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Factors Governing the Retention of Starches Added to Pulp in the Beater

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Factors governing the retention of
Starches.

Submitted
in
Partial Requirement in
Course 436A, Pulp and Paper Technology
by
Gordon J. Gill

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Factors Governing the Retention of Starches

Added to Pulp in the Beater

Index

I	Introduction	page	1
II	Theories of Retention		2
III	Factors Governing Retention		3
IV	Retention of Raw Native Starch		6
V	Preparation of Starches for Use in the Paper Industry		8
VI	Retention of Starches Other than Raw Native Starch		11
VII	Literature Cited		17
VIII	Outline of Proposed Laboratory Experiments		18
IX	Special Equipment and Chemicals to be Used in Proposed Experiments		19

Factors Governing the Retention of Starches

Added to Pulp in the Beater

I

Introduction

The information presented in this literature survey was obtained through Western Michigan College Library, Kalamazoo Public Library, St. Regis Central Laboratory, and Kalamazoo Vegetable Parchment Research Library.

The following survey is the result of twelve weeks of library research and was done in accordance with the methods and rules prescribed by Course 436A, Pulp and Paper Technology, Western Michigan College of Education.

Considering retention, from a general point of view, we find in Webster's New International Dictionary that it is, "A retaining or holding fixed in some place or position; state of being kept in place." Sutermeister (20) gives the paper makers definition as being the percentage of filler added to the furnish which appears in the finished paper.

II

Theories of Retention

Haslam and Steele (20) state that filler is retained in three ways, the first of which is filtration. Filtration is the actual straining effect caused by the interlocking of the fibers to form a web which in effect acts as the strainer. This is not a very important retention agency from the overall filler point of view but appears to be important to starch retention. (10)

By mechanical attachment, the second agency, is meant retention not governed by flocculation laws. Filler particles may be wedged into imperfections of the surface of the fibers, or they may be imbedded in a layer of plastic material. (10)

The third agency is coflocculation. This is by far the most important in the retention of fillers. Coflocculation is the attachment of filler particles to the fiber walls because of the play of interfacial forces. Willetts (21) refers to this as colloidal attraction. (10)

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III

Factors Governing Retention

The actual retention of fillers may vary from 30 to 90% but averages about 60%. This statement does not apply for starch but for fillers in general. (20)

The factors affecting this retention are many and varied. One of the most important is the degree of beating. The effectiveness is, of course, dependent on the type of stock being used. In general the slower the stock the better the retention. The improvement brought about by greater hydration is both coflocculation and filtration. Landt and Rulon (8) state that beating breaks down the fibers to fibrils and dissolves the pectic substances and other cementing materials which separates the fibrils from each other. This exposes the surface of the cellulose micelles which are studded with hydroxyl groups. When sheet is being formed these hydroxyl groups establish a continuous structure between fibrils through exercise of their residual attractive or cohesive force. This effect is increased with continued beating. Beating, then, in increasing attractive force and raising density of the sheet greatly affects retention. This effect is also noted by Willetts (21) and in Vol IV of Manufacture of Pulp and Paper (9). Sutermeister (20) mentions that high retention is most favorable with the use of long fibers of good fibrillation. In an unsized, unbeaten sheet filler is retained purely by

filtration although filler itself has nothing to do with the forming of a mat.

Increasing basis weight improves retention because of thickening of the web. This effect is shown only to a certain point. Past this point retention is much lower because of increased suction being required to remove water from the sheet.

Retention is somewhat dependent on the dilution of the stock. Low dilution gives good retention, but very low does not because of more rapid removal of water.

Actual machine construction is important. The finer the fourdineir wire used the better the retention. Suction regardless of where applied reduces the retentive properties, therefore, a machine with a short Fourdineir section and high suction on the suction boxes and suction roll will tend to give poor filler retention. Also higher machine speed, with increased suction being used, will react similarly.

Willetts (21) maintains that retention is improved by addition of alum up to about 3%. Further additions cause a small decline. pH appears to be important but alum may not be replaced by acid thus leading one to believe that the alumina floc to be the important phase and pH only an incidental affect when used in conjunction with alum. Alum used without rosin size does not seem to effect retention to a very great degree.

Order of addition of furnish sometimes shows a very

great effect. Retention may vary as much as 25% with the point of addition of alum, the best being closest to the head box.

More filler is retained when high concentrations are used because of saturation affect. Saturation of white water as well as the sheet. This effect levels off at a certain point. The more highly the colloidal properties of a filler are developed, the more the filler will tend to adhere to the fibers.

Small effect is seen with the use of wetting agents such as Duponal, Sodium Silicate, etc. because of lowering of surface tension. Temperature, use of starch, and particle size all show retentive affects but to only a minute degree. (9)

IV

Retention of Raw Native Starch

Lutz (11 and 19), Rowland (7), Strasser (18), Nivling (11), Richard (15), and Sutermeister (19) all state that raw starch is retained better than cooked starch but is ineffective.

Strasser (18) maintains that starch is retained exclusively by mechanical action. He says that raw starch is retained better than cooked starch because cooking enlarges the granules and renders it easy to distort, thereby allowing the granules to slide between the fibers. Slowing the stock will lessen the differential between the two by effecting closer spacing of fibers.

In Nivlings (11) article he stated that Lutz found that 50% more potato starch is retained than rice starch. He also includes photographs to illustrate the difference in granule size. Sutermeister (19) reported that Lutz's investigation using handmade sheets in which 10% starch had been added retained the following percentages:

Potato	73.6% retained
Wheat	71.7% retained
Rice	53.4% retained

Kerr (6) says that raw starch used in beaters (normally 1 to 3%) only about 30% is retarded and this is poorly dispersed and not very effective as a bond.

Due to the comparative ineffectiveness of raw starch

over cooked starch research has been concerned primarily with the latter.

Preparation of Starches for Use in the Paper Industry

Four kinds of starches are used in the paper industry.

Potato and corn starch are used to a greater extent than wheat and tapioca. These starches are used in many different forms. They may be used as beater additives in both native or modified form.

Cooking starch is the most important treatment and the condition which is used as a starting point in most retentive methods. According to Kerr (3), when starch is cooked in the absence of other chemicals the changes take place in three distinct phases.

Phase I

Water is slowly and reversibly taken up and limited swelling occurs.

Phase II

At about 65°C. the granules suddenly swell, increasing many times in size, taking up a great deal of water. Viscosity raises sharply and granule loses its structure with some of it dissolving.

Phase III

Granules become almost formless sacs and the more soluble starch is leached out.

When starch is cooked it is sometimes converted by the

use of enzymes. When this is done the starch is slurried with water and the enzyme added. It is then brought to the gelatinization point and held there until the degree of conversion desired is reached. This temperature is 160° F. to 180° F. The conversion process is completed and the enzyme killed by raising the temperature to 200 to 205° F. This process^{is} essentially breaking down of the starch particles into smaller sized groups thus changing the physical form from a jell to a thick liquid which may be diluted to the consistency desired. (5)

Starch may also be oxidized by hypochlorite, Sodium perborate, alkaline peroxides, and alkaline permanganates. This starch dissolves in hot water giving a thinner bodied solution than raw starch and has a shorter cooking time. The starch has higher fluidity, increased adhesive powers, lower rate of congealing and produces a cleaner solution. It is called chlorinated starch by the industry. (4)

Rowland and Bauer (16) describe in **their patent a preparation of starch** formed by making an alkaline dispersion of starch produced by treating a raw starch with formaldehyde and an acid catalyst such as hydrochloric acid. In use this is precipitated on the stock fiber by use of sufficient acidic material. A variation of this is pretreatment with formaldehyde and then cooking with caustic soda.

Corn starch may be solubilized in hot water and then

dried. This process has a tendency to precipitate the amylose contained in the starch granule thereby producing a granular appearing paste. This paste may not be completely disintergrated. The granules aid retention but are ineffective in the improvement of paper strength characteristics. By grinding before using the efficiency is improved but at a sacrifice in percentage of retained starch. (6)

Allen, in a patent for textile use, gives a method of dispersing starch which may be applicable to the paper industry. "A homogeneous prepared starch for use on textiles comprising a semi-liquid dispersion of starch, sodium benzoate, the reaction product of stearic acid and an excess of trietanamine formed in situ, and zinc stearate." (14)

VI

Retention of Starches Other than Raw Native Starch

Lutz (19) showed that, when starch which had been boiled was added in a 10% proportion and then made into hand sheets, the following retention values were found.

Potato	46.2%
Wheat	58.3%
Rice	58.9%

Cooked starch has a lower retention than raw starch of the same type because the swollen sacks have a tendency to disintegrate in the beater as investigated by Kerr (6).

Best retention of cooked starch (in the absence of chemicals) are those forming the stiffest pastes.

Work at the Institute of Paper Chemistry (18) showed that different starches cooked at 87°C. for 70 minutes had retention varying from 6.84% to 23.00%.

The main manner of retention of starch is thought to be due to an interaction of the anionic pulp colloid, the anionic starch colloid, and the cationic materials such as those derived from alum. In most cases research and patents are the direct outgrowth of this theory.

Starch and cellulose will normally bear negative charges in contact with aqueous media and so conditions favor the neutralization and the precipitation of starch and alumina,

or the absorption of alumina by cellulose, to give an effect of positive fiber agency. Starch may adhere through the agency of what TAPPI (1) referred to as an "electro-static cement." Both of these possibilities would favor an improved starch retention.

The quantity of starch being added to the beater will be limited by the starch's absorption of all surface energies of the pulp fibers. Cooked starch has better retention than raw starch of the same type because the swollen sacks have a tendency to disintegrate in the beater, as investigated by Kerr (16).

Fues (2), devised a process of precipitating starch by addition of sodium silicate, along with cooked starch and alum, but it is not a practical method due to the fact that the stock solution must be exactly neutralized.

Pattiloch (19) has obtained a patent on a process by which the starch is precipitated in the presence of soda or sodium aluminate. Starch and fibers are both negatively charged. The alumina carries a positive charge and carries the starch with it when it precipitates on the Cellulose fiber, as was stated in a fore-going paragraph.

He also states (13) in his patent that sodium meta-silicate or sodium sesquisilicate may be used as the positive bonding agent.

Kesler and Black (7) proposed adding fatty material

and precipitating with metallic ions to improve retention. They state that the viscosity of starch may be increased by the addition of soap. Adding small amounts of certain positive ions decreases this viscosity. The addition of these ions causes only the soap ions to precipitate which take the starch along with them, thereby effecting a mass precipitation without decomposition. At the Institute of Paper Chemistry (1) it was noted that tapioca starch when treated with suitable amounts of fatty acid soaps could be so completely precipitated from a solution by the addition of alum that no trace of color could be found with the addition of iodine to the supernatant liquid.

Potato, tapioca or corn starches which have been cooked with sodium or ammonium oleate, sodium stearate, or a cheap cottonseed oil soap, could be precipitated completely by addition of one of the following compounds: alum, aluminum chloride, copper sulfate, or lead nitrate. Experimenting with tapioca starch showed that good precipitation was not found with the use of neutral rosin soaps, Duponal, sodium silicate or phosphate used as precipitants. Also certain starches which are modified by oxidation or hot roll treatment did not precipitate when added to sodium stearate. (1)

With additions of soap, the viscosity of the starch raises. The amount of rise is dependant on both the soap and the starch used. "The greater the chain length of the

soap, the higher the viscosity effect on the starch. Rosin soap gives only a moderate rise in viscosity and, although alum or acids precipitate the fatty soap complex at or below pH 4.5 - 5.0, in the presence of rosin, the precipitation carries down only a part of the starch. Duponal likewise gives only a slight rise in viscosity." (1) "The precipitability of the starch-soap complex by alum or acids decrease as the soap viscosity effect disappears." (1)

The mechanism of retention of the fore-going soap viscosity principle appears to be as follows: the soap and starch colloid form a complex ion which is negative. The total negative charge carried by the soap starch complex will be higher than the individual charge exhibited by the starch.

The report from the Institute of Paper Chemistry states (1), "the addition of soap is known to increase the electrophoretic mobility of starch." Thus, due to the higher negative charge shown by the starch soap complex, the bond between the cellulose-alumina-soap starch complex will be stronger than the cellulose-alumina-starch bonding.

A method given in an article by Kesler and Black (7) for the use of the soap starch complex for retention is as follows:

1. Starch is suspended in water in a concentration of 0.4 to 0.7 pounds per gallon. This is heated

to at least 185° F.

2. Soap is then added during the process of diluting starch to a useable concentration, about 1 to 2% soap to starch needed, but the strength increase 3.6% is used.
3. The use of alumina in beater is sufficient amount of metallic ions to cause precipitation.
4. It does not matter which is added first to beater, starch-soap complex or alumina. Retention was given as being practically 100%.

With the use of extremely hard water, high quantities of alum is needed. As much as 4 to 5% of furnish weight. The starch jel becomes so fully occupied with the neutralization of positive charge alumina that its adhesive polar nature is no longer available for cellulose interface. (12)

Nivling (11) discovered that treating starch to swell the granules improved retention because of increased particle size.

Cobb (6) states that starch modified by enzymes acts like highly hydrated cellulose, slows stock, adds retention. As can be seen from the fore-going information the use of aluminum rosin size, fillers, and the hardness of water effects the final starch retention. (17)

The improvement of retention could possibly be obtained by adding a considerable quantity of rosin soap. The alum

would favor a hydrolysis of the soap to yield a alkali which in turn would form alumina. Reserve alkalinity in the pulp would play a similar part. With this method mechanical agitation should be kept at a minimum. (17)

Some special beater additives such as taprosize C, a highly converted tapioca starch and rosin size, and Tufjel by the Meincke Company, are on the market at the present time but no data on their retention has been published.

VII
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VIII
Outline of Proposed Laboratory Experiments

Pulp to be used: Weyerhouser Bleached Sulfito.

pH to be used: 4.8 using papermakers alum.

<u>Experiment</u>	<u>Variable</u>	<u>Measurement to be made</u>
(1) Beater runs to Canadian Standard freeness.	Occ, 100cc, 300cc, 500cc.	Canadian Standard freeness.
(2) (a) Retention of raw native starch using Occ freeness (b) Using 100cc freeness (c) Using 300cc freeness (d) Using 500cc freeness	Raw native potato starch. Raw native corn starch.	% retention and distribution. Freeness after starch addition.
(3) Repetition of No.2 using cooked native starch.	Cooked native potato starch. Cooked native corn starch.	% retention and distribution. Freeness after starch addition.
(4) Repetition of No.2 using raw modified starch.	Chlorinated potato starch. Chlorinated corn starch. Converted potato starch. Converted corn starch.	% retention and distribution. Freeness after starch addition.
(5) Repetition of No.2 using soap-starch complex.	Soap-potato starch complex. Soap-corn starch complex.	% retention and distribution. Freeness after complex addition.
(6) Repetition of No.2 using Quaternary Ammonium-starch complex.	Quaternary Ammonium potato starch complex. Quaternary Ammonium corn starch complex.	% retention and distribution. Freeness after complex addition.

IX

Special Equipment and Chemicals to be Used in Proposed Experiments

Equipment:

Canadian standard freeness tester

Laboratory beater

Noble and Wood Sheet Machine

Microscope and microscope slides

Chemicals:

Universal Indicator

Fehling's solution

Asbestos for Gooch crucibles

A quaternary ammonium compound such as methyl ammonium
chloride.