult to maintain a constant low temperature in the stock in the flocculation tester. Cooling water at 8° C. was passed through the copper coil in the head-box, but this cooling capacity was inadequate. The actual temperature variations from the mean, however, were not much greater than those tolerated for flocculation runs at room temperature, and the one variation from the standard procedure which occurred was the fact that only seven flocculation values were determined. During the run some difficulty was encountered with moisture condensation on the observation tube, but this was finally overcome by keeping the air around the tube well stirred, using four electric fans.

The results of these high and low temperature runs are shown graphically in Figure 22 and are compared with the average flocculation tendencies of the standard runs made at 25° C. The $\log \bar{Y} - \log Y$ relation for this latter condition is given by the dotted line on the graph. The dispersion index for run 26-h made at 55° C. was calculated to be 0.90, while the value for the run made at 10.5° C. (27-c) was 1.40. Comparing these values with the average dispersion index of 1.24 obtained for six standard runs made at 25° C., it is

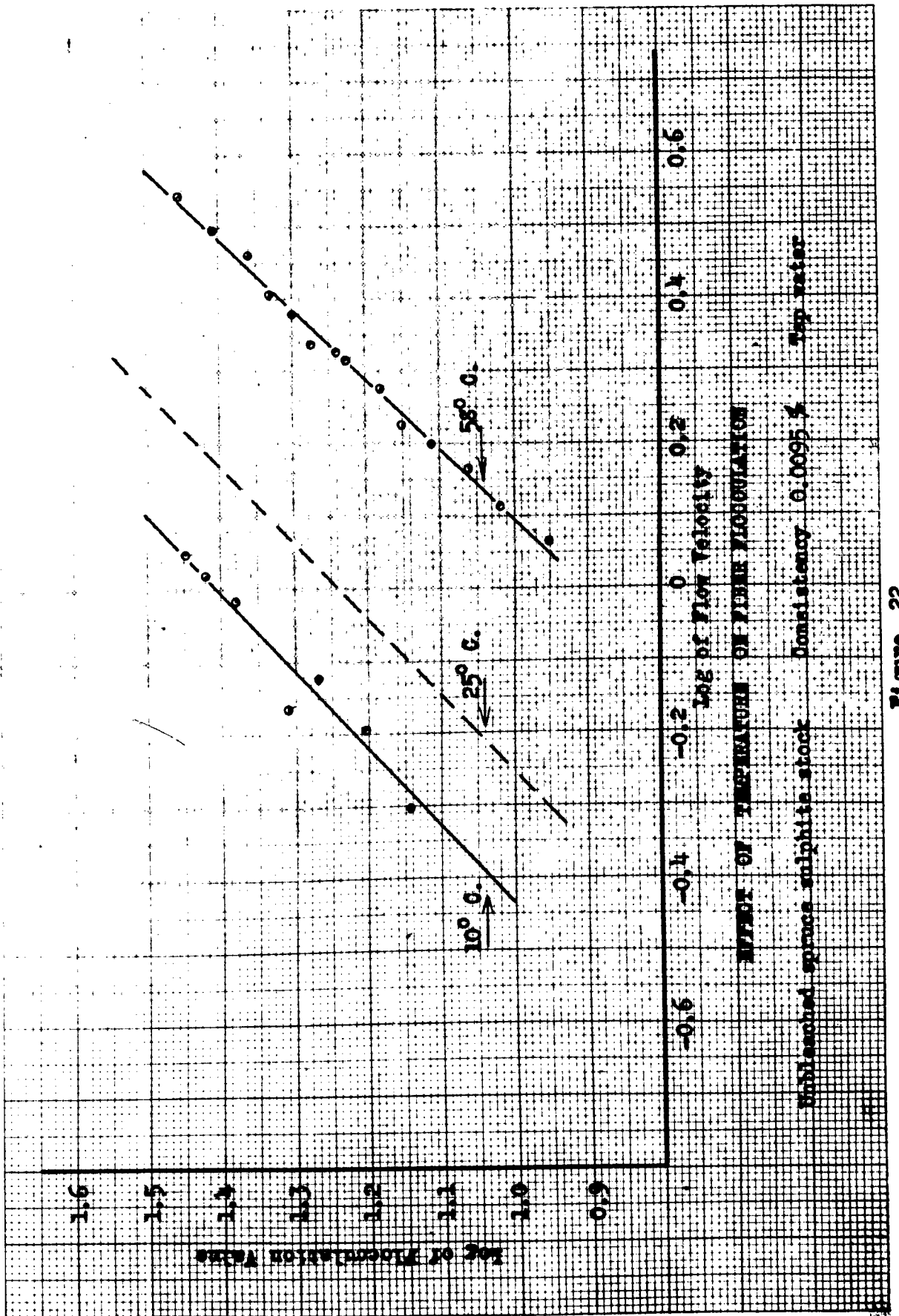


Figure 22

evident that temperature has a marked effect on the fiber dispersion, higher temperatures effecting flocculation.

This effect can be visually evaluated from the photographs shown in Figure 23. The three pictures are directly comparable, having been taken at essentially the same flow velocities through the observation tube. The actual flocculation values observed at the given flow rates for each condition are listed below the photographs. For the 58° C. run, the 26° C. run, and the 10.5° C. run these values are 5.5, 18, and 27, respectively. Precisely, it is not correct to make a direct numerical comparison of the degree of dispersion as expressed by these data, since I is not a linear function of Y , but actually a power function which becomes linear only when written in the logarithmic form:

$$\log I = K_1 + K_2 \cdot \log Y \quad .$$

Further, the values of the dispersion indices (K_2) for the various conditions do not give a directly proportional numerical evaluation of the degree of dispersion. To obtain the latter it is necessary to compare the parameter constants (K_1) of the power equations of the form:

$$I = K_1 \cdot Y^{K_2} \quad ,$$

where $K_1 = 10^{K_3}$. From the dispersion indices of the three runs,

$$(58^\circ \text{ C.}), \quad K_3 = 0.90 \quad ,$$

$$(26^\circ \text{ C.}), \quad K_3 = 1.24 \quad ,$$

Run # 26h Temperature 58° C. Water viscosity - 4.8 millipoise pH 7.8 - 8.4
Floculation - 8.5

Run # 22 Temperature 27° C. Water viscosity - 8.7 millipoise pH 7.2 - 8.0
Floculation - 12

Run # 27c Temperature 11° C. Water viscosity - 12.8 millipoise pH 7.2 - 7.5
Floculation - 27

TEMPERATURE EFFECTS - 1

Unbleached spruce sulphite stock Consistency 0.0095 %
Flow velocity 1.07 cm./sec. Tap water

Figure 23

$$(10.5^{\circ} \text{ C.}), K_3 = 1.40 ,$$

the corresponding K_1 values are:

$$(58^{\circ} \text{ C.}), K_1 = 8.0 ,$$

$$(26^{\circ} \text{ C.}), K_1 = 17.0 ,$$

$$(10.5^{\circ} \text{ C.}), K_1 = 25.5 .$$

These numerical values of K_1 , for each of the three temperatures, may be considered to directly evaluate the degree of fiber dispersion provided the power constant, K_2 , or (as it has previously been designated) the slope constant of the logarithmic relation between \bar{Y} and \bar{X} , is the same for all three conditions. This is essentially the case, since these slope constants were found to be 1.04, 0.96, and 0.93, respectively, for the high, medium, and low temperature runs. It will be noted that the K_1 values are practically equivalent to the actual flocculation values originally given, which is due to the fact that the power constant is essentially equal to one, and the flow rates were essentially the same.

Comparing the K_1 values for each of the three temperatures, it is evident that an increase in temperature of 32° (from 26° to 58° C.) produced the same change in degree of flocculation as was obtained by increasing the temperature by approximately 16° (from 10.5° to 26° C.). The viscosity of water at 58° C. is 4.6 millipoise, at 26° C. , 8.7 millipoise, and at 10.5° C. , 12.8 millipoise. Therefore, the increments in temperature of 16° and 32° have produced equal decrements in the viscosity of the white water, and it would

appear that the decrease in fiber dispersion with an increase in temperature is directly proportional to the viscosity change in the suspending fluid produced by the temperature variation.

In laminar flow through the observation tube, as the viscosity of the white water is decreased with an increase in temperature, the viscous fluid forces, due to relative motion of the fluid particles, are decreased in direct proportion. Hence, at elevated temperatures, there would be less shearing apart of the fibers (which had collided randomly), which would account for the proportional increase in flocculation. There is also the vague possibility that temperature changes may alter adhesion forces between individual fibers, but a discussion of this point will be left until the measurement of such forces is described.

When the fiber suspension at 58° C. was cooled to approximately 25° C., the dispersion index was increased from 0.90 to 1.09. Similarly, when the 10.5° C. run was warmed to 25° C., the dispersion index decreased from 1.40 to 1.21. Again comparing these values with the average value of 1.24 for the dispersion indices of six standard fiber-tap water runs, it would appear that, at least in the case of the low temperature run, the fiber dispersion was decreased to its normal value when the temperature was raised to duplicate standard conditions. In the former case, where the high temperature run was cooled to the standard temperature of 25° C., the fiber dispersion was increased, but did not reach its normal value, as indicated by the dispersion index of 1.09. This run, however, behaved anomalously, exhibiting a reversion in fiber

dispersion, which occurred when the stock was allowed to settle for several hours with no agitation. After the 58° C. temperature run was made, the fiber suspension was immediately cooled to 25° C. while circulating in the flocculation tester. Following the cooling operation, six flocculation values were determined for different flow velocities; the equipment was then shut down for several hours and the fibers allowed to settle. The dispersion index calculated from these first six flocculation points on the $\log \bar{Y} - \log \bar{Y}$ relation was 1.19, which checks the standard value of 1.24 within the limits of experimental error. After the 2-hour period of standing, however, ten flocculation values, determined at various flow rates, gave a dispersion index of 1.09, showing a slight reversion in the degree of fiber dispersion analogous to effects observed when alumina flock-fiber suspensions were allowed to settle. Why such reversion occurs is not at once evident, although several possibilities have been suggested earlier in this discussion. Figure 24 shows the photographs taken of runs 26-c and 27-h, and allows a direct comparison to be made with the degree of flocculation of a fiber suspension which was not subjected to preheating or precooling (run 22).

The Use of a Deflocculating Gun to Aid Fiber Dispersion

Deacetylated karaya gum is a patented gum preparation (34, 35) which has been developed to increase fiber dispersion in a stock suspension and thus improve sheet formation. It has been used with success in the manufacture of light weight tissue sheets where good formation can be obtained only with difficulty. The product, as

Run # 26c Stock from 58° cooled to 25.5° C. pH - 8.4 Flocculation - 13

Run # 22 Temperature 27° C. pH 7.2 - 8.0 Flocculation - 18

Run # 27a Stock from 11° warmed to 25.2° C. pH - 8.2 Flocculation - 17

TEMPERATURE EFFECTS - 2

Unbleached spruce sulphite stock Consistency 0.0095 %
Flow velocity 1.07 cm./sec. Tap water

Figure 24

marketed by the John A. Manning Paper Co., is a 50 per cent alcoholic dispersion of the deacetylated gum. When added to water, the material, being extremely hydrophilic, swells enormously and becomes colloiddally dispersed in the aqueous solution. As little as one part in 10000 parts of water, or 0.02 per cent of gum, is said to produce a marked fiber dispersion.

The addition of as little as 0.02 per cent of the gum to water also produces an increase in the viscosity of the latter. Further, it is known that the fiber-dispersing action of the gum is appreciably decreased if the aqueous gum dispersion is subjected to mechanical agitation. Combining these facts, it seemed logical to assume that the initial fiber-dispersing action of the gum is due to an increase in the viscosity of the fiber-suspending medium, while the subsequent decrease in fiber dispersion, resulting from agitation, is due to a decrease in viscosity. This latter effect could be the result of breaking down a gel structure in the gum dispersion, originally responsible for the viscosity increase. An investigation of the fiber dispersing action of the gum was thus of interest in relation to the temperature-viscosity-flocculation effects previously observed.

Flocculation run 25 was made using the standard unbleached soruce sulphite pulp suspended in tap water at 25° C., and at a fiber consistency of 0.0097 per cent. Eighty-four grams of the 50 per cent alcoholic dispersion of the gum were dissolved in 8.5 liters of tap water by slowly adding the gum to water with vigorous stirring. This viscous one per cent gum solution was screened through a 70-mesh wire

to eliminate any lumps and was then added to the head-box of the flocculation tester. After addition of the gum solution, the flocculation tester contained 464 ± 1 pounds of water and the standard weight of fiber, so that the fiber consistency was 0.0097 per cent and the gum consistency was 0.02 per cent. After the gum was added the white water had a pH value of 7.4, which was increased to 7.9 during the course of the run.

Since the agitation due to circulation through the centrifugal pump and to the stirrers in the head-box of the flocculation tester was expected to decrease the fiber-dispersing effect of the gum, run 25 was divided into three sections. Within 1 1/2 hours after the gum had been added to the head-box, six flocculation values were determined for different flow rates through the observation tube. These were used to determine a dispersion index defining the initial degree of fiber dispersion. The equipment was then shut down for several hours, after which the stock was recirculated for 1 hour, and a second series of seven flocculation values determined, which permitted the calculation of a second dispersion index. Finally, the flocculation tester was shut down for 20 hours, the fiber suspension then recirculated for an additional hour, and a third series of ten flocculation values determined, so that a final dispersion index could be calculated.

The results of these three fiber dispersion evaluations are shown graphically in Figure 25. The dispersion indices obtained for the three successive sections of the run were 1.43, 1.36, and 1.34.

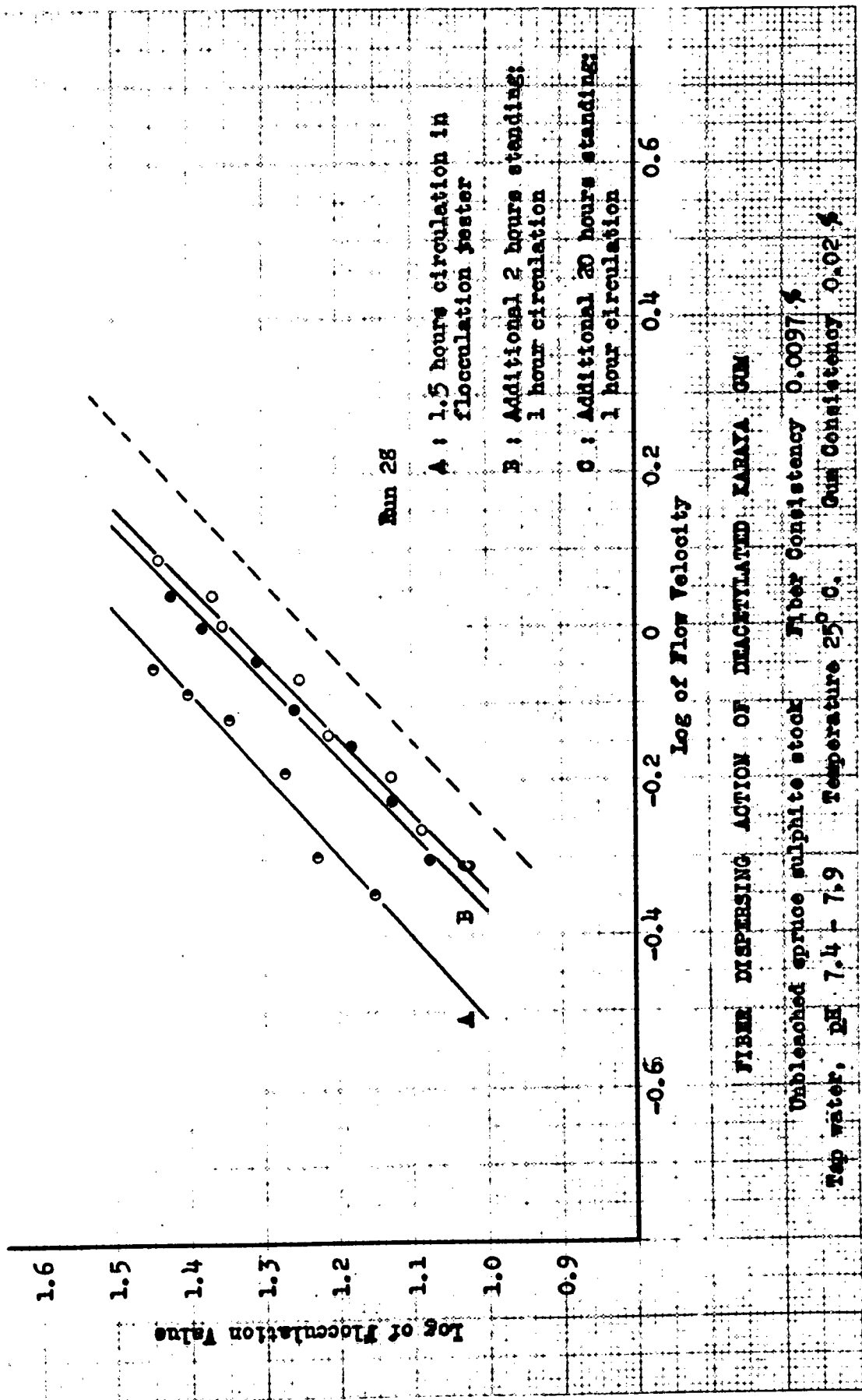


Figure 25

respectively, with the corresponding slope constants, 0.93, 1.04, and 1.00, agreeing within the accepted limits of error. Comparing the dispersion index values with 1.24, the average constant expressing the degree of dispersion for fibers suspended alone in tap water, it is apparent that 0.02 per cent of the deacetylated karaya gum initially produced an appreciable increase in fiber dispersion, approximately comparable to that obtained by merely lowering the temperature of the stock suspension from 25° to 10.5° C. (dispersion index in this latter case was 1.40). Further, the efficiency of the dispersing action of the gum was decreased as the suspension was allowed to circulate in the flocculation tester.

To determine whether this decrease in dispersion was due to a viscosity change of the dilute aqueous gum dispersion, a second flocculation run, 30, was made with all conditions the same as those described for run 28. However, instead of determining flocculation values at different flow rates during several intervals of the test, a photographic record of the degree of dispersion was made at various times throughout the run, simultaneously with viscosity measurements on samples of the white water.

The fiber consistency for this run was 0.0098 per cent, and the white water contained 0.02 per cent of the deacetylated karaya gum. The pH of the white water at the start of the run was 7.6 and was increased to 8.2 at the end of the run. Viscosity determinations on the white water and photographs showing the degree of dispersion in the observation tube at a given flow rate were made at intervals of 15, 90,

190, 325, and 505 minutes of circulation in the flocculation tester. The photographs were taken at a flow rate of 0.80 ± 0.015 centimeters per second.

The white water samples for viscosity determinations were removed at the specified intervals, filtered through a Jena 1-G-1 fritted glass crucible to remove the fibrous material and the viscosity then measured with an Ostwald viscosity tube. During most of the run the flow rate through the observation tube was about 2 centimeters per second, but at the time each white water sample was removed for a viscosity determination, this velocity was slowed down to 0.80 centimeters per second, at which the photographs were taken.

All viscosity determinations were made at 25° C. with a 5 milliliter sample of white water in an Ostwald viscosity tube which had been calibrated with distilled water at the same temperature. The specific gravity of the white water samples was determined with a Westphal balance, calibrated to give a value of 1.000 for distilled water. Absolute viscosities for the white water samples were calculated, using the equation:

$$\eta_{\text{abs.}} = \frac{8.94 \cdot d_2 \cdot t_2}{77.5} .$$

where, $\eta_{\text{abs.}}$ is the absolute viscosity in millipoises, 8.94, the absolute viscosity of distilled water at 25° C. (International Critical Tables), d_2 , the specific gravity of the white water relative to the value 1.000 for distilled water, t_2 , the flow time in seconds of the white water sample through the capillary of the Ostwald tube, and 77.5,

the flow time in seconds for distilled water through the same tube. Table VI shows the variation of the white water viscosity with time of circulation in the flocculation tester, as well as the flow rates through the observation tube at which each of the photographs were taken. The viscosity of the white water before the deflocculating gum was added was 9.07 millipoise.

Table VI

EFFECT OF CIRCULATION IN FLOCCULATION TESTER ON THE VISCOSITY
OF WHITE WATER CONTAINING 0.02% OF KARAYA GUM DEFLOCCULANT

Unbleached Spruce Sulphite Stock
Gum Consistency 0.02%

Fiber Consistency 0.0096%
Temperature 26° C.

Time of Circulation in Flocculation Tester (min.)	Absolute Viscosity of White Water (millipoise)	Flow Rate Through Observation Tube for Photographs (cm./sec.)
15	10.9	0.797
90	10.8	0.818
195	10.6	0.812
325	10.6	0.801
505	10.6	0.795

Photographs of the degree of dispersion existing after 15 minutes of circulation and then after 8.5 hours are shown in Figure 26. The top photograph gives the condition which existed when the fiber was suspended in tap water alone and flowed through the observation tube at a velocity of 0.80 centimeters per second. It allows a direct visual comparison to be made with the other two photographs showing the initial dispersing action of the deacetylated karaya gum, as well as the increase in flocculation of the fiber-gum-tap water dispersion

Runs # 38x and 22 Tap water White water viscosity - 9.1 millipoise pH 7.2 - 8.0

Run # 30(a) Tap water plus 200 % Deacetylated Karaya gum White water
viscosity - 10.9 millipoise pH 7.6 - 8.2 0.25 hour circulation

Run # 30(f) Tap water plus 200 % Deacetylated Karaya gum White water
viscosity - 10.6 millipoise pH 7.6 - 8.2 8.5 hours circulation

VISCOSITY EFFECT OF KARAYA GUM DEFLOCCULANT

Unbleached spruce sulphite stock Consistency 0.0096 %
Flow velocity 0.80 cm./sec. Temperature 26° C.

Figure 26

with continued circulation and agitation in the flocculation tester.

It is evident from Figure 26 that 8.5 hours of circulation have decreased the dispersing action of the gum to such an extent that the fibers have flocculated to practically the same degree as existed with no gum present in the aqueous suspension medium. From Table VI it will be seen that these effects do not correlate very well with the viscosity changes observed to occur in the white water. With no gum present the viscosity of the white water was 9.07 millipoise. Two hundredths of one per cent of the gum dispersed in the water increased this viscosity to 10.9 millipoise, and then 8.5 hours' circulation in the flocculation tester only lowered this viscosity value to 10.6 millipoise as measured by the Ostwald viscosimeter.

As previously mentioned, the initial dispersion produced by the deacetylated karaya gum was practically equivalent to the fiber dispersion obtained by merely decreasing the temperature of a fiber-tap water suspension from 26° to 10.5° C. In this latter case there was also an attendant viscosity increase in the white water from 8.7 to 12.8 millipoise. If the dispersing effect of the karaya gum was simply due to a white water viscosity increase, then such an increase would be expected to be comparable to the viscosity figures cited above for the dispersion effect observed with the temperature decrease. With the addition of the deacetylated karaya gum, however, the observed viscosity increase was only half that produced by the change in temperature from 26° to 10.5° C. Further, since the viscosity was only lowered to 10.6 millipoise when the fiber-gum dispersion was

agitated for 8.5 hours, causing the fibers to reflocculate. It is tentatively concluded that the dispersing action of the deacetylated karaya gum was due to factors other than its effect of slightly increasing the viscosity of the white water to which it was added. Such factors possibly may involve changes in fiber to fiber adhesion forces.

This conclusion is tentative, however, since some question might be raised concerning the procedure of filtering the white water samples before making the viscosity measurements. It was necessary to remove the suspended fibers, however, if measurements were to be made with the Ostwald capillary tube. In addition, it did not seem likely that very precise measurements could be made with a torsional type viscosimeter, since the viscosities involved were so very small. If an instrument of this type, more sensitive than the usually used MacMichael viscosimeter could be obtained, it would be of interest to check the viscosity data obtained with the use of the Ostwald capillary tube. Ordinarily, it would have been possible to check the effect of the filtering action on a gum suspension having no fibers present. However, the gum dispersion itself contained a small percentage of solids which may have interfered with viscosity measurements. Incidentally, the presence of these "impurities" in the gum would definitely limit its use.

The Effect of a Wetting Agent on Fiber Flocculation

It is conceivable that the addition of a surface active material to a fiber suspension could have some effect on the fiber flocculation characteristics because of possible changes in surface

tension forces at the fiber-fluid interfaces. Since no observation of any such effects has been reported in the literature, it was of interest to make at least a few exploratory experiments.

Flocculation run 22 was carried out by using the standard unbleached spruce sulphite stock suspended in tap water at 0.0093 per cent consistency and at a temperature of 27° C. The flocculation characteristics of the stock suspended in tap water alone were first obtained, determining ten flocculation end-points at various flow rates. During this part of the run the white water pH increased from 7.2 to 8.0. After the flocculation characteristics of the stock alone were determined, 15 per cent of a wetting agent, sold under the trade name of "DuPontol," was added to the fiber suspension in the head-box. This percentage of the wetting agent, based on the dry weight of the fiber, decreased the surface tension of the white water from 72 to 51 dynes per centimeter as measured on a DuPont tensometer. After sufficient time had been allowed for dispersion of the chemical, the flocculation tendencies of the stock were redetermined at ten different flow rates through the observation tube.

The results of these tests are shown graphically in Figure 27. For the blank run giving the flocculation characteristics of the fiber suspended in tap water alone, a dispersion index of 1.23 was obtained. The addition of 15 per cent of the wetting agent to the fiber dispersion decreased this index to 1.13, indicating a small but significant decrease in fiber dispersion. For the two runs the calculated slope constants of the $\log I - \log \bar{I}$ relations were 0.95 and 1.02, respectively.

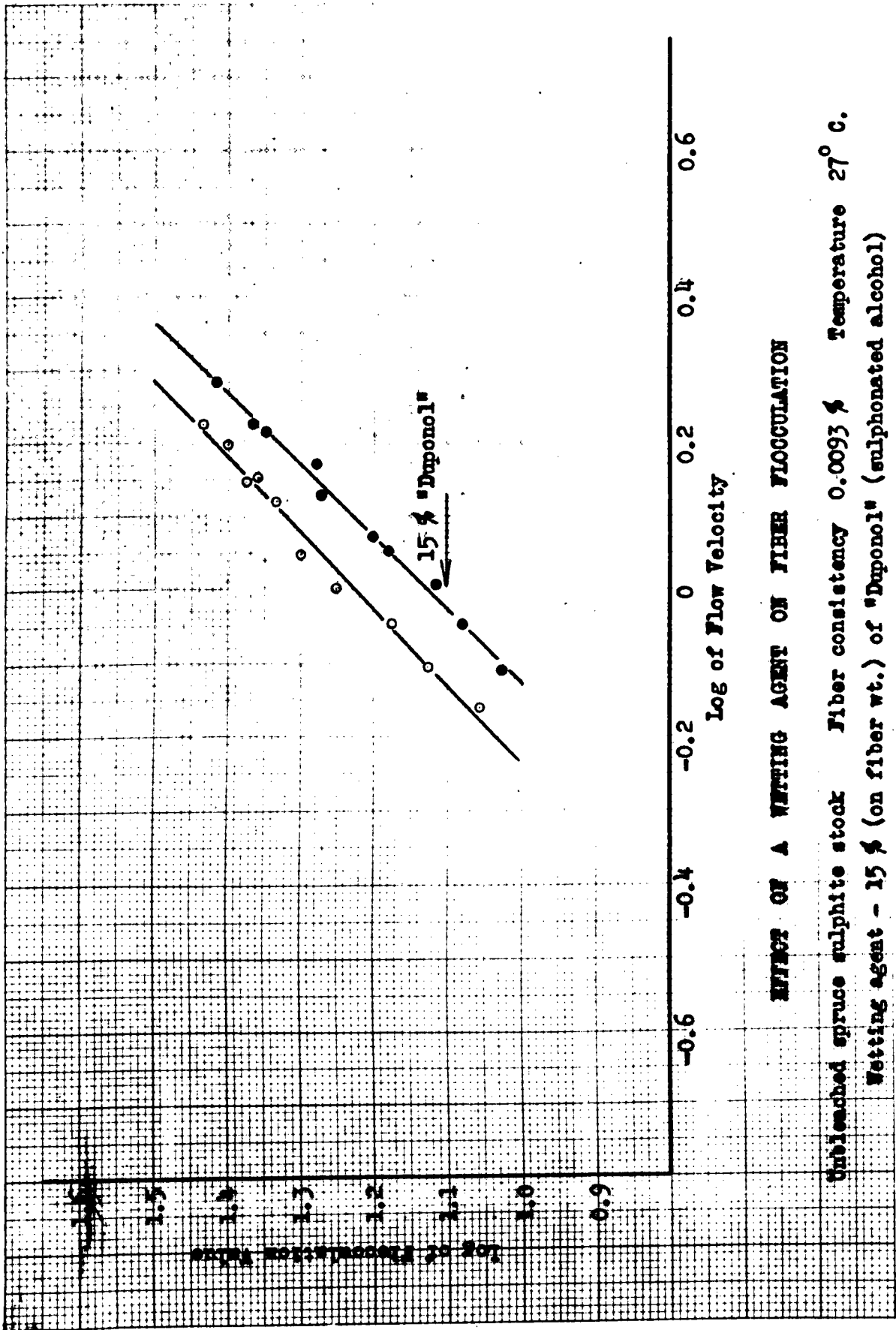


Figure 27

in agreement within the limits of experimental error.

The small increase in fiber flocculation due to the addition of 15 per cent of the wetting agent is substantiated photographically in Figure 25. The top photograph shows the dispersion obtained in tap water alone (surface tension 72 dynes per centimeter) and is directly comparable with the lower photograph showing the effect of 15 per cent "Duponol" on the fiber dispersion.

Because of the minor effect observed in this flocculation run, no further work was done on determining the effect of other surface active materials on fiber flocculation. From this single experiment it is indicated that an active wetting agent only slightly increases the flocculation in a fiber suspension. Additional investigations, using various other surface active materials, and at higher concentrations, might well be made before further definite conclusions are drawn.

The Effect of Beating on Fiber Flocculation

Most of the postulations, which have been made in the literature concerning the effects of beating on fiber flocculation, have been arrived at indirectly by considering the effects of beating on sheet formation. There are obvious objections to such inductions since other factors, such as drainage characteristics of the stock, must enter the picture. From purely hypothetical reasoning, it may be presumed that beating, if it is essentially a reduction in fiber length obtained with sharp tackle, will decrease the flocculation tendencies

Run # 22a Tap water pH 7.2 - 8.0 Surface tension of white
water - 72 dynes/cm. Flocculation - 18

Run # 22b Tap water plus 15 % "Dapenol" pH 8.2 Surface
tension of white water - 51 dynes/cm. Flocculation - 14

EFFECT OF A WETTING AGENT ON FIBER FLOCCULATION

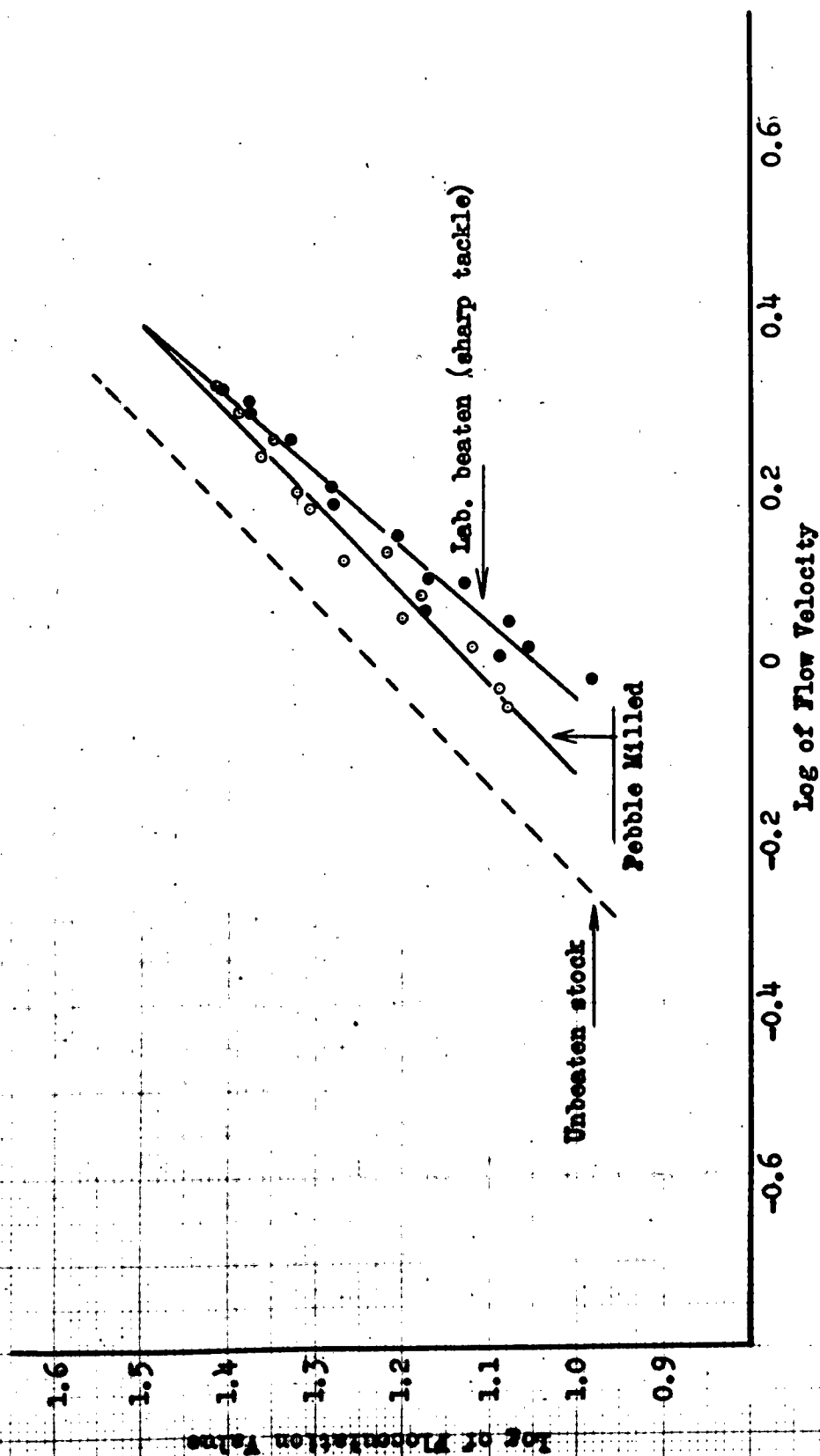
Unbleached spruce sulphite stock Consistency 0.0093 % Temperature 27° C.
Flow velocity 1.07 cm./sec. "Dapenol" Wetting agent - Sulphonated Alcohol

Figure 25

of a given type fiber. This would be a simple mechanical effect, assuming that the shorter the fiber, the less likely would be the possibility of fiber to fiber entanglement. On the other hand, if the beating action is less drastic and is continued over a longer period of time, so that hydration and fibrillation of the cellulosic fiber occurs with only a reasonably small reduction in fiber length, it is conceivable that the flocculation characteristics of the stock would be enhanced.

To investigate these possibilities two flocculation runs, 19 and 20, were made. Run 19 was made with the standard unbleached spruce sulphite stock which had been beaten in an Abbe pebble mill to a freeness of 578 cc. S.R. The milling was done with 90 grams of oven-dry pulp, a total of 3 liters of water and with 77 pebbles weighing 5,000 grams in the mill. Before milling, the stock was disintegrated in the standard British disintegrator for 75,000 revolutions. Actual milling time of the pulp was 75 minutes, equivalent to a total of 4,500 revolutions of the pebble mill.

For the flocculation test the proper amount of milled pulp (578 cc. S.R. freeness) was added to 464 pounds of tap water in the flocculation tester to give a fiber consistency of 0.0094 per cent. The run was made at a temperature of 24° C., and the pH of the white water before and after the run was 7.2 and 5.0, respectively. Flocculation end-points were determined for thirteen different flow rates through the observation tube, these data being presented graphically in Figure 29. The calculated dispersion index for this pebble-milled stock was



EFFECT OF HEATING ON FIBER FLOCCULATION

Unbleached spruce sulphite stock Consistency 0.0092 % Temperature 25° C.
 Freshness : Unbeaten stock - 850 cc. S. R. ; Pebble milled - 578 cc. S. R. ;
 Lab. beaten - 540 cc. S. R.

Figure 29

1.13 and the slope constant of the $\log \bar{Y} - \log Y$ relation was 0.96.

The second flocculation run of this series was made with the standard unbleached spruce sulphite stock which had been beaten in a small 1 pound Valley laboratory beater of the Niagara type. The roll and bed plate of this equipment were in excellent condition and reasonably sharp. The stock was processed according to the Standard TAPPI Method, T 200 m-74, with the exception that, instead of using a 5,500 gram weight on the bed plate, 6,500 grams were used to increase the cutting action on the fibers. The total beating time was 25 minutes and the stock freeness was reduced from 850 cc. S.R. to 540 cc. S.R. The beaten stock (1467 grams of 1.15 per cent consistency) was dispersed in the flocculation tester with 484 pounds of water, giving an actual fiber consistency of 0.0089 per cent. The temperature was 26° C. and the pH of the white water increased from 7.6 to 8.1 during the course of the run. Fourteen flocculation values for various flow rates through the observation tube were obtained; these are also shown graphically in Figure 29. The dispersion index for this beaten stock was calculated to be 1.05, and the slope constant for the $\log \bar{Y} - \log Y$ relation was 1.14.

From the dispersion indices, 1.13 and 1.05, for the milled and beaten stock, respectively, and from Figure 29, it is apparent that both milling and beating of the fibers tended to increase their flocculation characteristics. Further, a comparison of these dispersion indices with the average value of 1.24 for the dispersion index of the unbeaten stock shows that the effect of beating is not an extreme one,

although there is a definite decrease in the degree of fiber dispersion. These results are substantiated photographically in Figure 30. In this figure the top photograph shows the degree of dispersion obtained with unbeaten fiber, while the second and third photographs show the slight decrease in dispersion, resulting from pebble milling and laboratory beating, respectively.

A further comparison of the dispersion indices for these beaten pulps shows that a small difference existed between the pebble-milled and laboratory-beaten stock, although this variation is just beyond the possible limits of experimental error. Accordingly, it is not desirable to base any conclusions on these data alone. However, a somewhat unusual observation was made in the case of the stock processed in the Valley beater, which may indicate that this difference may be significant. In this case, (run 20), it was observed during the course of the flocculation run that the fibers bunched themselves into stringy masses around the high speed stirrer blades in the head-box. This same phenomenon had never been observed before with this beaten stock, however, it occurred to such an extent that the stirrers were actually slowed down by the agglomerating fibers, and it was necessary to remove these bunches from the stirrer blades at various times throughout the course of the run. Incidentally, it is probable that this accounts for the low fiber consistency value obtained at the end of the run.

This "balling up" of the pulp beaten in the sharp tackle was not observed in the case of the pebble-milled stock, although both types

Run # 22 Undeaten stock Freshness - 850 cc. S. R. pH 7.2 - 8.0 Flocculation - 18

Run # 19 Pebble Milled stock Freshness - 578 cc. S. R. pH 7.2 - 8.0 Flocculation - 14

Run # 20 Laboratory beaten stock Freshness - 540 cc. S. R. pH 7.6 - 8.1 Flocculation - 12

Run # 1981A Pebble Milled stock (from run 19) plus 100 % alum pH 6.8

EFFECTS OF BEATING

Unbleached spruce sulphite stock Consistency 0.0092 %
Flow velocity 1.06 cm./sec. Temperature 26° C.

Figure 30

of beating seemed to increase slightly the flocculation characteristic of the fiber. It is possible that the sharp tackle of the Valley laboratory beater not only cut the stock, but also bruised the fiber to such a degree that a kind of "macro-fibrillation" occurred, which enhanced its flocculation characteristics because of increased mechanical entanglement. Unfortunately, no microscopic examination of the milled and beaten fibers was made.

An additional difference between the pebble-milled and the beaten stock is that between the slope constants of the $\log \eta - \log \eta$ relations obtained for the two runs. It has been previously suggested that an increase in the slope constant may indicate a decrease in fiber to fiber adhesion forces. Since the slope constant of the beaten stock was 1.14 as compared to 0.96 for the pebble-milled fibers, this line of reasoning would indicate that the adhesion forces between the fibers of the beaten stock were smaller than those existing between the fibers of the milled pulp. These adhesion forces may be the resultant of several components, including surface energy forces at the fiber-fluid interfaces and simple mechanical entanglement, due possibly to fibrillation, or perhaps even to a sharp fracture of the fibers. The slope constants given above for the beaten and milled stocks would indicate that hydration and fibrillation increased the adhesion forces as compared to a fiber cutting action presumably obtained with the laboratory beater. Too extensive interpretation of the slope constants and their relation to fiber adhesion forces, however, may not be justified at the present. It is conceivable that other factors, such as fiber

density and settling characteristics, may also be concerned with a change in the slope constants of the $\log \bar{I} - \log \bar{V}$ relations obtained for the various conditions. Settling rates of fibers would have more significance at the lower flow rates through the observation tube than in the case of higher velocities; this could account for appreciable differences in flocculation values at low flow rates for pulps which had practically the same flocculation characteristics at higher velocities of flow.

It is thus obvious that, with the limited amount of data on the effects of beating, only one definite conclusion can be drawn, namely: beating, including hydration, fibrillation, and a sharp cutting action of the fibers, tends to increase the flocculation characteristics of the latter. As measured by the flocculation tester the effect is not marked, but it is still large enough to be significant. Further experimentation designed to isolate the effect of factors such as fiber length, width, and specific surface on fiber flocculation would aid materially in the interpretation of the data now available.

In Figure 30 there is also included a photograph at the bottom of the figure showing the dispersing effect of 100 per cent alum on the pebbled mill stock.

In connection with the effects of beating on fiber flocculation characteristics, it may be of interest to mention again the results obtained in the case of run series 18, which has been previously discussed on page 110 with reference to reversion of fiber dispersion which occurred when the fiber suspension was allowed to settle

under quiescent conditions in the flocculation tester. This run was made using the standard unbenton, unbleached spruce sulphite pulp suspended in tap water at 0.0097 per cent consistency and a temperature of 24° C. The initial flocculation characteristics of the fibers were obtained by determining ten flocculation end-points at different flow rates and calculating the $\log X - \log Y$ relation. Following this, the stock was allowed to stand 24 hours in the flocculation tester and its flocculation characteristics redetermined. This procedure was repeated a second time after another standing period of 24 hours. The $\log X - \log Y$ equations obtained were, respectively:

$$\log X = 1.23 + 0.93 \log Y \quad (\text{Initial})$$

$$\log X = 1.19 + 0.92 \log Y \quad (24 \text{ hours})$$

$$\log X = 1.12 + 0.99 \log Y \quad (48 \text{ hours})$$

As previously discussed, a slight decrease in fiber dispersion due to recirculation in the flocculation tester is shown by the change in dispersion indices from 1.23 to 1.12. Since beating has been shown to effect a similar small decrease in the dispersion index, it was thought that the fiber was possibly hydrated, to some extent, by circulation through the small centrifugal pump in the flocculation tester. To check this possibility, the stock from run 15, which had been in the tester 48 hours, was allowed to settle and sufficient of it removed to make a freeness test. The results of the latter gave a freeness value of 350 cc. S.R., which checked exactly the freeness of the original pulp, indicating that no significant hydration of the fibers was incurred by circulation during the course of three flocculation runs

over a period of 48 hours. This result seems quite probable because of the very dilute fiber consistency at which the flocculation runs were made.

The Effect of Consistency on Fiber Flocculation

Four flocculation runs (31, 32, 33, and 34) were made to determine the variation of fiber dispersion with consistency. The standard unbleached worme sulphite pulp, suspended in tap water at 25° C., was used. The consistency range investigated was 0.0047 to 0.0195 per cent dry fiber. It was not feasible to attempt an investigation of flocculation effects at consistencies above or below this range because of the difficulty of making visual observations. At the high stock densities it became very difficult to differentiate between flocculated fiber bunches and the more or less solid background of fibers in the observation tube which were not agglomerated. Likewise at the low consistencies, the fiber flocks did not stand out very markedly against the black background behind the observation tube, since almost as much of this background could be seen through the section of the tube where fiber dispersion was complete. The value of 0.01 per cent consistency gave the optimum contrast between fiber flocks and dispersed fibers and was originally selected as the standard consistency for this reason.

The results of the four flocculation runs made at 0.0047, 0.0116, 0.0133, and 0.0195 per cent fiber consistency are given in Table VII and also graphically in Figure 31.

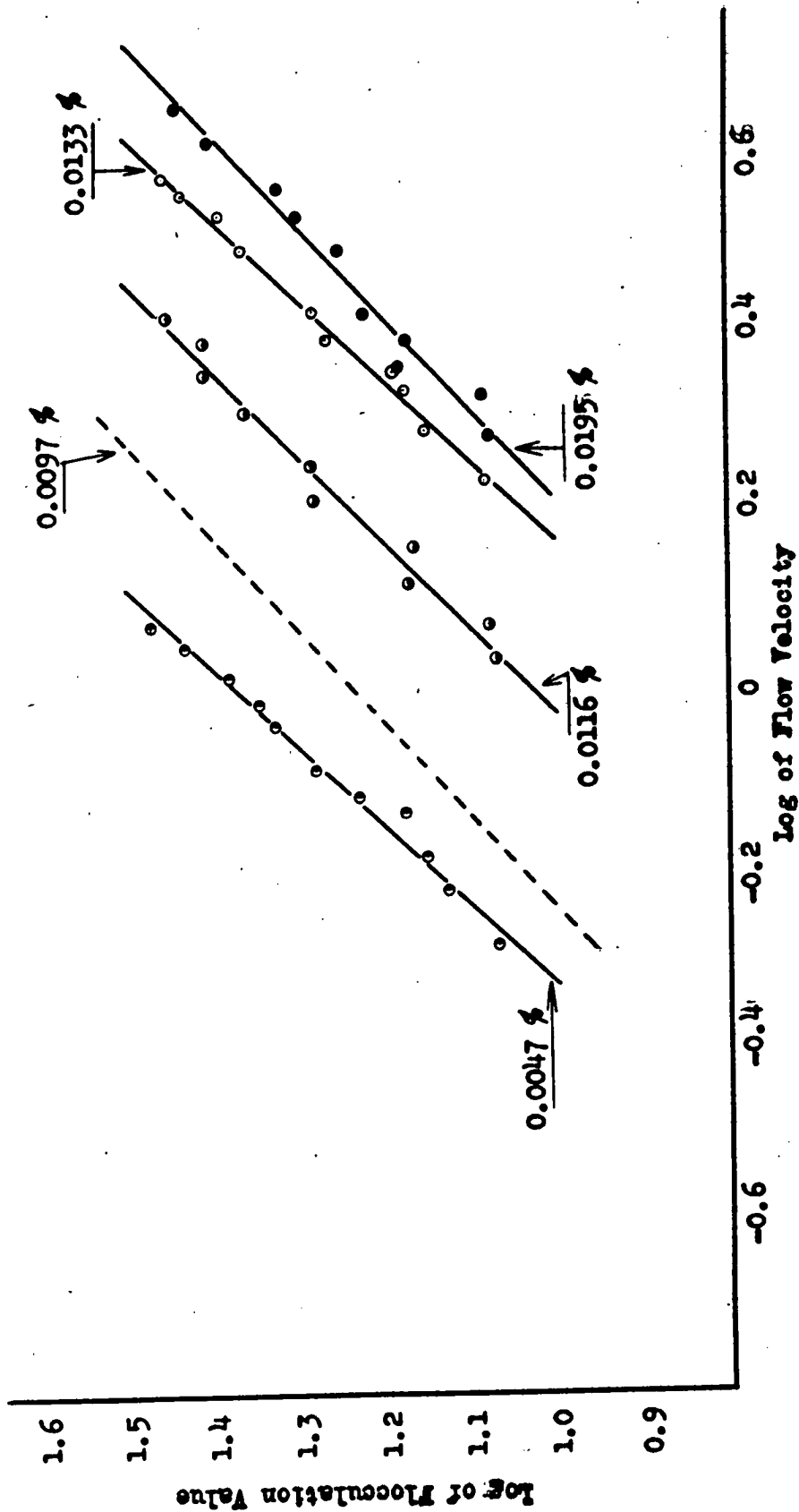
Table VII

EFFECT OF CONSISTENCY ON FIBER FLOCCULATION

Unbleached Spruce Sulphite Stock Tap Water					Temperature 25° C.	
Run No.	Average Consist- ency (%)	Temperature Limits °C.	White Water pH Start Finish		Dispersion Index (\bar{K}_1)	Slope Constant (\bar{K}_2)
31	0.0047	24.0-27.2	7.7	8.1	1.38	1.12
34	0.0116	23.8-24.8	7.5	8.2	1.04	1.02
33	0.0133	25.0-26.5	7.7	8.1	0.827	1.10
32	0.0195	24.6-26.5	7.6	8.1	0.807	0.96

From the dispersion indices given in the above table, it is evident that at the higher consistencies fiber flocculation was appreciably increased. This is also evident from Figure 31, which allows a comparison to be made of the results obtained at these four consistencies with the average $\log \bar{X} - \log \bar{Y}$ curve for 0.0097 per cent fiber consistency (dotted line on Figure 31). Figure 32 allows a visual evaluation to be made of the effect of consistency on fiber flocculation.

From theoretical considerations, increasing the fiber consistency up to a definite limit might well be expected to increase the degree of flocculation. This increase would be simply a statistical effect, since the greater the number of fibers in suspension, the greater the number of fiber-fiber collisions and, hence, the greater probability of increased flocculation. However, the motion of fibers moving past one another should tend to separate fiber bunches and,



EFFECT OF CONSISTENCY ON FINE FLOCCULATION

Unbleached spruce sulphite stock Temperature 25° C. Tap water, pH 7.5 - 8.1

Figure 31

Run # 31 0.0047 % Consistency pH 7.7 - 8.1 Flocculation - 26

Run # 22 0.0093 % Consistency pH 7.2 - 8.0 Flocculation - 18

Run # 33 0.0133 % Consistency pH 7.7 - 8.1 Flocculation - 7.3

Run # 32 0.0195 % Consistency pH 7.6 - 8.1 Flocculation - 6.8

EFFECT OF CONSISTENCY

Unbleached spruce sulphite stock Tap water Flow velocity 1.08 cm./sec. Temperature 26° C.

Figure 32

accordingly, when the fiber consistency exceeds some definite limit, the degree of flocculation might be expected to reach a constant maximum value.

From the results given in Table VII and Figures 31 and 32, it is indicated that such a constant maximum degree of flocculation was approached at approximately 0.02 per cent consistency, since the difference in the degree of flocculation occurring at 0.0133 and at 0.0195 per cent consistency was reasonably small. However, as has already been mentioned, at least a portion of this effect may be attributed to the anomalous flocculation values which may be obtained at the comparatively high consistencies because of lack of contrast between the fiber bunches and the dispersed fibers. Therefore, conclusions from the data must be limited, and it may be said that within the limits of 0.005 and 0.02 per cent fiber consistency, increments in the latter have been observed to appreciably increase the degree of flocculation. However, such increases in flocculation were not found to be proportional to the consistency changes, being noticeably smaller for equal consistency changes in either the high or low values of the range investigated.

The fact that changes in flocculation proportional to the consistency changes were not found in the lower consistency range (0.005 to 0.01 per cent) may be due to a subjective variation in the flocculation end-point. Analogous to the condition which exists when alum is present as a dispersing agent, the maximum size of the fiber flocks formed at 0.005 per cent density is quite small as compared

with that observed at the higher consistencies. This may have caused the flocculation end-points for the low consistency run to be judged too high in the flocculation tube, giving an abnormally low dispersion value.

In concluding the experimental work on the consistency runs, it was of interest to check the dispersing effects of alum both at the 0.0047 and 0.0195 per cent fiber consistencies. Photographs of the results observed are shown in Figure 33. The marked fiber dispersion resulting from the formation of alumina flock in the white water, analogous to the effects observed at 0.01 per cent consistency, is evident. The fact that this dispersing effect of alum has been observed for all consistencies in the range 0.005 to 0.02 per cent indicates that similar effects may be expected to occur at consistencies from 0.2 to 1.0 per cent used in paper machine operation.

The Flocculation Characteristics of Air-Dried Pulp

To determine whether air drying of the pulp fibers would alter their flocculation characteristics, a batch of the standard unbleached spruce sulphite pulp was air-dried over a period of several days to 92.9 per cent oven-dry pulp.

A quantity (22.82 grams) of this air-dried stock, sufficient to give a fiber consistency of 0.0096 per cent when dispersed in the flocculation tester, was soaked in water 4 hours and disintegrated in the British disintegrator according to the standard procedure. It was then dispersed in the head-box of the flocculation tester at 24.5° C.,

Run # 31 0.0047 % Fiber pH White water 7.7 - 8.1 Flow velocity 0.38 cm./sec.

Run # 31a 0.0047 % Fiber plus 200 % alum pH 6.9 Flow velocity 0.38 cm./sec.

Run # 32 0.0195 % Fiber pH White water 7.5 - 8.1 Flow velocity 1.06 cm./sec.

Run # 32a 0.0195 % Fiber plus 50 % alum pH 6.7 Flow velocity 1.05 cm./sec.

DISPERSING EFFECT OF ALUM AT 0.0047 % AND 0.0195 % FIBER CONSISTENCIES

Unbleached spruce sulphite stock Tap water Temperature 25° C.

Figure 33

and ten flocculation values were determined for different flow rates through the observation tube. From these values a dispersion index of 1.16 and a slope constant of 0.98 for the $\log \bar{X} - \log Y$ relation were calculated. Comparing these values with the average dispersion index of 1.24 and the average slope constant of 0.96 obtained for the $\log \bar{X} - \log Y$ relation expressing the degree of flocculation for the undried pulp, it is apparent that no significant change in the flocculation characteristics of the fibers occurred during air drying.

It is possible that this air drying of the fibers was not sufficient to produce appreciable change in the wettability of the fiber surfaces. If the latter did occur, it is possible that fiber flocculation characteristics would be altered due to changes in fiber to fiber adhesion forces. Further investigation along this line, using completely desiccated fibers, might be of interest.

The Flocculation of Douglas Fir and Birch Sulphite Fibers Relative to that of Spruce Sulphite Fibers

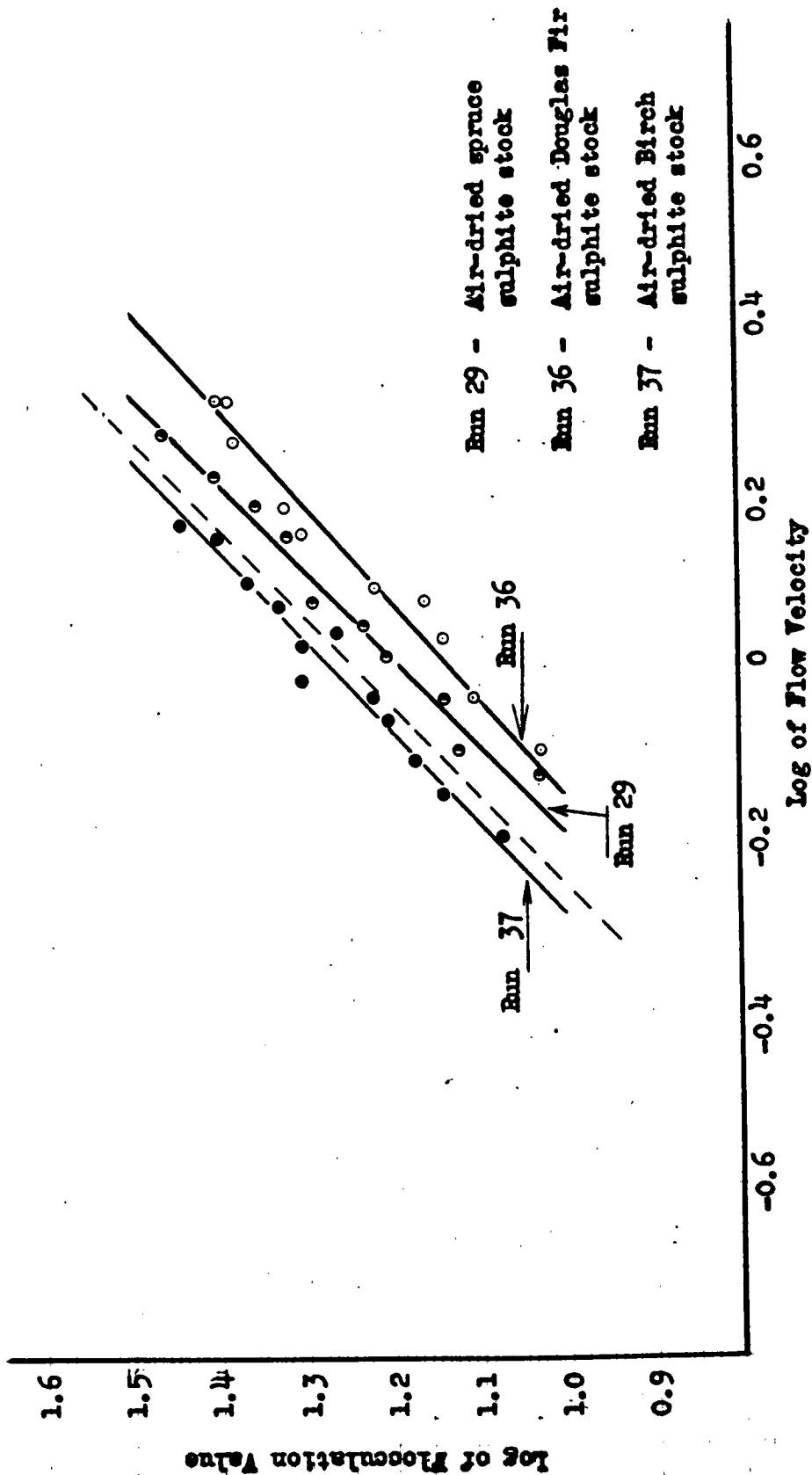
This final set of two flocculation runs was made to give some indication of the role played by fiber length in the flocculation phenomenon.

An unbleached Douglas fir sulphite pulp was used in the first of these runs (no. 36), since its average fiber length was known to be appreciably greater than the average fiber length of the standard unbleached spruce pulp used in the previous experiments. The Douglas fir pulp as obtained for use in the flocculation run was 93.6 per cent

oven-dry. A sufficient quantity of this air-dried pulp was dispersed in tap water in the head-box of the flocculation tester to give a fiber consistency of 0.0087 per cent, which was somewhat lower than the consistency usually obtained. The temperature at which the run was made was 25° C. and the pH of the white water at the start was 7.7, increasing to 8.1 at the end of the run.

An unbleached birch sulphite pulp was used for the second run of this series (no. 37), because of its lower average fiber length as compared with that of the spruce fibers. This pulp was also air dried, having a moisture content of 6 per cent. For this flocculation run, 22.6 grams of the air-dried stock were dispersed in tap water in the flocculation tester at a consistency of 0.0099 per cent. The run was made at a temperature of 25° C., with the pH of the white water increasing from 7.5 to 8.1 during the course of the run.

For both runs 36 and 37, at least ten flocculation values were determined at different flow rates through the observation tube. The results are given graphically in Figure 34 where comparison can also be made with the flocculation characteristics of both the air-dried and wet-lap standard unbleached spruce sulphite stocks. Run 29 was made with the air-dried spruce pulp, while the dotted line in Figure 34 gives the average flocculation characteristics of the wet stock. The dispersion indices and other pertinent data for each of the runs are given in Table VIII.



FLOCCULATION CHARACTERISTICS OF DOUGLAS FIR AND BIRCH SULPHITE FIBERS

Consistency 0.0093 % Temperature 25° C. Tap water

Figure 34

Table VIII

FLOCCULATION CHARACTERISTICS OF DOUGLAS FIR AND BIRCH SULPHITE FIBERS RELATIVE TO THAT OF SPRUCE SULPHITE FIBERS

Fiber Consistency $0.0093 \pm 0.0005\%$ Temperature 25°C .
Tap Water

Run No.	Unbleached Sulphite Pulp	Consistency (%)	White Water pH Start	White Water pH Finish	Dispersion Index (K_1)	Slope Constant (K_2)
-	Spruce (wet stock)	0.0097	7.2	8.0	1.24	0.96
29	Spruce (air dry)	0.0096	7.5	8.0	1.18	0.98
36	Douglas fir	0.0087	7.7	8.1	1.13	0.88
37	Birch	0.0099	7.5	8.1	1.27	0.94

These results, in general, show that neither the longer fibered Douglas fir nor the shorter fibered birch pulp exhibited flocculation characteristics markedly different from those of the standard spruce sulphite pulp. Actually, the Douglas fir fibers did show increased flocculation tendencies as compared with the spruce pulp, but the difference between the dispersion indices, 1.24 and 1.13, is considerably smaller than that which might be expected from the difference in fiber lengths of the two pulps. The same opinion may be expressed concerning the small difference between the dispersion indices of the hardwood birch and the spruce fibers. In conclusion, it may be said that only reasonably small differences in the flocculation characteristics of birch, Douglas fir, and the standard unbleached spruce sulphite pulps were observed. This would indicate that the factor of fiber length, as it concerns fiber flocculation, is of less importance

than a number of other factors which have been investigated.

This concludes the experimental work in which the flocculation tester was used. Before summarizing the results, however, the work which has been done on the torsion balance developed for the measurement of fiber to fiber adhesion forces will be presented.

Results Using the Torsion Balance for Measurements of Fiber to Fiber Adhesion Forces

A number of the results obtained by the use of the flocculation tester, and discussed in the previous section, have indicated that fiber to fiber adhesion forces may be involved in the phenomenon of fiber flocculation. The initial flocculation effect of alum followed by a marked dispersing action, the difference that was found to exist between the degree of fiber dispersion in tap water and that in distilled water and the very definite fiber flocculation resulting from temperature increases could be related, at least in part, to changes in surface energy forces existing at the fiber-fluid interfaces when the fibers are suspended in water. Therefore, as already stated, it was of interest to attempt some measurement of these forces.

The work which has been done thus far along these lines is essentially of an exploratory nature. The torsion balance originally designed for investigating the fiber to fiber adhesion effects has not proved to be entirely satisfactory. However, with its use the existence of adhesion forces between individual fibers has been established and some techniques which may be applicable in subsequent work have been developed.

Actual fiber to fiber adhesion measurements have been made with fibers suspended in tap water, distilled water, and in tap water at an elevated temperature. The individual fibers used in the experiments were isolated from the standard unbleached spruce sulphite pulp used in the experimental work with the flocculation tester.

On pages 60 to 72 the details of the torsion balance, as well as the specific procedures used in making the adhesion force measurements, have been described. For each condition, such as the investigation of adhesion forces in tap water, five sets of fibers (ten individual fibers) were used. For each set of fibers, at least five individual measurements of the displacement of the lower light beam beyond the zero point were made. The average of these five displacement values was used to calculate an average adhesion force for each pair of fibers.

The results obtained when measurements were made with the fibers submerged in tap water and in distilled water are shown in Tables IX and X, respectively.

Table IX

FIBER - FIBER ADHESION MEASUREMENTS
UNBLEACHED SPRUCE SULPHITE - TAP WATER

Average Temperature $22.3^{\circ} \pm 0.6^{\circ} \text{C.}$
Torsion Wire No. 1; $t = 0.0611 \text{ dyne}\cdot\text{cm./rad.}$
Length of Optical Lever Arm (q) = 107 cm.

Fiber Pair No.	Back Dis- place- ment (cm.)	Rate of Fiber Motion (cm./sec.)	Rest point (Scale read.)	Max. Swing (Scale read.)	Dis- place- ment (x) (cm.)	Adhesion Force	
						$F = \frac{t \cdot x}{2 \cdot q \cdot y}$	(dynes)
						Uncorr.	Corr.
						($\times 10^{-4}$)	($\times 10^{-4}$)
Torque arm (y) = 1.70 cm.							
1	5.6	.0074	74.1	74.6	0.5	1.3	2.4
	6.0	.0078	74.1	74.7	0.6		
	5.3	.0059	73.7	74.4	0.7		
	5.7	.0059	73.2	73.9	0.7		
	5.6	.0068	73.2	73.6	0.4		
	5.6	.0068			0.58		
Torque arm (y) = 1.70 cm.							
2	5.2	.0059	74.5	74.0	-	0.82	1.9
	5.9	.0059	73.8	74.2	0.4		
	5.1	.0065	74.0	74.1	0.1		
	5.3	.0063	73.6	74.0	0.4		
	5.6	.0058	73.7	74.2	0.5		
	5.4	.0061			0.37		
Torque arm (y) = 1.77 cm.							
3	4.8	.0083	71.2	71.9	0.7	1.5	2.6
	5.0	.0070	75.5	75.7	0.2		
	5.1	.0060	76.0	76.1	0.1		
	5.0	.0060	74.6	76.2	1.6		
	5.0	.0057	74.5	75.5	1.0		
	5.0	.0066			0.72		
Torque arm (y) = 1.75 cm.							
4	5.0	.0060	76.0	76.5	0.5	1.1	2.2
	5.0	.0060	75.4	75.9	0.5		
	5.0	.0059	75.3	75.8	0.5		
	5.5	.0057	75.5	76.0	0.5		
	5.0	.0051	75.1	75.7	0.6		
	5.1	.0057			0.52		

Table IX (continued)

Fiber Pair No.	Back Dis- place- ment (cm.)	Rate of Fiber Motion (cm./sec.)	Rest point (Scale read.)	Max. Swing (Scale read.)	Dis- place- ment (\bar{x}) (cm.)	Adhesion Force	
						$\bar{F} = \frac{t \cdot \bar{x}}{2 \cdot q \cdot y}$ (dynes)	
						Uncorr. ($\times 10^{-4}$)	Corr. ($\times 10^{-4}$)
		Torque arm (y) = 1.74 cm.					
5	4.6	.0069	75.1	75.5	0.4		
	5.0	.0060	75.0	75.3	0.3		
	5.5	.0061	74.6	75.2	0.6	0.92	2.0
	5.0	.0059	74.5	74.9	0.4		
	4.9	.0060	74.3	74.7	0.4		
	5.0	.0062			0.42		
Total Average					0.52	1.13	2.22

Table X

FIBER - FIBER ADHESION MEASUREMENTS
UNBLEACHED SPRUCE SULPHITE FIBERS - DISTILLED WATER

Average Temperature $21.2 \pm 1.4^{\circ}$ C.
Torsion Wire No. 1; $t = 0.0811$ dyne-cm./rad.
Length of Optical Lever Arm (q) = 107 cm.

Fiber Pair No.	Back Dis- place- ment (cm.)	Rate of Fiber Motion (cm./sec.)	Rest point (Scale read.)	Max. Swing (Scale read.)	Dis- place- ment (\bar{x}) (cm.)	Adhesion Force	
						$\bar{F} = \frac{t \cdot \bar{x}}{2 \cdot q \cdot y}$ (dynes)	
						Uncorr. ($\times 10^{-4}$)	Corr. ($\times 10^{-4}$)
		Torque arm (y) = 1.74 cm.					
1	4.9	.0059	71.1	71.9	0.8		
	5.0	.0048	73.2	74.3	1.1		
	5.0	.0057	73.2	74.3	1.1	3.0	4.1
	4.9	.0053	73.1	75.6	2.5		
	5.1	.0046	72.5	73.9	1.4		
	5.0	.0053			1.4		

Table X (continued)

Fiber Pair No.	Back Dis- place- ment (cm.)	Rate of Fiber Motion (cm./sec.)	Rest point (Scale read.)	Max. Swing (Scale read.)	Dis- place- ment (g) (cm.)	Adhesion Force	
						$F = \frac{1 \cdot X}{2 \cdot q \cdot y}$	(dynes)
						Uncorr.	Corr.
						($\times 10^{-4}$)	($\times 10^{-4}$)
			Torque arm (y) = 1.88 cm.				
	5.0	.0062	76.6	77.2	0.6		
	5.2	.0060	76.7	77.2	0.5		
2	5.0	.0065	76.5	77.0	0.5	1.2	2.2
	5.1	.0053	76.4	77.2	0.8		
	5.4	.0065	76.6	77.1	0.5		
	5.1	.0061			0.58		
			Torque arm (y) = 2.34 cm.				
	4.9	.0040	75.3	75.6	0.3		
	5.1	.0071	75.8	76.3	0.5		
3	5.0	.0074	76.1	76.6	0.5	0.68	1.5
	5.1	.0077	75.7	76.0	0.3		
	5.0	.0073	76.3	76.8	0.5		
	5.0	.0067			0.42		
			Torque arm (y) = 1.75 cm.				
	5.1	.0030	75.4	75.8	0.4		
	5.6	.0030	75.5	75.8	0.3		
4	5.0	.0049	75.1	75.7	0.6	0.91	2.0
	5.0	.0031	75.8	76.1	0.3		
	5.1	.0052	75.8	76.3	0.5		
	5.2	.0038			0.42		
			Torque arm (y) = 1.66 cm.				
	5.0	.0055	74.4	77.3	2.9		
	5.0	.0055	73.8	77.0	3.2		
	5.0	.0042	73.3	73.8	0.5		
5	5.0	.0055	73.2	73.3	0.1	3.0	4.1
	4.0	.0052	72.9	73.2	0.3		
	5.0	.0052	74.4	76.0	1.6		
	5.0	.0049	72.2	72.6	0.4		
	4.9	.0051			1.3		
Total Average					0.82	1.76	2.78

The last two columns in the tables give an uncorrected and a corrected adhesion force value. The former was obtained from the formula:

$$F = \frac{j \cdot X}{2 \cdot X \cdot g}$$

where F is the adhesion force (dynes), j , the torsion constant of the gold wire (dyne-cm./radian), X , the average displacement of the lower light beam beyond the rest point of the suspension (cm.), g , the length of the optical lever arm (cm.), and X , the torque arm, or the horizontal distance from the point of contact of the two fibers to the vertical axis of the torsion suspension.

However, as already mentioned on pages 75 and 76, this evaluation of the adhesion force does not take into consideration the effect of fluid frictional drag on the upper horizontal glass arm on which one of the fibers was mounted. The obvious effect of this fluid friction was to decrease the fiber to fiber adhesion force as measured by the displacement of the light beam.

Direct calculation of the adhesion force from the displacement value, X , also neglects the effect of the momentum of the suspended system, which would tend to displace the latter slightly beyond its zero or rest point. The effect of this inertial force is opposite to that of the frictional drag, tending to increase the apparent fiber to fiber adhesion force as measured by the light beam displacement.

The magnitude of these frictional and inertial forces depends

upon the speed at which the fibers are pulled apart and upon the viscosity of the fluid in which the measurements are made. For the former reason, the rate of fiber motion during all the measurements was held reasonably constant as indicated by column 3 in tables IX and X. Actual variations in the rates of motion were sometimes as large as 30 per cent, due to a rather crude speed regulation on the driving mechanism of the balance, but even variations as large as these are not significant at the very slow rates of movement used. Accordingly, since the rate of motion of the fibers and the viscosity of the liquid in which the adhesion measurements were made, were sensibly constant for all experiments, the uncorrected adhesion forces calculated directly from the observed displacement of the lower light beam are relatively comparable. However, to give a more absolute value to the adhesion forces a constant correction factor for the effect of frictional drag and inertial force of the torsion suspension was applied to the average displacement values, \bar{x} .

The procedure for determining the correction factor for viscous fluid drag on the glass arm of the suspension has already been described on page 76. The value of the factor in terms of centimeters displacement on the optical scale was approximately +2 centimeters.

To obtain an approximation for the inertial force tending to increase the observed adhesion forces, the following procedure was used. The suspension was mounted exactly as in the experimental work with the upper horizontal glass arm in the platinum saddle and submerged in the water in the glass-copper cell; the motor was connected to the upper drive shaft of the balance. The entire suspension was

first rotated to the right at the same speed as that used during the fiber measurements. After the light beam, reflected from the upper mirror of the torsion suspension (r. Figure 5), was observed to move exactly 5 centimeters along the top optical scale, the rotation of the entire suspension was stopped and the maximum swing of the lower light beam to the right was observed on the bottom optical scale. The entire suspension was rotated to the right an additional 5 centimeters as indicated by the movement of the upper light beam on the top scale. After arresting the motion of the suspension, it was allowed to come to equilibrium in this position. Then, by reversing the motor, the entire suspension was rotated to the left, again at the same speed used in the adhesion force measurements. After the light beam on the upper scale had moved through a distance of 5 centimeters, it was stopped at exactly the same point on the scale as in the preceding case of the left to right measurement. The maximum swing to the left of the lower light beam was the observed. The difference between the two scale readings obtained for the maximum left and maximum right swing of the lower light beam was divided by two, and this quotient considered to be the correction factor in centimeters as measured on the lower optical scale for the inertial effect of the suspended system. The average of this correction factor, for a number of readings taken in water, was -1.5 centimeters.

Combining the positive correction factor of 2 centimeters for the effect of fluid viscosity on the glass balance arm with the negative inertial force factor of 1.5 centimeters, an overall correction

factor of +0.5 centimeters was obtained. This was then added to the average displacement value, \bar{x} , in the calculation of the corrected fiber to fiber adhesion force.

The average corrected value of the fiber to fiber adhesion force obtained for the unbleached spruce sulphite fibers in tap water was 2.2×10^{-4} dynes (Table IX). Corresponding to this force value, the average displacement of the light beam on the lower optical scale was 0.52 centimeters. Further, it will be observed that the average variation in the rest point during any series of measurements on a fiber pair was approximately 1 centimeter. Accordingly, it must be concluded that the adhesion forces measured for the specific conditions were at the lower limit of sensitivity of the balance and, for this reason, their accuracy may be questioned. The maximum deviation from the mean of the force values was of the order of 40 per cent. Further, because of this latter variation, the significance of the "average" force values for measurements, made on only five fiber pairs, may be questioned.

The average adhesion force between the fibers submerged in distilled water was 2.8×10^{-4} dynes, which is an increase of approximately 25 per cent over the average force of adhesion between the fibers measured in tap water. From the flocculation measurements, it will be recalled that a somewhat greater flocculation was observed in distilled water relative to that obtained in tap water. However, the proposed interpretation of the $\log \bar{X} - \log \bar{Y}$ relations, indicated that the adhesion forces in distilled water might be expected to be smaller

than those existing between fibers suspended in tap water. It was then postulated that the greater flocculation in distilled water could be due to factors other than adhesion forces. The results of the measurement of these latter values on the torsion balance, however, indicate that the increased fiber flocculation in distilled water may be due to an increase in fiber to fiber adhesion forces. A mechanism accounting for such an increase is not at once evident, and, admittedly, the torsion balance measurements are subject to a large experimental error. However, the 25 per cent increase in the adhesion forces obtained in distilled water relative to those in tap water seems likely to be of some value in indicating a trend. It has already been mentioned that too extensive interpretation of changes in slope constants of the $\log \bar{I} - \log \bar{Y}$ relations is probably not desirable until further experimentation has shown more definitely some of the factors that influence these changes. Therefore, it may be concluded that rather crude measurements, using the torsion balance, have indicated an increase in fiber to fiber adhesion forces in distilled water as compared to those obtained in tap water. This increase correlates with an increase in flocculation of the fibers in distilled water as measured by the dispersion index, calculated from data obtained using the flocculation tester. By improving the present techniques used for the measurement of fiber to fiber adhesion forces a considerably greater insight into the fundamental factors involved in fiber flocculation may be expected.

The results of the fiber adhesion measurements made in tap water at an elevated temperature (approximately 37° C.) are given in

Table XI. To make these measurements at 37° C. it was necessary to encase the entire torsion balance in a chamber which could be kept at this temperature; this was required so that the balance would be isothermal to eliminate eddy currents, both in the air within the balance case and in the fluid in the glass cell. The temperature chamber was improvised from a large cardboard box in which glass windows were built so that the necessary optical measurements on the system could be made. The temperature within the chamber was maintained with several small nichrome wire resistors.

Table XI

FIBER - FIBER ADHESION MEASUREMENTS							
UNBLEACHED SPRUCE SULPHITE FIBERS - TAP WATER							
Average Temperature $37.9^{\circ} \pm 0.3^{\circ}$ C.							
Torsion Wire No. 1; $t = 0.0811$ dyne-cm./radian							
Length of Optical Lever Arm (q) = 107 cm.							
Fiber Pair No.	Back Dis- place- ment (cm.)	Rate of Fiber Motion (cm./sec.)	Rest point (Scale read.)	Max. Swing (Scale read.)	Dis- place- ment (z) (cm.)	Adhesion Force $F = \frac{t \cdot z}{2 \cdot q \cdot y}$ (dynes) Uncorr. ($\times 10^{-4}$)	Corr. ($\times 10^{-4}$)
Torque arm (y) = 1.70 cm.							
1	5.0	.0055	72.9	73.2	0.3	1.3	2.4
	5.0	.0057	71.2	71.8	0.6		
	5.0	.0058	71.3	71.9	0.6		
	4.9	.0058	71.3	72.0	0.7		
	5.2	.0060	71.3	72.0	0.7		
	5.0	.0058			0.58		
Torque arm (y) = 1.56 cm.							
2	5.1	.0048	70.1	71.5	1.4	2.2	3.4
	5.0	.0053	71.0	71.4	0.4		
	5.2	.0053	71.1	72.5	1.4		
	5.0	.0054	72.2	72.9	0.7		
	5.3	.0053	72.4	73.0	0.6		
	5.1	.0052			0.90		
Total Average					0.74	1.75	2.9

Only two sets of fibers were measured, which very definitely limits the accuracy of the average corrected adhesion force value of 2.9×10^{-4} dynes. However, the make-shift construction of the outer chamber used for temperature control made the test procedure very lengthy, since it was necessary to remove the chamber to change each set of fibers, and a considerable amount of time was then required to bring the system back to temperature equilibrium. The results do indicate a slight increase in the adhesion forces between the fibers at increased temperature, which is in agreement with the marked increase in fiber flocculation under the same conditions as measured by the flocculation tester. Again the accuracy of the adhesion force measurements is in question, and no further conclusions are warranted until improvements in the torsion balance sensitivity have been made.

Summarizing the exploratory work which has been done on the measurements of fiber to fiber adhesion forces, it may be said that there is some indication that such forces exist, but their importance in fiber flocculation has not yet been determined. An approximate order of magnitude for the forces was found to be 10^{-4} dynes. The torsion balance which was constructed to measure the fiber to fiber adhesion effects was not entirely satisfactory for several reasons. To begin with, its lower range of sensitivity was of the order of the adhesion forces being measured, which left the accuracy of the latter values in question. This could be remedied by using a more sensitive gold torsion wire or, perhaps preferably, a more sensitive quartz filament. A gold torsion wire approximately seven times more sensitive than the one originally used could be obtained, but because of

lower tensile strength it would require a much lighter lower saddle and mirror which is supported at its lower end to hold the horizontal glass arm.

A second objection to the balance was that it was not thermally insulated. This is an important factor and is believed to be responsible for the difficulties encountered in obtaining equilibrium rest points for the torsion suspension. It was observed during the course of the experiments that the heat radiated from a 40-watt light bulb, some 12 inches distant from the balance case, and for only a period of several minutes, shifted the light beam on the optical scale about 10 centimeters. Further, body heat from the operator, sitting more than 18 inches in front of the balance, was observed to produce a slight but definite shift in the rest point. These heat effects were presumably due to eddy currents set up within the air in the balance case, which acted on the comparatively large area of the mirror mounted on the lower end of the suspension. Accordingly, improvement in the sensitivity of the balance could be expected if it were thermally insulated. Such improvement was even observed when the hastily constructed outer cardboard chamber was used in the high temperature run.

Finally, improvement might also be effected in the mounting of the individual fibers. The necessity of mounting in warm wax raises a question concerning possible desiccation of the fiber. It is possible that a micro-clamp arrangement could be used on mounting arms other than glass, to overcome this difficulty.

VI. SUMMARY AND CONCLUSIONS

1. Equipment and procedures have been developed which have enabled a study to be made of the flocculation of papermaking fibers in a flowing suspension. The equipment, referred to as the flocculation tester, permitted investigation of flocculation effects in a pulp suspension flowing laminarily through a large glass observation tube. Eddy currents were eliminated from the flowing stream before it was introduced into the observation tube and in this manner the important variable of agitation on fiber flocculation was held constant. The procedures developed included a method of visual observation, as well as a photographic technique, for evaluating the degree of fiber flocculation.
2. From visual observations and data thus obtained a mathematical relation between the degree of flocculation and the rate of flow of a fiber suspension through the flocculation tester was established. This relation enabled a comparative numerical evaluation to be made of the degree of fiber dispersion in any given suspension. The flocculation tester and procedure used were found capable of reproducing this numerical dispersion index for a given fiber suspension to within 15 per cent experimental error.
3. With the flocculation tester and both the visual and photographic procedures for evaluating the degree of flocculation, the following results, using an unbleached spruce sulphite fiber suspension at approximately 0.01 per cent consistency, have been obtained:

- (a) Alum was shown to produce a marked fiber dispersion when added to a suspension of unbleached sulphite fibers in tap water.
- (b) Experiments using distilled water indicated that this dispersing effect of alum was due to the formation of an alumina flock from the reaction of the alum with the alkalinity of the hard tap water.
- (c) Further investigation showed that the initial effect attained when alum was added to a tap water suspension of fibers was not a dispersing action but rather a marked flocculation. However, several minutes after the alum was added and completely dispersed, the originally observed dispersing effect was obtained. It has been postulated that an isoelectric point may occur with regard to the adsorption of the positively charged alumina by the electronegative fibers.
- (d) When the alum flock and fibers were allowed to settle from suspension, it was observed that a reversion in the degree of dispersion took place. If the settled suspension was recirculated in the flocculation tester, a degree of fiber dispersion was obtained (as measured by the dispersion index) that was lower than that which originally existed. The same reversion phenomenon was also observed in the case of a fiber-tap water suspension alone, but to a smaller extent. It has not been possible to definitely isolate factors responsible for this effect. The phenomenon, as observed, is of a smaller order of magnitude than a number of other effects which have been

discerned to produce appreciable changes in fiber flocculation. Accordingly, it may be of less significance as far as sheet forming characteristics of a given stock are concerned. Attention has been given to the effect, however, because of the possibility that it may be fundamentally concerned with the fiber flocculation phenomena.

- (e) The addition of 25 per cent bentonite clay to a fiber suspension increased the fiber flocculation; the effect was assumed to be due to the gelatinous nature of the hydrophilic clay.
- (f) Temperature of the white water was shown to have a marked effect on fiber flocculation, the latter being greatly increased at the higher temperatures. The effect was considered to be due to a decrease in the white water viscosity at the high temperature.
- (g) Deacetylated karaya gum was found to increase fiber dispersion when added to a suspension of unbleached sulphite fibers in tap water. The initial dispersing effect was lost when the fiber-gum-tap water suspension was circulated and agitated in the flocculation tester for several hours. It was thought that the initial dispersing action of the gum was due to an increase in viscosity resulting from the addition of the gum to the white water, but measurements made on the changes in viscosity which occurred when the gum dispersion was agitated did not agree entirely with this theory. Additional investigation will be necessary before further postulations can be made concerning the mechanism by which the gum effects dispersion.
- (h) A wetting agent was shown to produce only a very small increase

in the flocculation tendencies of the unbleached sulphite pulp in tap water.

- (i) The work done with respect to the effect of beating on fiber flocculation was not extensive, but indicated that the factors involved in beating, such as hydration, fibrillation, and a cutting of the fibers, tend to increase the flocculation characteristics of the latter. It is indicated that improvement in sheet formation resulting from beating is, perhaps, more intimately concerned with other factors, such as drainage characteristics of the beaten pulp, rather than flocculation characteristics. More investigation along this line would be desirable.
- (j) The fiber consistencies which could be used in the flocculation tester fell in the range of 0.005 to 0.02 per cent dry fiber. Above or below this range it was found difficult to make very accurate observations of the degree of flocculation. However, within this consistency range, appreciable differences in fiber dispersion were observed; the higher the consistency, the greater the degree of flocculation. The effect has been assumed to be due simply to a statistical effect, enhanced flocculation resulting from the larger number of fibers present at the higher consistencies.
- (k) The marked dispersing effect of alum was observed to occur also at 0.005 and 0.02 per cent fiber consistency, as well as with beaten pulp. These results indicate that the effects may have a bearing on sheet formation under similar conditions.

- (1) Air drying pulp was observed to have little or no effect on the flocculation characteristics of the fiber. It is conceivable that complete desiccation of the stock might alter its flocculation characteristics due to changes in the wettability of the fiber surfaces, resulting in changes in fiber-fiber adhesion forces. More experimentation on such effects would seem desirable.
- (m) The flocculation characteristics of Douglas fir sulphite pulp and birch sulphite pulp were observed to differ only very slightly from the flocculation characteristics of the standard unbleached spruce sulphite stock. The Douglas fir fibers tended to show a little greater flocculation than the spruce fibers under analogous conditions, but the difference was not nearly as great as might be expected from the differences in fiber lengths of the pulps. Likewise, the birch fibers showed less flocculating tendencies than the spruce, but again the difference was not concordant with the differences in fiber lengths. These experiments indicate that fiber length may have only a small effect on the flocculation characteristics of a stock. It does not directly follow that fiber length is of no importance with regard to the sheet forming characteristics of such a stock. Short fibers may flocculate almost as readily as longer fibers, but the size of the fiber bunches in the former case will be considerably smaller than those flocks formed by the longer fibers. Hence, with the short fibered stock, formation of a sheet may not appear as "wild" as in the

case of paper made under similar conditions with long fibered pulp; however, in the former case a general cloudy formation may still result with considerable nonuniformity of structure throughout the sheet.

4. From these results it may be concluded that a number of non-mechanical factors play important roles in the phenomenon of fiber flocculation. The marked dispersing effect of alumina flock on a fiber suspension, the flocculating effect of high temperatures, and the dispersing action of the deacetylated karaya gum had much greater influences on fiber flocculation than mechanical factors such as beating of the pulp. How important some of these non-mechanical factors may be in sheet formation has not been definitely established, but the results obtained with the flocculation tester suggest that they may be quite intimately concerned with the formation of the sheet and matting of the fibers on the paper machine.
5. Finally, to determine some of the fundamental causes of fiber flocculation, an attempt was made to measure fiber to fiber adhesion forces which may exist when fibers are submerged in a white water medium and brought into contact. A torsion balance was developed to measure the forces, but it was not entirely satisfactory, principally because of lack of sensitivity. The exploratory experiments made to date indicate that fiber to fiber adhesion forces do exist and are of the order of 10^{-11} dynes. With the development of greater sensitivity in the torsion balance, further work along these lines may be of considerable aid in

elucidating the phenomenon of fiber flocculation and the attendant problems of fiber dispersion and sheet formation.

VII. LITERATURE CITED

- (1) Moss, L. A., and Bryant, K. O., Paper Trade J. 106, no. 15: 46-57 (Apr. 14, 1938).
- (2) McNeill, D., Worlds' Paper Trade Rev. 101:847-8, 850, 888, 890, 928, 966, 969-70, 972 (1934).
- (3) Strachan, J., Paper Maker 89: Ts 1-2, 17, 20 (1935).
- (4) Ibid., 88: Ts 177 (1934).
- (5) Ibid., 89: Ts 33-4 (1935).
- (6) Rubin, M. M., Paper Trade J. 101, no. 6:39-43 (Aug. 8, 1935).
- (7) Anon., Paper 25, no. 11:19-21 (Nov. 19, 1919).
- (8) Venneman, F., Paper 35:113 (1924).
- (9) Specht, H., Paper Trade J. 104, no. 8:108, 110, 112, 114, (Feb. 25, 1937).
- (10) Specht, H., and Connor, C. M., Paper Mill 61, no. 10:11, 13, 15 (Mar. 5, 1938).
- (11) Rowland, B. W., J. Phys. Chem. 41:997-1005 (1937).
- (12) Willets, W. R., Paper Trade J. 101, no. 13:81-6 (Sept. 26, 1935).
- (13) Loddenggaard, P. M., Paper Trade J. 105, no. 9:37-42 (Aug. 26, 1937).
- (14) Robinson, E. H., J. Chem. Soc. Trans. 89: 1496-1505 (1906).
- (15) Anon., Chem. Industries 40:171 (1937).
- (16) Kress, O., and Bialkowaky, H., Paper Trade J. 93, no. 20:35-44 (Nov. 12, 1931).
- (17) Harrison, E. A., Worlds' Paper Trade Rev. 99, Technical Convention no.: 27 (1933).
- (18) Campbell, W. B., Paper Trade J. 100, no. 7:35-8 (Feb. 14, 1935);
see also, Ibid., 95, no. 6:29-33 (Aug. 25, 1932).
- (19) Campbell, W. B., and Yorsten, F. H., Forest Products Labs. Canada, Pulp Paper Lab., Quarterly Rev., no. 10:38-47 (April-June, 1932).
- (20) Bell, J. H. P., J. Soc. Chem. Ind. 52: T 109-16, 119-30 (1933).

- (21) Yorsten, F. H., Forest Products Labs. Canada, Pulp Paper Lab.,
Quarterly Rev., no. 16:7-14 (October-December, 1933).
- (22) Skaperdas, G., Forest Products Labs. Canada, Pulp Paper Lab.,
Quarterly Rev., no. 20:11 (October-December, 1934).
- (23) Anon., Wochbl. Papierfabr. 62:152-3 (1931).
- (24) Bearce, G. D., Paper Trade J. 76, no. 9:52-3 (Mar. 1, 1923).
- (25) McGrath, L. E., Paper Trade J. 80, no. 9:46-8 (Feb. 26, 1925).
- (26) Bechtel, A. R., Paper Trade J. 102, no. 1:29-33 (Jan. 2, 1936).
- (27) Graef, O. K., Paper Ind. 15:249-53, 310-3 (1933-34).
- (28) Booth, L. W., Paper Trade J. 100, no. 4:33-4 (Jan. 24, 1935).
- (29) Brecht, W., and Rausch, B., Papier-Fabr. 35:449-55 (1937)
- (30) Brecht, W., Eberstadt, L., and Kilpper, W., Papier-Fabr. 33:404-16
(1935).
- (31) Anspach, S., Worlds' Paper Trade Rev. 103:420, 422, 462, 464, 500,
502, 504, 542, 544; 104:755-6, 758, 801-2 (1935).
- (32) Lindovsky, K., Papier-Fabr. 35:429-32 (1937).
- (33) Suckdorff, B., Pappers- Trävarutid. Finland 19:475-6, 478-80, 482
(1937); Bull. Inst. Paper Chem. 7, no. 11:380
(July, 1937).
- (34) Le Compte, T. R., Assignor to John A. Manning Paper Co., Inc., U. S.
patent, 2,069,766 (Feb. 9, 1937).
- (35) Ibid., U. S. patent, 2,065,479 (July 27, 1937).
- (36) Sveen, K., U. S. patent, 1,622,474 (Mar. 29, 1927).
- (37) Van den Akker, J., "Mechanics, Hydraulics, Heat and Thermodynamics."
Vol. 1, p. 156-7, Appleton, The Institute of
Paper Chemistry, 1937.
- (38) Perry, J. H., "Chemical Engineers' Handbook," 1st ed., p. 727-8.
New York, N. Y., McGraw-Hill Book Co., Inc., 1934.
- (39) Corning Glass Works, "Pyrex Brand Piping and Heat Exchangers,"
Bulletin 814, p. 4, New York, N. Y.