

#1102-8 THE INSTITUTE OF PAPER CHEMISTRY  
(Physical Chemistry)  
Project Reports (1)

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# PROJECT REPORT FORM

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PROJECT NO. 1102-8  
COOPERATOR I. P. G.  
REPORT NO. 1  
DATE June 11th, 1951  
NOTE BOOK 885  
PAGE 13 TO 25  
SIGNED *Nicholas Stolica*  
Nicholas Stolica

## COLLOID CHEMISTRY

### SUMMARY

Pearl cornstarch was converted with hydrogen peroxide at two peroxide concentrations and the solutions were used to tub size 100% rag paper. Superfilm No. 4 solutions of the same concentrations as the cornstarch solutions were prepared and also used to tub size 100% rag paper. The data indicate that superfilm solutions are distinctly superior to converted cornstarch solutions for this purpose. The physical properties of paper tubsized with high viscosity converted cornstarch did not show a consistent variation from those of paper tubsized with low viscosity converted cornstarch.

### INTRODUCTION

Project 1102-8 was established by The Institute of Paper Chemistry for the purpose of making a preliminary study of the use of hydrogen peroxide converted cornstarch as a tub size. The present report is concerned with a comparison of the physical properties of 100% rag paper sized with 8.30 and 4.15% converted cornstarch and with superfilm No. 4 at these concentrations. Studies were also made using 8.30 and 4.15% converted cornstarch which had been cooked with enough peroxide to lower the viscosity to that of superfilm solutions of the same concentration.

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## EXPERIMENTAL RESULTS AND DISCUSSION

### Conversion of the Cornstarch

The following formula for the conversion of cornstarch was adapted from bulletin SPG-1, "Modification of Starches, Proteins and Gums with Peroxygen Compounds," obtained from the Buffalo Electrochemical Co. The beaker was filled in the order given and with constant stirring with:

1945 ml. of water

0.0312 g.  $\text{CuSO}_4$  (dissolved in water before addition)

0.998 g. soda ash ( $\text{Na}_2\text{CO}_3$ )

250 g. of cornstarch

1.397 g. of 50%  $\text{H}_2\text{O}_2$  dissolved in 13.9 cc. of water.

This amount of copper sulfate was chosen because a glass vessel was used for cooking instead of a copper one. The mixture was heated by steam injection to 95°C. rapidly, and maintained at that temperature for 25-30 minutes.

From the weight of the beaker and contents plus stirrer at the end of this period, and the weight of beaker plus stirrer the percent solids was calculated. It happened to be 8.30 in the first experiment. Since this value is of the desired magnitude future starch conversions were carried out to this solids content by adding water after the cooking had been completed. The 4.15% starch solution was prepared from the 8.30% solution by adding 500 g. of water to 500 g. of the starch solution.

The converted cornstarch solution of low viscosity was prepared by using three times as much hydrogen peroxide as listed in the above cooking formula.

#### Dispersion of Superfilm No. 4

Two hundred fifty grams of superfilm No. 4 were placed in about 900 ml. of water and heated at 95°C. for 15 minutes by direct steam injection. The mixture was then diluted to 8.30% solids content by the procedure described above for cornstarch. Five hundred grams of water were added to 500 g. of this solution to obtain a 4.15% solids solution.

#### Determination of Viscosity

A Mac Michael viscosimeter and an Ostwald viscosimeter No. 300 were used to determine viscosity of the solutions. The viscosities of the two converted cornstarch solutions (of high viscosity) and of the superfilm solutions were determined with a Mac Michael viscosimeter. Since the torsion wire used in these experiments was accidentally broken before being calibrated with a solution of known viscosity the viscosity of a 4.15% superfilm solution was determined with an Ostwald viscosimeter. The viscosities of the other solutions were then calculated from the Mac Michael viscosimeter data and the value for the viscosity of 4.15% superfilm solution. The viscosity of the cornstarch which had been modified by the larger amount of hydrogen peroxide was determined by an Ostwald viscosimeter.

#### Tub Sizing Procedure

A laboratory tub sizing apparatus was used. The temperature of the sizing solution was 55°C. in all cases. A ten to seventeen foot length was marked off on each strip of paper tubsized. No weight was placed on the weight rod on the rollers. After the paper had been sized the sections on each side of the markings were discarded and the paper of known length weighed. Several sections of uncoated paper of the same length as that tubsized were weighed and the average taken. From this average weight of uncoated paper corresponding to the given length, the weight of the coated paper and the solids content of the coating solution the amount of starch solids taken up per foot of paper was calculated.

The tub sized paper was tested for basis weight. Mullen Burst (Model B), M. I. T. fold, in and across, Gurley porosity, Elmendorf tear, in and across.

The results are given in Table I.

The data indicate that paper tub sized with superfilm has a greater bursting strength than that sized with converted cornstarch. It is seen that the paper sized with converted cornstarch has very nearly the same bursting strength regardless of the amount of peroxide used in the conversion.

Paper sized with superfilm has greater folding endurance, both in the in and across directions than that sized by converted

TABLE I

PHYSICAL PROPERTIES OF PAPER TUBSIZED WITH  
PEROXIDIZED AND SUPERFILM STARCHES

Sizing Solution	Viscosity (poises) at 55°C.	Starch solids taken up g./ft.	Basic Weight lb.		Points	Mullen Burst (Model B)		Point per 100 lb.	M.I.T. Fold Porosity, sec/100 cc. In		Curley Porosity, g./sheet	Elmendorf Tear Across
			17x22/500	18.7		29.8	159		230	50		
-----	--	---										
Cornstarch, 8.30%	0.0500 <sup>a</sup>	0.12	19.8	39.4	199	335	79	2120	89	102		
Cornstarch, 4.15%	0.0152 <sup>a</sup>	0.062	19.3	36.6	190	314	70	486	90	100		
Superfilm No.4, 8.30%	0.0182	0.16	20.0	43.7	218	493	100	353	88	96		
Superfilm No.4, 4.15%	0.00918	0.060	19.3	38.4	199	267	85	212	92	99		
Cornstarch, 8.30%	0.0179 <sup>b</sup>	0.119	19.7	39.0	198	288	96	595	89	97		
Cornstarch, 4.15%	--	0.0423	19.5	37.3	191	248	79	243	90	99		

<sup>a</sup>Converted with 1.397 g. of 50% H<sub>2</sub>O<sub>2</sub> per 250 g. of starch

<sup>b</sup>Converted with 4.191 g. of 50% H<sub>2</sub>O<sub>2</sub> per 250 g. of starch

Notes: 100% rag paper used in these experiments  
Tub sizing performed at 55°C.

cornstarch. There seems to be an exception in the case of 4.15% converted cornstarch of high viscosity. The folding endurance of paper sized with this solution in the "in" direction is better than that sized with superfilm No. 4. Paper sized with high viscosity converted cornstarch has a greater folding endurance in the "in" direction than paper sized with low viscosity converted cornstarch. Just the opposite relationship holds for folding endurance in the across direction.

The data given for the Gurley porosity show that paper sized with superfilm is more porous than paper sized with converted cornstarch. Paper sized with high viscosity converted cornstarch has a much lower porosity than that sized with low viscosity converted cornstarch.

There seems to be almost no difference in the tear strength in the "in" direction between paper sized with superfilm and that sized with the two converted cornstarches. The two cornstarch-sized papers have identical values for tear; the 8.30% superfilm has a slightly lower value and the 4.15% superfilm one which is slightly higher.

The tear strength in the "across" direction is less for paper sized with superfilm than for that sized with converted cornstarch. Paper sized with high viscosity converted cornstarch has a greater across direction tear strength than that sized with low viscosity converted cornstarch. There is no difference in the tear strength in the across direction between 4.15% superfilm sized

paper and paper sized with 4.15% low viscosity cornstarch. The tear strength in the across direction of paper sized with 8.30% superfilm is only slightly less than that of paper sized with 8.30% cornstarch of low viscosity.

We may conclude that superfilm No. 4 solutions are distinctly superior to hydrogen peroxide converted cornstarch solutions as a tub size for 100% rag paper. A comparison of the physical properties of paper tubsized with high viscosity converted cornstarch with those of paper tubsized with low viscosity cornstarch shows no consistent pattern.

#### SUGGESTIONS FOR FURTHER WORK

Since hydrogen peroxide converted cornstarch is definitely inferior to superfilm as a tub size it is recommended that no further studies be made with converted cornstarch.

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# PROJECT REPORT FORM

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## ANALYSIS OF THE DISTRIBUTION OF SUBSTITUENTS ON CARBOXYMETHYL- CELLULOSE BY IONOPHORESIS

### INTRODUCTION

In the hydrolygate of carboxymethylcellulose 8 different substances may theoretically be present. These are: unsubstituted glucose, the three mono-substituted glucoses, the three di-substituted glucoses and the tri-substituted glucose.

The amount of each of these can be determined by chemical means as shown by Timell (1). Thus the distribution of carboxymethyl groups on a cellulose chain can be found. It is known that the degree of substitution has great influence on the properties of a cellulose derivative. Little is known, however, about the influence of the distribution of the substituents. This is largely due to the fact that the chemical method of distribution analysis is complicated and time-consuming.

The present work is an investigation of the possibilities of using a combination of paper electrophoresis and chromatography for this analysis.

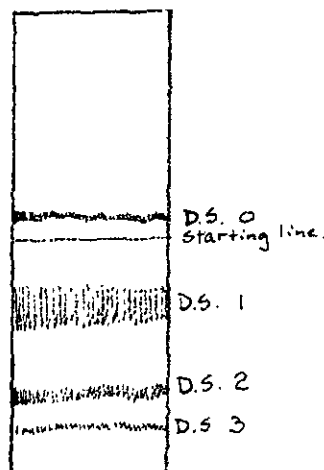
### EXPERIMENTAL AND DISCUSSION

The carboxymethylcellulose used in this work was a Hercules Powder Company "Cellulose Gum" with a degree of substitution = 1.2.

The hydrolysis was carried out as recommended by Timell (1). 50 ml. of sulfuric acid (72%), cooled down to +2°C. (Timell cooled to -6°C.), was added to log GNC in a 200 ml. flask with a ground glass stopper. The flask was shaken for 24 hours and after standing for 20 hours, the dark solution was diluted to 800 ml. with water and boiled under reflux for 8 hours. The acid solution was then filtered for removal of undissolved, ~~basic~~ substances and neutralized to pH 3.4 with the weak ion exchanger Amberlite IR-4B (Rohm and Haas). Finally the solution was concentrated to 200 ml. on a steambath.

When this hydrolyzate was put on paper and run in the ionophoresis apparatus, an ionogram was obtained as shown in Figure 1. A phosphate buffer of pH 9.9 and ionic strength 0.05 was used.

Four well defined zones can be seen and it is assumed that they represent the four possible degrees of substitution as shown on the figure. The D.S.0. zone has moved toward the cathode because of the electro-osmotic flow. D.S.1 is the heaviest one as might be expected when the D.S. of the original carboxymethyl-cellulose was 1.2. D.S.2 has moved about twice as far from the starting



line as D.S.1. D.S.3 is the faintest of the zones and lies quite close to the D.S.2 zone. The migration distances under different conditions

were as shown in Table 1. The distances were measured from the front of the D.S.O zone to the front of each of the three other zones.

TABLE 1

Run nr.	1	2	3	4
pH	9.9	9.9	9.9	12.5
Voltage	500	1000	2000	1000
Duration hrs.	2	1	1/2	1

Migration Distance mm.

D.S. 1	85	84	85	58
D.S. 2	136	135	130	93
D.S. 3	151	152	145	106

Relative migration distance mm.

					Theoretical
D.S. 1	1	1	1	1	1
D.S. 2	16.0	1.61	1.53	1.60	1.61
D.S. 3	1.78	1.81	1.71	1.83	2.01

The theoretical relative migration distances are calculated on the assumption that the charge mass ratio is directly proportional to the migration distance. The observed migration checks very well with the calculated in the case of the D.S. 2 zone, but not by far as well for the D.S. 3 zone. Run nr. 4 which is identical with run nr. 2 except for the pH was made to see if incomplete dissociation of the third carboxyl group might be the reason of the discrepancy. This does not seem to be the case.

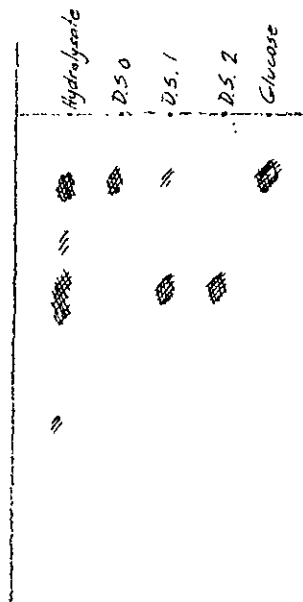
By cutting out and spraying guide strips the three heaviest zones were localized in an ionogram. The sugars were then eluted and

spotted on paper. The paper was developed with an ethyl acetate-acetic acid-water (8:2:2) solvent. After 10 hours the paper was dried and sprayed with aniline hydrogen phthalate solution. The resulting chromatogram is shown in Figure 2.

As expected D.S. 0 shows only the glucose spot.

The very faint glucose spot of D.S. 1 is probably due to incomplete separation of the D.S. 0 and D.S. 1 zones on the ionogram.

The main material of D.S. 1 and D.S. 2 has the same  $R_f$  values when this solvent is used. Two faint spots shown by the total hydrolyzate fail to appear in the chromatogram of the fractions.



#### CONCLUSION

The hydrolyzate of a carboxymethylcellulose can be fractionated with respect to charge by paper electrophoresis. Further fractionation of the mono- and di-substituted material into isomers by chromatography will probably be difficult. It should however be possible to determine the amount of the material belonging to the different charge-groups.

Colorimetric determination of the anthrone complex might be the best method. If analyses of this kind could be made, the degree of substitution of carboxymethylcellulose could be determined using very

small amounts of material. In addition one would get a fairly good idea about the distribution of the substituents on the cellulose chain.

#### REFERENCES

- (1) Timell. Sv. Papperstidn. 55, 649. (1952).

# PROJECT REPORT FORM

PROJECT NO. 1102-8  
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## A PRELIMINARY EVALUATION OF MINNESOTA MINING AND MANUFACTURING COMPANY'S FC-804 AS A SURFACE SIZING AGENT

### SUMMARY

The first portion of the work consisted in surface sizing a 45 lb./ream Weyerhaeuser bleached sulfite stock with solutions of 3.0, 1.5, 0.75, and 0.50% of Minnesota Mining and Manufacturing Company's product, FC-804. The sizing ability of this product was determined by measuring the time of penetration of several oils and greases into the treated stock. Also, the change in contact angle between the oils and paper surface was measured in some instances by a horizontal microscope technique. The oils used were peanut, castor, white carnation, and corn. The greases were spray, butter, and oleomargarine.

Sheets treated with 3.0 and 1.5% of FC-804 resisted penetration of the oils for periods of time exceeding three weeks with the exception of turpentine which penetrated in 20 minutes and 15 seconds, respectively.

Penetration occurred more readily on the sheets sized with a 0.75% solution. It was found that carnation oil penetrated most rapidly (3-1/2 hours) while castor oil penetrated the slowest (6-1/2 hours).

The time of penetration on sheets sized with a 0.5% solution was measured by means of the Feuss penetration apparatus (Institute Method 523). This method allows a standard size drop to fall on a section of the sheet. The time of penetration is measured from the moment the drop makes contact with the paper surface until the portion of paper under the drop is completely wetted. Five runs were made with each oil along with a blank control. It was found that peanut oil penetrated most rapidly (3 seconds) while castor oil penetrated the slowest (65 seconds).

The rate of penetration of greases was also noted. Oleomargarine and spry did not penetrate sheets sized with 3.0 and 1.5% solutions of FC-804 over a period of one week. Butter initially penetrated the sheets sized with a 1.5% solution of FC-804 in 24 hours and complete penetration took place in 72 hours. Butter penetrated the sheets sized with 0.75% of FC-804 the most rapidly (6 hours), while spry penetrated the slowest (26 hours). Butter, oleomargarine and spry penetrated sheets sized with 0.50% FC-804 in 60, 90, and 45 seconds, respectively. On a control sheet butter penetrated in 30 seconds, oleomargarine in 40 seconds, and spry in 15 seconds.

By use of the horizontal microscope technique it was observed that castor and corn oils had the greatest initial contact angles, 94-102° and 100-103°, respectively. Of the two, however, the castor oil had the lower rate of decrease in contact angle which would tend to bear out the previous penetration data. The carnation oil had the lowest initial contact angle, 90-92°, and decreased most rapidly.

## INTRODUCTION

FC-804 is a water soluble chromium derivative of perfluorocaprylic acid. Its molecular structure is believed to consist of two parts, a polar group which can interact with cellulose and a nonpolar fluorinated "tail," which is both hydrophobic and organophobic.

The mechanism which is proposed for its action on paper involves the conversion of the water soluble form into a water insensitive form, with the water and oil repellent group arranged away from the paper.

The most effective use of FC-804 consists of three operations. They are (1) preparation of a dilute treating solution, (2) application of solution to the paper, and (3) application of heat sufficient to properly cure.

## EXPERIMENTAL

The raw stock employed in the surface sizing experiments consisted of laboratory prepared 45 pound per ream sheets of Weyerhaeuser bleached sulfite which had been beaten to an S.-R. freeness of 700 cc.

Four sets of ten sheets each (5 by 8 inches) were tub-sized at room temperature in aqueous solutions composed of 3.0, 1.5, 0.75, and 0.50% of Minnesota Mining and Manufacturing Company's product FC-804 and an equal amount of 20% urea.

Tub sizing was accomplished by dipping the sheets through the solution and then passing between the tub-sizing rolls under a load of



2,200 grams. The sized sheets were then heat cured for 5 minutes on the steam drier at a pressure of 3.5 pounds of steam.

The sheets were coded according to the percentage of 3M's FC-804 in solution. The coding is as follows:

Percentage of FC-804 in Sizing Solution	Code No.
3.0	1102-8-FC-804-A
1.5	1102-8-FC-804-B
0.75	1102-8-FC-804-C
0.50	1102-8-FC-804-D

The size pickup was determined by weighing the sheets before and after tub sizing. The pickup is an average of the ten sheets and the results are shown below:

Code No.	Percentage Pickup
1102-8-FC-804-A	1.03
1102-8-FC-804-B	0.60
1102-8-FC-804-C	0.24
1102-8-FC-804-D	Unable to determine due to change in relative humidity during the interval from the initial weighing to weighing after sizing.

Those sheets sized with 3.0, 1.5, 0.75, and 0.50% FC-804 were tested by merely placing a drop of the given oil, peanut, white carnation, castor, corn, and turpentine, on the wire side of the treated stock and measuring the time required for initial and complete penetration. The

lightly sized sheets (0.50% of FC-804) were tested on the Fuess apparatus (Institute Method 523) employing the above oils. The results of these measurements are listed in Table I.

TABLE I

PENETRATION TIMES FOR SEVERAL OILS ON SHEETS SURFACE SIZED WITH  
0.50% OF FC-804

Oil Used	Penetration Time on Control Sheet, sec.	Penetration Time on Sized Sheets, sec.
Peanut	Instantaneous	3
Castor	35	65
Corn	3	15
Carnation	4	14

Penetration of greases was noted by merely placing a smear of grease on the sheets sized with 0.0, 0.50, 0.75, 1.50, and 3.0% solutions of FC-804. The greases used were butter, spay, and oleomargarine. They did not penetrate the sheets sized with 1.5 and 3.0% solutions over a period of one week with the exception of butter which penetrated the lightly sized sheet.

The penetration times on the more lightly sized sheets are presented in Table II.

TABLE II

PENETRATION RATE OF GREASES

Greases Used	Code No.	Time of Initial Penetration	Time of Final Penetration
Butter	1102-8-FC-804-B	48 Hours	120 Hours
Butter	1102-8-FC-804-C	2-1/4 hours	6 Hours
Butter	1102-8-FC-804-D	Instantaneous	1 Minute
Oleomargarine	1102-8-FC-804-C	3 Hours	8 Hours
Oleomargarine	1102-8-FC-804-D	Instantaneous	1-1/2 Min.
Spry	1102-8-FC-804-C	2-1/2 Hours	7 Hours
Spry	1102-8-FC-804-D	Instantaneous	45 Sec.

Butter penetrated a control sheet in 30 seconds, oleomargarine in 40 seconds, and spry in 15 seconds.

Contact angle measurements of the oils on the sized sheets were made. The technique used was a horizontal microscope apparatus with a rotating stage graduated in degrees. A glass slide with a scratch on it was attached to the stage. A strip of the paper was placed on a rack behind the stage and a drop of oil was placed on the paper. The measurements were taken by aligning the scratch on the glass slide with the tangent of the drop at the interface. The method is believed to be accurate to  $\pm 2^\circ$ .

The results of the foregoing measurements are given in Tables III to VI.

TABLE III

CONTACT ANGLE MEASUREMENTS BETWEEN PEANUT OIL AND PAPER SIZED WITH FC-804

Code No.	Time Interval, hr.	Contact Angle, deg.
1102-8-FC-804-A	0	95
"	1/2	90
"	1-1/2	90
"	4	87
"	7	87
"	31	87
1102-8-FC-804-B	0	94
"	1/2	84
"	1-1/2	80
"	4	75
"	7	75
"	31	75
1102-8-FC-804-C	0	91
"	1/2	88
"	1-1/2	79
"	4	79
"	7	71
"	31	69

TABLE IV

CONTACT ANGLE MEASUREMENTS BETWEEN CASTOR OIL AND PAPER SIZED WITH FC-804

Code No.	Time Interval, hr.	Contact Angle, deg.
1102-8-FC-804-A	0	102
"	1/2	94
"	1-1/2	94
"	4	90
"	7	90
"	31	90
1102-8-FC-804-B	0	100
"	1/2	96
"	1-1/2	93
"	4	90
"	7	90
"	31	90
1102-8-FC-804-C	0	94
"	1/2	89
"	1-1/2	89
"	4	87
"	7	87
"	31	84

TABLE V

CONTACT ANGLE MEASUREMENTS BETWEEN CORN OIL AND PAPER SIZED WITH FC-804

Code No.	Time Interval, hr.	Contact Angle, deg.
1102-8-FC-804-A	0	100
"	1/2	92
"	1-1/2	90
"	4	90
"	7	90
"	31	85
1102-8-FC-804-B	0	102
"	1/2	86
"	1-1/2	86
"	4	86
"	7	79
"	31	77
1102-8-FC-804-C	0	103
"	1/2	87
"	1-1/2	82
"	4	79
"	7	78
"	31	58

TABLE VI

CONTACT ANGLE MEASUREMENTS BETWEEN WHITE CARNATION OIL AND PAPER SIZED  
WITH FC-804

Code No.	Time Interval, hr.	Contact Angle, deg.
1102-8-FC-804-A	0	92
"	1/2	89
"	1-1/2	85
"	4	81
"	7	75
"	31	69
1102-8-FC-804-B	0	90
"	1/2	81
"	1-1/2	80
"	4	77
"	7	77
"	31	63
1102-8-FC-804-C	0	90
"	1/2	78
"	1-1/2	68
"	4	68
"	7	65
"	31	32

# PROJECT REPORT FORM

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REPORT NO. 4  
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PAGE 38 TO 50  
SIGNED Gerald Hoffman  
Gerald Hoffman

A Preliminary Evaluation of American Cyanamid  
Company's Product Cyron as a Sizing Agent for  
Paper Prepared from Bleached Sulfite Pulp

## SUMMARY

Handsheets were made from Weyerhaeuser bleached sulfite with 0.0, 0.1, 0.5, 1.0, 2.0 and 5.0% of Cyron added to the furnish. Sheets were also prepared with rosin at 0.5, 1.0 and 2.0% addition levels with an additional set at the 2.0% level omitting heat drying. The sheets were tested for basis weight, caliper, Schopper tensile, Mullen burst, TAPPI and Galvanic size, and ink penetration. It was found that the sizing ability of Cyron was inferior to that of rosin when employed at the same addition levels. When comparing the results of the Galvanic size test it was found that, at the 1% addition level, Cyron resulted in a value of 3 seconds and rosin 8 seconds. At the 2% level Cyron produced a value of 5 seconds and rosin 23 seconds. Sheets sized with rosin also possessed higher tensile and bursting strength than those sized with Cyron at corresponding addition levels. Sheets sized with 1% of rosin had a tensile strength of 18.3 pounds per inch compared to 15.9 for a sheet with an equal amount of Cyron. The bursting strength decreased with increased additions of Cyron. The resistance to ink penetration increased greatly on those sheets sized with 5% of Cyron. The penetration time was 233 seconds for these sheets as compared with only 8 seconds for sheets sized with 2% Cyron. It is interesting to note that air dried sheets sized with 2% of Cyron had lower values for TAPPI and Galvanic size, but higher values for Schopper tensile, Mullen burst and ink penetration tests than heat dried sheets sized in the same manner.



An attempt was made to measure the contact angle of water and sheets sized with Cyron by the use of a horizontal microscope technique. The water penetration of these sheets was instantaneous and therefore it was impossible to make measurements, however measurements were made on sheets heat cured for two hours at 105°C.

In a separate set of experiments an attempt was made to correlate contact angle and smoothness. Additional sheets were made at the 2% rosin level. One set was not pressed. Two other sets were pressed in contact with stainless steel plates at 50 and 100 pounds respectively. These sheets were submitted for basis weight, caliper, Gurley porosity, TAPPI and Galvanic size and ink penetration tests. Chapman smoothness tests were also run on the plate side of the sheets. The porosity for unpressed sheets was 45 seconds per 100 cc. of air. Sheets pressed at 100 pounds had much lower porosity, 541 seconds per 100 cc. of air. The values of Galvanic and TAPPI size, and time of ink penetration were higher on these sheets pressed in contact with the plates. It is believed that in the case of a water repellent surface such as rosin sized paper the contact angle would be higher for a rough surface than for a smooth one. A definite correlation between contact angle and smoothness, however, was not found.

#### INTRODUCTION

Cyron, developed by American Cyanamid, is an alkaline sizing material for paper and supposedly has been successful in alkaline and acid stocks. Cyron is believed to be especially effective as a beater additive when high water and ink resistance specifications are to be met. No wax, rosin and alum is required.

The coating of raw stock sized with Cyron reportedly results in more uniform coatings with a lesser depth of penetration than conventionally sized papers, resulting in smoother, better printing surfaces. Surface sizing with Cyron is also believed to be effective in producing water resistant paper.

Cyron should not be added to stock when the pH is above 8.5. Inferior sizing values have been noted when Cyron is added to the stock at higher pH values.

Rosin and Cyron should not be used together. They are not compatible and their sizing effects are not additive.

#### EXPERIMENTAL

Three hundred and ninety grams of Weyerhaeuser bleached sulfite were soaked for one hour in six liters of tap water. The Valley beater was filled to the 17 liter mark with tap water which had been adjusted to 25°C. and a pH of 7.0 with 2% sulfuric acid. The soaked pulp was added to the beater and slushed for 5 minutes with balance weight on the bed plate. The pulp was beaten for 46 minutes to a SR freeness of 560 cc. The beater consistency was measured at 1.56%.

Twenty gram aliquots (o.d. basis) of beaten pulp were placed in a bucket. A 2% Cyron solution was prepared by dissolving 15 grams of the product in 750 milliliters of distilled water by heating and agitating for 30 minutes on the steam bath at 175-180°F.

Portions of the Cyron solution were added to the furnish at 0.0, 0.1, 0.5, 1.0, 2.0 and 5.0% based on the weight of the fiber. The Cyron was allowed to stir into the pulp one minute prior to dilution to 0.5% consistency. One and a half gram sheets were made on the Valley sheet mold in the usual manner with pH adjustments. All sheets were pressed for 5 minutes with 50 pounds pressure and dried for seven minutes sheetside up on the steam drier at 3.5 pounds of steam with the exception of a set of sheets prepared at the 2.0% Cyron level which was air dried.

Additional sheets were prepared with rosin at the 0.5, 1.0 and 2.0% addition levels.

The sheets were coded according to the percentage of Cyron and rosin added. The coding is as follows:

Code No.	Percentage of Cyron or Rosin Added Based on Fiber Weight
1102-8-H-C-0	- First set of controls
1102-8-H-C-0.1	- 0.1% Cyron
1102-8-H-C-0.5	- 0.5% Cyron
1102-8-H-C-1.0	- 1.0% Cyron
1102-8-H-C-2.0	- 2.0% Cyron
1102-8-H-C-2.0'	- 2.0% Cyron, air dried
1102-8-H-C-5.0	- 5.0% Cyron
1102-8-H-C-0'	- Second set of controls
1102-8-H-R-0.5	- 0.5% rosin
1102-8-H-R-1.0	- 1.0% rosin
1102-8-H-R-2.0	- 2.0% rosin

All of the above mentioned sheets were tested for basis weight, caliper, TAPPI and Galvanic size, Schopper tensile, Mullen burst and ink penetration. The following table is a list of the data.

TABLE I

Physical Test Data on Paper Sized with Cyron and Rosin

Code No.	Basis Weight, lb. 25 x 40/500	Caliper, inch	TAPPI Size, sec.	Galvanic Size, sec.	Schopper Tensile, lb./inch	Bursting Strength (Mullen)		Ink Penetration, sec.
						points	pt. per 100 lb.	
1102-8-H-C-0	41.9	.0037	1	2	17.4	33.3	80	1
1102-8-H-C-0.1	42.9	.0038	2	2	17.7	31.3	73	2
1102-8-H-C-0.5	42.6	.0040	1	2	16.3	29.9	70	2
1102-8-H-C-1.0	44.8	.0041	1	3	15.9	27.7	62	4
1102-8-H-C-2.0	43.8	.0041	3	5	13.9	22.0	50	6
1102-8-H-C-2.0'	43.9	.0039	2	4	17.4	32.0	73	8
1102-8-H-C-5.0	42.9	.0041	8	18	11.1	17.3	40	233
1102-8-H-C-0'	43.8	.0038	1	2	20.2	34.6	79	1
1102-8-H-R-0.5	43.5	.0039	5	6	19.9	34.6	80	10
1102-8-H-R-1.0	42.0	.0038	6	8	18.3	29.2	70	10
1102-8-H-R-2.0	48.1	.0042	17	23	20.6	34.1	71	77

Gurley porosity was also noted on the sheet coded 1102-8-H-R-2.0.

A reading of 300 seconds for 100 cc. of air was obtained.

Contact angle measurements were made of water on representative samples of handsheets sized with rosin and sheets sized with Cyron and heat cured for two hours at 105°C. It was not possible to make measurements on

the non-cured sheets because water penetrated the sheets too rapidly. The technique used was a horizontal microscope apparatus with a rotating stage calibrated in degrees. A glass slide with a scratch on it was attached to the stage. A strip of the paper was placed on a rack behind the stage and a drop of water was placed on the paper. The measurements were taken by aligning the scratch on the glass slide with the tangent of the drop at the interface. The method is believed to be accurate to  $\pm 2^\circ$ .

The results of the foregoing measurements are given in TABLES II and III.

TABLE II

Contact Angle Measurements Between Water and  
Paper Sized with Cyron and Heat Cured at 105°C.

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-C-0.1	1/6	30
"	1	20
"	2	15
"	3	immeasurable
1102-8-H-C-0.5	1/6	30
"	1	30
"	2	22
"	3	20
"	4	20
"	5	15
"	6	immeasurable
1102-8-H-C-1.0	1/6	33
"	1	30
"	2	30
"	3	28
"	4	25
"	5	25
"	6	22
"	7	15
"	8	11
"	9	11
"	10	10
"	11	immeasurable

TABLE II (Cont.)

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-C-2.0'	1/4	71
"	1	66
"	2	64
"	3	63
"	4	63
"	5	63
"	6	55
"	7	48
"	8	41
"	9	40
"	10	42
"	11	41
"	12	42
"	13	40
"	14	39
"	15	37
"	16	34
"	17	31
"	18	32
"	19	29
"	20	30
"	21	30
"	22	29
"	23	26
"	24	28
"	25	26
"	26	25
"	27	25
"	28	24
"	29	23
"	30	23
"	31	22
"	32	22
"	33	21
"	34	20
"	35	19
"	36	17
"	37	15
"	38	immeasurable
1102-8-H-C-2.0	1/4	30
"	1	25
"	2	20
"	3	19

TABLE II (Cont.)

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-C-2.0	4	19
"	5	17
"	6	17
"	7	16
"	8	17
"	9	15
"	10	15
"	11	13
"	12	12
"	13	immeasurable
1102-8-H-C-5.0	1/4	40
"	1	35
"	2	33
"	3	33
"	4	35
"	5	31
"	6	26
"	7	26
"	8	25
"	9	23
"	10	23
"	11	17
"	12	18
"	13	17
"	14	16
"	15	15
"	16	15
"	17	14
"	18	14
"	19	13
"	20	12
"	21	immeasurable

TABLE III

Contact Angle Measurements Between  
Water and Paper Sized with Rosin

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-R-0.5	0	89
"	5	60
"	10	51

TABLE III (Cont.)

<u>Code No.</u>	<u>Time Interval, Min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-R-0.5	15	47
"	20	42
"	25	35
"	30	24
"	35	15
"	40	8
"	45	immeasurable
1102-8-H-R-1.0	0	93
"	5	81
"	10	78
"	15	76
"	20	72
"	25	60
"	30	52
"	35	35
"	40	24
"	45	20
"	50	8
"	55	immeasurable
1102-8-H-R-2.0	0	100
"	5	88
"	10	85
"	15	71
"	20	70
"	25	67
"	30	66
"	35	65
"	40	61
"	45	54
"	50	42
"	55	16
"	60	immeasurable

In separate experiments three sets of four handsheets each was prepared at the 2.0% rosin level. The first set was not pressed but dried for seven minutes on the steam drier. Two other sets were pressed for five minutes in contact with stainless steel plates at 50 and 100 pounds pressure respectively.



The sheets were coded according to the percentage of rosin added and the extent of pressing. The coding is as follows:

<u>Code No.</u>	<u>Percentage of Rosin Added Based on Fiber Wt.</u>
1102-8-H-R-2.0-0	- 2.0% rosin, no press
1102-8-H-R-2.0-50	- 2.0% rosin, pressed at 50 pounds pressure in contact with stainless steel plates
1102-8-H-R-2.0-100	- 2.0% rosin, pressed at 100 pounds pressure in contact with stainless steel plates.

These sets of handsheets were submitted for basis weight, caliper, Gurley porosity, TAPPI and Galvanic size, and ink penetration tests. The following is the data on the above mentioned tests.

TABLE IV

<u>Sheet No.</u>	<u>Basis Weight, lb. 25 x 40/500</u>	<u>Caliper, inch</u>	<u>Gurley porosity, sec./100 cc.</u>	<u>TAPPI Size, sec.</u>	<u>Galvanic Size, sec.</u>	<u>Ink Penetration, sec.</u>
1102-8-H-R-2.0-0	43.3	.0049	45	9	15	38
1102-8-H-R-2.0-50	44.9	.0036	311	26	56	147
1102-8-H-R-2.0-100	45.4	.0034	541	26	43	173

Chapman smoothness tests were run on the above mentioned sheets and a control. The following table is a list of the readings.

TABLE V

Chapman Smoothness Tests on Sheets Sized  
with Rosin and Pressed at Different Levels

<u>Code No.</u>	<u>Nominal Test Pressure, p.s.i.</u>	<u>Smoothness, percentage</u>	<u>Average Smoothness percentage</u>
1102-8-H-R-2.0			
(Sample I)	35	4	
"	100	6	
"	200	7	
"	300	9	
"	500	12	
1102-8-H-R-2.0			
(Sample II)	35	5	5
"	100	6	6
"	200	7	7
"	300	9	9
"	500	11	12
1102-8-H-R-2.0-0			
(Sample I)	35	5	
"	100	6	
"	200	7	
"	300	8	
"	500	11	
1102-8-H-R-2.0-0			
(Sample II)	35	5	5
"	100	6	6
"	200	7	7
"	300	8	8
"	500	10	10
1102-8-H-R-2.0-50			
(Sample I)	35	6	
"	100	8	
"	200	10	
"	300	13	
"	500	16	
1102-8-H-R-2.0-50			
(Sample II)	35	6	6
"	100	7	8
"	200	10	10
"	300	11	12
"	500	15	15

TABLE V (Cont.)

<u>Code No.</u>	<u>Nominal Test Pressure, p.s.i.</u>	<u>Smoothness, percentage</u>	<u>Average Smoothness, percentage</u>
1102-8-H-R-2.0-100			
(Sample I)	35	6	
"	100	7	
"	200	9	
"	300	11	
"	500	15	
1102-8-H-C-2.0-100			
(Sample II)	35	6	6
"	100	8	8
"	200	10	10
"	300	12	12
"	500	15	15

Contact angle measurements were made between water and sheets sized with rosin and pressed at different levels. The results of these measurements are listed in Table VI.

TABLE VI

Contact Angle Measurements Between Water and Sheets  
Sized with Rosin and Pressed at Different Levels

<u>Code No.</u>	<u>Time Interval, Min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-R-2.0	0	100
"	5	88
"	10	85
"	15	71
"	20	70
"	25	67
"	30	66
"	35	65
"	40	61
"	45	54
"	50	42
"	55	16
"	60	immeasurable

TABLE VI (Cont.)

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-R-2.0-0	0	90
"	5	71
"	10	61
"	15	55
"	20	47
"	25	44
"	30	40
"	35	40
"	40	38
"	45	35
"	50	32
"	55	28
"	60	22
"	65	20
"	70	14
"	75	11
"	80	immeasurable
1102-8-H-R-2.0-50	0	96
"	5	88
"	10	86
"	15	80
"	20	61
"	25	44
"	30	32
"	35	30
"	40	28
"	45	25
"	50	23
"	55	20
"	60	15
"	65	10
"	70	immeasurable
1102-8-H-R-2.0-100	0	97
"	5	91
"	10	89
"	15	89
"	20	85
"	25	80
"	30	64
"	35	47
"	40	39

TABLE VI (Cont.)

<u>Code No.</u>	<u>Time Interval, min.</u>	<u>Contact Angle, deg.</u>
1102-8-H-R-2.0-100	45	38
"	50	38
"	55	38
"	60	35
"	65	34
"	70	33
"	75	30
"	80	30
"	85	27
"	90	22
"	95	20
"	100	18
"	105	15
"	110	12
"	115	8
"	120	immeasurable

# PROJECT REPORT FORM

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✓ PROJECT NO. 1102-8  
COOPERATOR I.P.C.  
REPORT NO. 5  
DATE September 20, 1955  
NOTE BOOK 885  
PAGE 51 TO 54  
SIGNED *Gerald R. Hoffman*  
Gerald R. Hoffman

## A PRELIMINARY EVALUATION OF HERCULES POWDER COMPANY'S PRODUCT AQUAPEL 380 AS A SIZING AGENT FOR PAPER

### Summary

Sheets of 100% rag stock were tub sized with dispersions of Aquapel 380 at the following concentrations: 0.0, 0.1, 0.2, 0.3, 0.5, 1.0 and 2.0%. Additional sheets were coated with a 0.1% dispersion by means of Mayer rods 4 and 8. The sheets were submitted for the following physical tests: basis weight (17 x 22/500), caliper, Mullen burst, Elmendorf tear, M.I.T. fold, Schepper tensile, TAPPI and K.B.B. size, and ink flotation.

The results from the preliminary tests indicate that Aquapel 380 when used as a sizing agent for 100% rag stock is rather ineffective. The TAPPI size times of the blank control and sheets sized with various concentrations of Aquapel are comparable. The K.B.B. size time for sheets tub sized with dispersions at the 0.1 and 0.2% levels were slightly higher than the control. Only at one level, the 0.2% concentration of sizing agent, the K.B.B. size time was comparable to the blank control. The other values were all lower. Sheets coated at the 0.1% level by means of Mayer rods resulted in slightly higher K.B.B. size times. The ink flotation times for those sheets tub sized with dispersions at the 0.1 and 0.2% level and sheets coated with a 0.1% dispersion by means of Mayer rods were higher than the blank control. At the 0.3% level the time was comparable to the control, and with

higher additions of sizing agent, the flotation times progressively decreased. The physical strengths of the tub-sized sheets were not significantly affected by the presence of a small amount of sizing agent. Sheets sized with dispersions of 0.3% or more generally exhibited lower strength values than the control. The strength values progressively decreased with larger amounts of sizing agent present in the sheets.

#### Introduction

Aquapel 380 is a product of Hercules Powder Company. The following information is supplied by the manufacturer: Aquapel is a alkyl ketene dimer containing in admixture, a water-miscible emulsifying agent. The ketene dimer supposedly reacts readily with paper fibers under mild conditions of treatment. In the paper machine drier section, reaction with the cellulose hydroxyls occurs quickly. The paper is not sized until this reaction has occurred. Once the reaction, or cure has been effected the sizing is a permanent and integral part of the paper.

#### Experimental

Twenty-three foot lengths of six-inch width 100% rag stock were tub sized on the laboratory tub-sizing equipment with dispersions containing 0.0, 0.1, 0.2, 0.3, 0.5, 1.0 and 2.0% Aquapel 380. Dispersions were prepared by stirring the dry flake into deionized water at 140°F. The dispersions were a white milky consistency. Tub sizing was accomplished by passing the sheets through the dispersions and then between the tub-sizing rolls under a load of 1500 grams. The sheets were air dried and allowed to cure 24 hours before they were submitted for testing. The

sheets were weighed before and after tub sizing and the percentage pickup determined.

Additional sheets were coated with a 0.1% dispersion by the use of Mayer rods 4 and 8. These sheets and the tub-sized sheets were submitted for the following tests: basis weight (17 x 22/500), caliper, Mullen burst, Elmendorf tear, M.I.T. fold, Schopper tensile, TAPPI and K.B.B. size, and ink flotation.

The data for the foregoing tests are listed in Table I.



TABLE I  
PHYSICAL TEST DATA FOR SHEETS SIZED WITH AQUAPL 380

Concentration of Aquapel Sizing Solution	Pickup, %	Basic Weight, lb. 17 x 22/500	Caliper, in.	Bursting Strength, (Mullen)		Elmendorf Tear, G./sheet		Tear Factor		M.I.T. Fold		Schopper Tensile lb./inch	TAPPI Size, seconds		K.B.B. Size, seconds		Ink Flotation, seconds		
				Points	Points per 100 lb.	In	Ac.	In	Ac.	In	Ac.		Wire	Felt	Wire	Felt	Wire	Felt	
Blank Control	--	19.3	0.0038	30.0	155	83	95	4.30	4.92	191	53	26.2	13.7	24	22	64	56	90	108
1%, Sheets tub sized	0.17	19.5	0.0040	30.0	154	89	95	4.56	4.87	201	50	25.1	12.8	19	19	54	48	143	125
2%, Sheets tub sized	0.35	19.7	0.0041	30.6	155	87	98	4.42	4.97	212	46	24.6	12.7	22	22	65	57	129	107
4%, Sheets tub sized	0.58	19.5	0.0040	29.0	149	88	96	4.51	4.92	172	42	23.3	12.4	20	20	55	57	94	97
5%, Sheets tub sized	0.82	19.6	0.0040	28.6	146	87	95	4.44	4.85	169	41	24.8	12.4	20	20	56	50	73	69
6%, Sheets tub sized	1.97	19.7	0.0040	28.1	143	84	93	4.26	4.72	130	46	22.9	11.5	20	20	54	52	75	84
8%, Sheets tub sized	4.48	19.8	0.0040	26.2	132	82	98	4.14	4.95	129	34	23.0	11.4	20	20	39	38	71	59
1%, Sheets coated using Mayer Rod No. 4	0.10	19.5	0.0040	30.7	157	86	97	4.41	4.97	190	50	25.6	13.2	20	19	77	70	107	105
1%, Sheets coated using Mayer Rod No. 8	1.49	19.5	0.0040	30.2	155	86	97	4.41	4.97	189	58	25.2	13.2	19	20	72	73	119	106

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PROJECT NO. 1102-8  
COOPERATOR I.P.C.  
REPORT NO. 6  
DATE 6/26/57  
NOTE BOOK 1368  
PAGE 21 TO 42  
SIGNED *Norman L. Colson*  
Norman L. Colson

## MODIFICATION OF THE JAYME TECHNIQUE TO ACCOMODATE PULP WITH LARGE AMOUNTS OF FINES.

### SUMMARY

The first step in the further development of the modified Jayme technique was to try the old method on samples of highly beaten Jute pulp containing large amounts of fines. The results were highly erratic due to fines packing around the bead causing improper drainage.

To prevent the packing of the fines around the bead three methods were tried, two failed. The first trial was the placing of a 80-mesh screen disc on the top of the glass bead. The second trial was the chipping of the glass bead itself, this and the first method failed to improve drainage. The third method was the use of a .035 g. glass wool pad approximately one inch in diameter. This pad was packed over the top of the bead preventing the fines from packing around the bead.

An average water retention value of the glass wool pad itself was determined by centrifuging two runs of four pads each with just water. It was found that the glass wool pad retained a very small amount of moisture, an average of 2.8 milligrams. To correct for the moisture, the glass wool pad normally retained, the 2.8 milligrams were deducted from the wet weight of the sample pad.

Water retention values were run on samples of highly beaten Jute pulp employing the glass wool pad modification and the results showed a tremendous increase in precision.

The following are four water retention values simultaneously run employing the old method and four employing the glass wool modification method: (The same pulp was used for both methods.)

Values obtained using the old method:	Values obtained using glass wool pad modification:
873.62%	203.55%
852.73%	207.75%
632.69%	208.05%
908.94%	211.00%
Average: 816.99%	Average: 207.59%

#### INTRODUCTION

This is project report no. 6 on project 1102-8 and is concerned with a modification of the Jayme Technique to accomodate highly beaten pulp.

In the past a great deal of difficulty has been encountered in obtaining precise retention values on pulps with large amounts of fines. The lack of precision is believed to be due to a plugging action by the fines around the glass bead resulting in improper drainage. Consequently, the present report deals with ways and means of counteracting this effect.

#### EXPERIMENTAL PROCEDURES

The experimental work began with the employment of the old modified Jayme Technique. Water retention values were run on highly beaten jute pulp. The Modified Jayme Technique procedure was as follows:

Approximately two grams of pulp were soaked in deionized water for twenty four hours in a conditioned room at 72 degrees fahrenheit and 50%

relative humidity. After soaking, 0.1-0.2 g. portions (oven dry basis) were metered out into special centrifuge tubes (see Figure 1) and allowed to drain by gravity until the drainage rate diminished to approximately one drop per minute. Plyofilm covers were then fastened over the tops of the tubes to prevent evaporation. The tubes were placed in waxed wooden supports and the whole assembly was, in turn placed in the 250-ml. cups of a Model V International Centrifuge. The samples were spun at top speed allowing a total centrifuge time of ten minutes. With an effective radius of 13.6 cm. there resulted a relative centrifugal force of 1300 X gravity. After centrifuging, the pulp pads were transferred with tweezers to tared weighing bottles, weighed and dried overnight at 105 degrees centigrade, prior to reweighing. The water retention value in percentage was then computed from ---

$$\frac{\text{wet pad weight} - \text{dry pad weight}}{\text{dry pad weight}} \times 100.$$
 All determinations were made in

quadruplicate. The results may be seen on Table I., Section A. Results obtained from the preceeding method were extremely erratic due to improper drainage. Poor drainage is believed to be caused by fines settling and packing around the glass bead during centrifuging.

Three methods were tried to prevent the fines from packing around the bead. First a 80-mesh screen disc was cut to a size, (approximately 1/4-inch in diameter), so that it would just rest on the top of the glass bead in the special centrifuge tubes. This was found to be unsatisfactory because the fines passed through the screen during centrifuging and blocking of drainage resulted. Chipping and grooving of the glass bead with a three-cornered file was next tried. This method also failed because the fines stopped up the grooves and prevented proper drainage. The next method employed was with the use of glass wool pads. The pads, weighing .035 g., approximately one inch

in diameter, were cut and weighed on the analytical balance. These pads were then placed in the special centrifuge tubes over the glass bead. (See Figure 2). Plain glass beads were used with the glass wool pads. The best results were obtained when the tube was wetted with water prior to placing the glass wool over the bead. A glass rod approximately 1/8-inch in diameter was employed in packing the glass wool over the bead. If the pad did not pack well around the top of the bead one or two drops of water were put on the pad with the glass rod. This procedure prevented the fines from forming a closely packed mat around the bead which would normally hinder drainage and result in extremely erratic swelling values. Water retention values were then run on the highly beaten jute pulp employing the Jayme technique adopting the glass wool modification. The results can be seen on Table I Section B.

An attempt was made to correct for moisture held by the .035 g. glass wool pad and by the fines which had penetrated the pad. First of all four .035 g. pads of glass wool were placed in the special centrifuge tubes and 15 ml. of water were drained through each pad. Plyofilm covers were placed over the tubes and then centrifuged in the same manner as the pulp samples. After centrifuging the pads were transferred to tared weighing bottles, weighed, dried at 105 degrees centigrade overnight and reweighed. The water retention value of glass wool pads were then determined in the same manner as the pulp pads. The glass wool .035 g. pads had an average water retention value of 8.2%. Weight of moisture held by a .035 g. pad =  $.082 \times .035$  which equaled 2.8 milligrams. To enable the aforementioned correction value to be employed it was necessary to weigh each glass wool pad in the same manner as the pulp pad after centrifuging when running swelling values. The 2.8 mg. of moisture plus the dry weight of the glass wool pad was then subtracted from the wet weight of the glass wool pad. The difference was added to the

wet weight of the pulp pad since it was assumed that this difference was the weight of moisture held by fines which had penetrated into the glass wool pad.

A correction for the weight of fines that penetrated into the glass wool pad during centrifuging was considered to be necessary. However, there was a slight loss of glass fiber into the pulp pad during drainage and centrifuging, making it impossible to have a clear separation of the two pads. Therefore ashing of the glass wool pad was carried out to determine the amount of fines present in the pads. The procedure is as follows:

The pulp used was approximately two grams of highly beaten jute which was soaked in deionized water for at least 24 hrs. in a conditioned room (72 degrees F. and 50% R.H.). About 1.5 g. (oven dry basis) were metered out into the special centrifuge tubes and allowed to drain by gravity until the drainage rate diminished to approximately one drop per minute. Plyofilm covers were fastened over the tops of the tubes to prevent evaporation. The tubes were placed in waxed wooden supports and the whole assembly was, in turn, placed in the 250-ml. Cups of a Model V International Centrifuge. The samples were spun at top speed allowing a total centrifuging time of 10 minutes. With an effective radius of 13.6 cm. there resulted a relative centrifugal force of 1300 X gravity. After centrifuging the pulp pads and glass wool pads were separated and the glass wool pads were transferred to tared weighing bottles, dried at 105 degrees centigrade overnight and then weighed. The glass wool pads were then transferred to crucibles and put in the Lindberg muffle furnace and ashed at 600 degrees centigrade, then weighed. The ashed pad weight was then subtracted from the dry weight of the pad before ashing. The difference obtained represents the fines present before ashing. The determinations are shown on Table II. The maximum fines present in a glass wool pad was 1.4

milligrams. The 1.4 milligrams was added to the wet weight of the pulp pad and also to the dry weight of the pulp pad.

There was glass wool fiber that penetrated into the pulp pad during drainage and centrifuging that could not be readily separated with the glass wool pad. Therefore the dry weight of the glass wool pad was not .035 g. as before centrifuging. The difference between the .035 g. weight and the dry weight was then deducted from the wet pulp pad weight, and also dry pulp pad weight, as glass wool fiber weight.

Table III shows correction for moisture retained by .035 g. glass wool pad, for fines, moisture retained by fines and for glass wool retained in pulp pad.

To eliminate the lengthy process of weighing the glass wool pad and the pulp pad separately, it was decided to weigh them as one pad wet and as one pad dry. This would automatically decrease the number of correcting calculations. The only corrections would then be to take the sum of the weight of the .035 g. glass wool pad and the 2.8 mg. weight of moisture it retained and subtract it from the wet pad weight. Then from the dry weight of the pad subtract the .035 g. weight of the glass wool pad. The water retention value in percentage would then be computed from ---

$$\frac{\text{corrected wet pad weight} - \text{corrected dry pad weight}}{\text{corrected dry pad weight}} \times 100.$$

As Table I illustrated, the adoption of the glass wool pad modification greatly increased the precision of the Jayme technique.

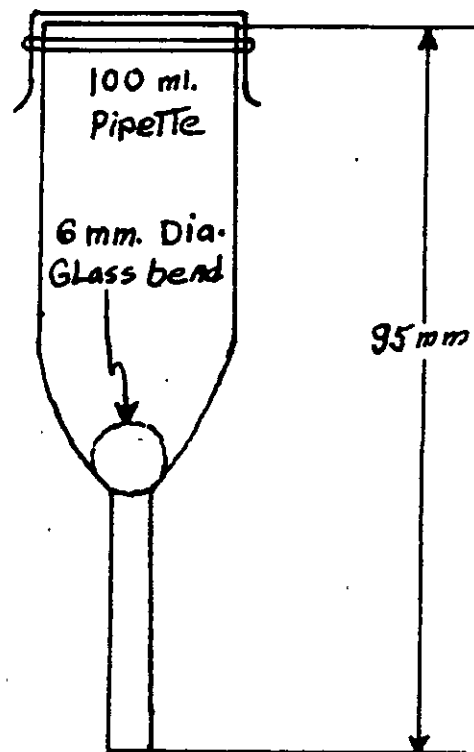


Fig. 1. SPECIAL CENTRIFUGE TUBE,  
GLASS BEAD

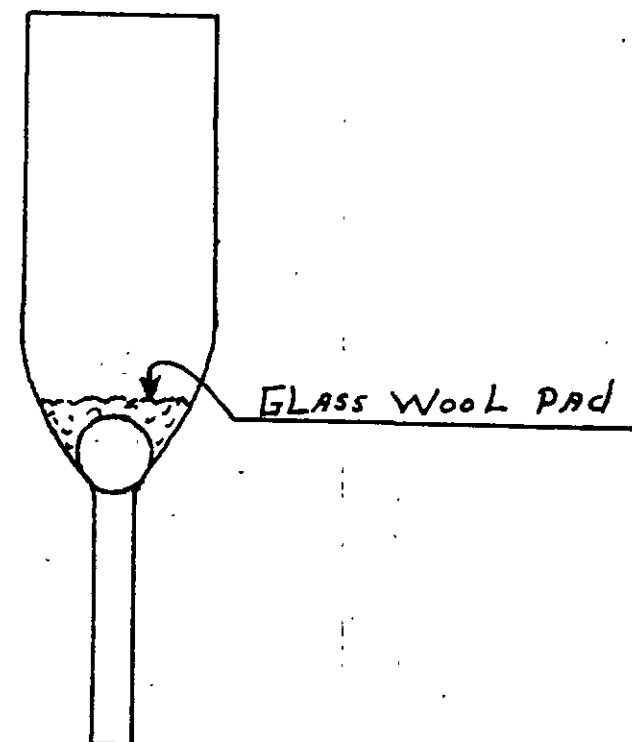


Fig. 2. GLASS WOOL PAD, GLASS BEAD,  
SPECIAL CENTRIFUGE TUB.



TABLE I

A COMPARISON OF SWELLING VALUES ON HIGHLY BEATEN JUTE PULP OBTAINED BY THE JAYME TECHNIQUE  
VALUES OBTAINED BY ADOPTING THE GLASS WOOL MODIFICATION TO THIS TECHNIQUE.

SECTION A Swelling values employing Jayme Technique

<u>Sample bottle No.</u>	<u>Wet weight, g.</u>	<u>Dry weight, g.</u>	<u>Moisture retained by pulp pad, g.</u>	<u>Swelling value, %</u>
1.	1.4098	.1448	1.2650	873.62
2.	1.3767	.1445	1.2322	852.73
3.	.9213	.1254	.7959	632.69
4.	1.3994	.1387	1.2607	908.94

Average of four determinations 816.99%

SECTION B Swelling values employing the Jayme Technique with the adoption of the glass wool modification.

<u>Sample bottle No.</u>	<u>Wet weight, g.</u>	<u>Dry weight, g.</u>	<u>Moisture retained by pulp pad, g.</u>	<u>Swelling value, %</u>
1.	.3679	.1212	.2467	203.55
2.	.4687	.1523	.3164	207.75
3.	.3407	.1106	.2301	208.05
4.	.3648	.1173	.2475	211.00

Average of four determinations 207.59%

TABLE II

ASHING DETERMINATIONS FOR FINES PRESENT IN GLASS WOOL PADS.

<u>Sample No.</u>	<u>Weight of glass wool with fines present</u>	<u>Weight of glass wool after ashing</u>	<u>Calculated fines present</u>
1.	.0355	.0342	.0013
2.	.0360	.0346	.0014
3.	.0361	.0352	.0009
4.	.0345	.0333	.0012
5.	.0336	.0335	.0001
6.	.0351	.0347	.0004

Maximum fines in a single pad: 1.4 milligrams.

TABLE III

Correction For Moisture Retained By Glass Wool, For Fines, Moisture Retained By Fines, And For Glass Wool Fiber Retained In Pulp Pad.

Glass Wool Pad Weights, g.							Pulp Pad Weights							
Sample No.	Wet Weight, g.	Dry Weight, g.	Moisture Retained By Glass Wool Pad and Retained Fines, g.	Correction Factor For Moisture Retained By Glass Wool Pad, g.	Weight Of Moisture Retained By Fines, g.	Glass Wool Weight Prior To Use, g.	Wet Weight, g.	Dry Weight, g.	Correction Factor For Weight Of Fines Retained By Glass Wool, g.	Wet Weight Plus Weight Of Moisture Retained By Fines And The Weight Of Fines, g.	Dry Weight Plus Weight Of Fines Retained By Glass Wool, g.	Corrected Wet Weight Minus Retained Glass Wool Fiber, g.	Corrected Dry Weight Minus Retained Glass Wool Fiber, g.	Swelling, Value, %
1.	.0383	.0330	.0053	.0028	.0025	.0350	.4727	.1456	.0014	.4766	.1470	.4746	.1450	227.31
2.	.0367	.0323	.0044	.0028	.0016	.035	.4302	.1344	.0014	.4332	.1358	.4305	.1331	223.44
3.	.0392	.0322	.0070	.0028	.0042	.035	.4688	.1422	.0014	.4744	.1436	.4716	.1408	234.94
4.	.0386	.0339	.0047	.0028	.0019	.035	.4826	.1472	.0014	.4859	.1486	.4848	.1475	228.68

# PROJECT REPORT FORM

Copies: ✓ Files  
C. L. Garey  
J. W. Swanson  
Reading Copy

PROJECT NO. ✓ 1102-8  
COOPERATOR Institute of Paper Chem  
REPORT NO. Seven  
DATE December 30, 1957  
NOTE BOOK 1368  
PAGE 42 TO 44  
SIGNED C. L. Garey

## EVALUATION OF "PROSEINATE" FROM HEINZKILL SOAP WORKS

### SUMMARY

A material called "Proseinate" was evaluated for its potential use as an adhesive in clay coating for paper. This material is a rapid preparation, from powdered milk, of a casein-like material developed by the Heinzkill Soap Works, Appleton, Wisconsin. The main feature of the product was its rapid preparation (40 minutes) in order to keep its cost low.

This material failed to meet the strength requirement as a coating adhesive in competition with Argentine casein. "Proseinate" gave a Dennison wax pick of -2A at 16% adhesive while Argentine casein gives a 5A pick at 14% adhesive.

### INTRODUCTION

The possibility of obtaining a source of casein that would compete in both quality and price with Argentine casein would be of interest to the paper industry. Casein enjoys some considerable use in paper coating as an adhesive since it does exhibit good film strength at rather low adhesive to clay ratios.

The Heinzkill Soap Works has been attempting to develop a quick, economical method for separating casein from powdered milk in an effort to make use of the large amount of powdered milk available. A sample of the

material was submitted for determination of the possible effectiveness of this quickly prepared casein, to be called "Proseinate," as an adhesive binder in clay coating.

#### EXPERIMENTAL

A prepared casein from powdered milk was submitted by the Heinzkill Soap Works of Appleton, Wisconsin, to be known as "Proseinate". This form of casein was made in 40 minutes from powdered milk. Evaluation was made from visual observation of the material, and from the results of strength of a coating color on paper with this "Proseinate" material as the adhesive. These coatings were then compared to Argentine casein by the use of the Dennison wax pick test. Argentine casein is known to have a wax pick value of 5A at 14% adhesive based on the weight of HT Clay. Coating colors with the "Proseinate" as the adhesive were made up at 45% total solids with HT Clay. The amounts of the adhesive used were 12, 14, and 16% based on the clay and the finally prepared colors were screened through a 200-mesh screen.

Draw downs were made using No. 14 and 20 Mayer rods on Kimberly-Clark Rotofect raw stock. The coated sheets were allowed to dry 1-1/2 hours at 72°F. and 50% relative humidity before Dennison wax pick tests were made.

#### RESULTS

A brief descriptive examination of the product as submitted indicated the possibility of the material to serve as an adhesive. The color was a light straw in appearance which would be good in a coating since it would tend to

change the color of the coating only slightly. A visual observation of foam in the sample indicated that at least in the suspension form it did not appear to possess excessive amounts of air bubbles. The solids concentration was found to be 25.67% which is a little higher concentration than at which Argentine casein is usually prepared. The viscosity of the sample at the above solids appeared to be quite low and thus it could be handled quite easily although no actual viscosity measurements were taken. The pH of the "Proseinate" was 9.15 which compares to Argentine casein when cut with concentrated  $\text{NH}_4\text{OH}$ .

The formulations for the coating colors at 45% total solids as prepared using HT Clay as the pigment are given in Table I together with the resulting pick test for the coated sheets. These coating colors appeared to have a lower viscosity than colors containing Argentine casein at the same percentages of adhesive. No lumps were formed and the colors screened easily.

As shown by the pick test, this material fails completely to meet the strength test as an adhesive in a coating. This "Proseinate" material at 16% adhesive gave a Dennison wax pick test of -2A. When compared to Argentine casein, which gives a 5A pick at only 14% adhesive, the "Proseinate" as prepared in the sample studied does not fulfill the requirements of an acceptable adhesive for paper coating. Coatings were also prepared using a No. 20 Meyer rod in order to increase the coat weight and the resulting pick was found to remain at -2A.

In preparing the coating colors, the stirring and screening of the mixtures tended to beat in a considerable amount of air. An attempt was made to deaerate these suspensions without success. It has been found to be much easier to deaerate colors containing Argentine casein as the adhesive than these colors prepared as above with the "Proseinate."

TABLE I

FORMULATION AND TEST STRENGTH OF PAPER COATING  
 WITH "PROSEINATE" AS THE ADHESIVE

<u>Component</u> Formulation	<u>Percentage of Adhesive</u>		
	12	14	16
HT Clay, g.	25.00	25.00	25.00
Proseinate, g.	11.69	13.64	15.58
Quadrofos, 1N cc.	0.75	0.75	0.75
NaOH, 1N cc.	0.25	0.25	0.25
H <sub>2</sub> O	24.53	23.69	22.86
Dennison Wax Pick Value	--	--	-2A