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# Measuring the Water Retention of Coating Colors

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# MEASURING THE WATER RETENTION OF COATING COLORS

by

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in partial fulfillment
of the
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# ABSTRACT

The water holding properties of coating colors are important for both finished sheet properties and proper runnability on the coater. A test cell was constructed which is capable of measuring water retention of coating slips and predicting water hold out of base papers. The study showed that enzyme conversion time of starch was inversely related to viscosity and water retention. Also the level of sizing was determined to have the greatest influence on water hold out of base stocks.

# INTRODUCTION

As machine speeds increase and more emphasis in placed on rapid drying of coatings, water retention will need to be critically controlled for maxium operation. Increased knowledge of water retention and adhesive migration will provide added information for the selection of coating components and production of base stocks (1). To gain an understanding of water retention, the areas of water retention measurements devices and factors effecting water retention will be investigated.

## Importance of Water Retention

The water holding properties of binders are very important for both finished sheet properties and proper runnability on the coater. Excessive water and adhesive migration to the surface caused by drying can effect surface properties and may cause coating failures (2). The amount of adhesive contained in the coating surface will effect the surface wettability, ink receptivity, wet-rub resistance and glueability (3). The loss of binding power can result in coating pick during printing or converting operations (4). It is important that enough adhesive penetrates the surface of the base stock to ensure proper binding between the coating and fibers, although excessive loss of adhesive to the base stock may cause dusting or picking (5). If the base stock absorbs to much water it could effect drying.

The amount of adhesive penetration into the base stock is related to the method of application and the characteristics of the coating and base sheet. The temperature, total solids, viscosity, pigment type and size, adhesive type and level may all influence the coating water release properties. The contact time (6) and degree of surface sizing (7) can be used to control vehicle penetration.

The right level of adhesive is a balance between many factors. Overuse of adhesive increases costs and reduces gloss and brightness, while insufficient adhesive causes strength problems (8).

In trailing blade and air knife coating operations an interrelationship exists between water retention and rheological properties which influences coating application. The instant the coating film is applied to the paper web the water penetrates the paper surface. The loss of water causes an increase in solids and decrease in fluidity of the coating film. The semi-solid portion is retained by the web, whereas the mobile portion is removed by the trailing blade or air knife. The amount of semi-solid coating formed is related to the water release properties of the coating, flow properties, and solids. This same relationship exists in roll and rod coating applications influencing the film splitting. In smoothing roll processes the relationship is also important (9).

## Water Retention Devices and Factor Influencing Water Retention

Water retention can be measured by using many different methods. One of the oldest methods is outlined by Frost (10). A standard test paper is sprinkled with dry indicator when dropped on a puddle of the coating to be studied. The water retention is the time in seconds needed for the water from the coating to penetrate the base stock and react with the indicator.

N.H. Soemers (11) measured water retention using a film splitting technique. A coating film equal to that used in the coating process to be studied is applied to a glass plate. The base paper is held in contact with the coating film for a set time and pressure. During this time the vehicle penetrates the base stock and reduces the solids and flow properties of the original coating. After the time period has elapsed the pressure is removed and the paper pulled away from the glass causing the coating layer to split. If the coating remains wet, readily deformable and coherent the critical pigment-volume concentration has not been reached. The procedure is repeated at longer contact periods until the critical pigment volume concentration is obtained. This period in seconds is taken as a measure of water retention.

The film splitting technique can be used to predict the runnability of new coating formulas. The film splitting technique uses a controlled film of coating and measures the contact period needed to dewater the coating film. The mill trials showed good correlation between water retention figures and runnability of the Massey and Blade coaters.

Stinchfield, Clift, and Thomas (12) described a water retention test that consisted of measuring the time in seconds that it takes for a current passing through a coated sheet of paper to reach 0.5 ma. The coating is applied to a steel plate terminal, then a test paper and dead weight terminal are placed on top of the coating. The test begins when simultaneously the current and timer are started. This method was found satisfactory for average viscosity coatings, but unable to accurately measure low solids or extremely high viscosity coatings.

Mark (13) developed a resevoir type device which is capable of measuring coating colors ranging from the low consistency of water to the high of putty. The terminal ring cell is versatile test instrument for measuring water retention of paper coatings and water holdout properties of base papers. The cell is easy to handle and clean. The removal of a plastic barrier starts the test by allowing the coating to penetrate the paper sample.

The use of heavy, bulky, filter paper increased test sensitivity and gave reproducible results. The evaluation of the terminal ring cell was conducted as a part of TAPPI Coating Committee Adhesives Task Group Round-Robin Testing Program. Also, Mark conducted tests with the terminal ring cell to determine the relationships between coating binder compositions, coating viscosity, solids, and water retention. In the first test four coatings of increasing ratios of oxidized starch to styrene butadine latex were evaluated. All the coatings contained 16 parts total binder to 100 parts No. 2 coating clay. The tests were run at 55% solids on four different base stocks. The results showed that bulky, porous paper D gave water retention values 10 times as large as paper A, B, and C. Table III demonstrates that increased ratios of starch to styrene-butadiene gave increased viscosity and proportional increases in water retention values.

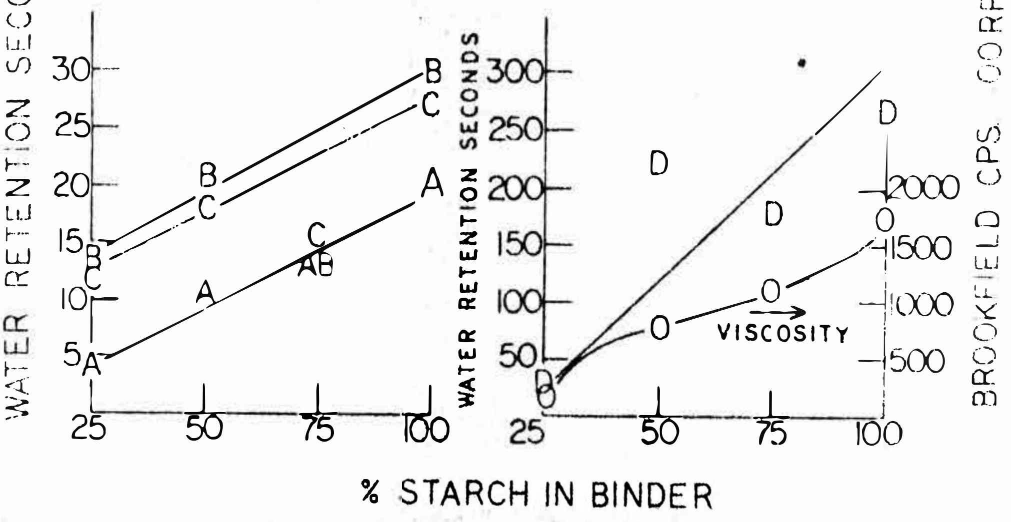
## TABLE III

### WATER RETENTION – EFFECT OF BINDER

| STARCH IN BINDER | | 100% | 75% | 50% | 25% |
|---|---|---|---|---|---|
| **COATING FORMULAE (DRY)** | | | | | |
| CALGON | | .35 | .35 | .35 | .35 |
| CLAY | | 100. | 100. | 100 | 100 |
| STARCH | | 16. | 12. | 8 | 4 |
| SBR | | – | 4. | 8. | 12. |
| COATING SOLIDS (%) | | 54.5 | 54.6 | 55.1 | 54.2 |
| ph | | 5.2 | 5.2 | 5.3 | 5.3 |
| RVT BROOKFIELD (CPS.) | | | | | |
| 100 RPM | | 1,660 | 1,040 | 760 | 120 |
| 10 RPM | | 7,000 | 4,600 | 3,600 | 500 |
| WATER RETENTION (SECONDS) | | | | | |
| "A" BASE PAPER | 1 | 24.0 | 13.0 | 11.6 | 3.9 |
| | 2 | 18.2 | 13.3 | 10.5 | 3.7 |
| | 3 | 17.7 | 12.6 | 10.1 | 3.4 |
| **AVERAGE** | | 20.0 | 13.0 | 10.7 | 3.7 |
| "B" BASE PAPER | 1 | 31.6 | 13.1 | 22.0 | 14.0 |
| | 2 | 29.8 | 11.7 | 19.5 | 13.6 |
| | 3 | 28.1 | 14.2 | 19.0 | 13.8 |
| **AVERAGE** | | 29.8 | 13.0 | 20.2 | 13.8 |
| "C" BASE PAPER | 1 | 26.3 | 12.2 | 18.4 | 11.2 |
| | 2 | 28.0 | 17.4 | 16.9 | 12.4 |
| | 3 | 26.8 | 16.6 | 18.6 | 13.0 |
| **AVERAGE** | | 27.0 | 15.4 | 18.0 | 12.2 |
| "D" BASE PAPER | 1 | 295. | 172. | 164. | 20.7 |
| | 2 | 242. | 188 | 301. | 18.5 |
| | 3 | 253. | 170 | 254. | 18.4 |
| **AVERAGE** | | 263. | 177. | 240 | 19.2 |

FIGURE 4

EFFECT OF STARCH-LATEX BINDER



% STARCH IN BINDER

A sonic method for measuring the extent of coating color drainage was developed by Taylor and Dill (14). The principle is that the migrating water from the coating color swells the fibers of the base stock and decreases the velocity through the base stock. The rate of sorption was measured with sonic probes placed on each side of the coated stock. A model IV sonic pulse progagation meter equipped with strip chart recorder was used to chart the rate of sorption. The sonic water retention value is expressed as a percentage velocity retained after a period of coating penetration, the test can be run in less than a minute because of the rapid clean up.

The sonic test in conjunction with a electronic type water retention device were used in an investigation by Taylor and Dill. The study was to evaluate the effects of additives, viscosity, latexes, clay, pinholes, and base stock properties on water retention.

Taylor & Dills investigation demonstrated that certain additives have a significant effect on water retention. They believed that viscosity is not always the essential factor in influencing water retention.

Three coatings of 58 percent solids with 18 pph latex and 1% carboxymethyl cellulose were prepared. Each of the coatings were equivalent in percent solids, percent latex and percent CMC, each CMC addition was of different viscosity (low, medium, high). Their results showed that water retention as measured by the sonic test is unaffected by viscosity. The two higher viscosity coatings were two viscous to be measured on the electrical conductivity equipment.

"There is a prevalent belief that an increase in coating color viscosity produces higher water retention. In fact, commercial products are being sold on this basis. The following experiments show that viscosity is not always the essential factor. Perhaps indications in the past of the effect of viscosity on water retention may have been due to the test methods used". (15).

Effect of Additives on Clay

| | | | Water Retention | | |
|---|---|---|---|---|---|
| Additive | pH | Viscosity, cp | Sonic, (15 sec),% | Electrical, sec. | Blotter, sec. |
| None | 8.7 | 584 | 51.8 | 12.8 | 15 |
| Scripset 500 | 8.6 | 1460 | 61.4 | 17.7 | 48 |
| Scripset 540 | 8.6 | 850 | 60.6 | 18.3 | |

A new method for measuring water retention was developed by Thomin, Heutew, Anic (16). The device uses the same principle of electrical conductivity for measurement as the S.D. Warren tester and other conductivity testers. The difference is that the coating is applied to both sides of the paper simultaneously without any external application of pressure. Thomin, Heuten, Anic believe that electrical contact problems between the test paper and measuring electrodes are source of error in other testers. This measuring cell uses coating on both sides of the test sheet to reduce contact problems.

Thomin, Heuten and Amic used the test cell to measure the effects of temperature, solids, adhesive level on water retention.

# STATEMENT OF PROBLEM

The initial purpose of this project was to evaluate the effects of starch viscosity on water retention, using a previously constructed cell. However, the cell was not readily available and the main thrust of the project had to be shifted to an evaluation of the cell. The cell was initially evaluated by measuring the water retention of clay slips containing no adhesive at a range of solids levels. Next the cell was used to evaluate the relationship between starch viscosity and water retention. Finally a comparison of base stocks believed to have different holdout characteristics was evaluated.

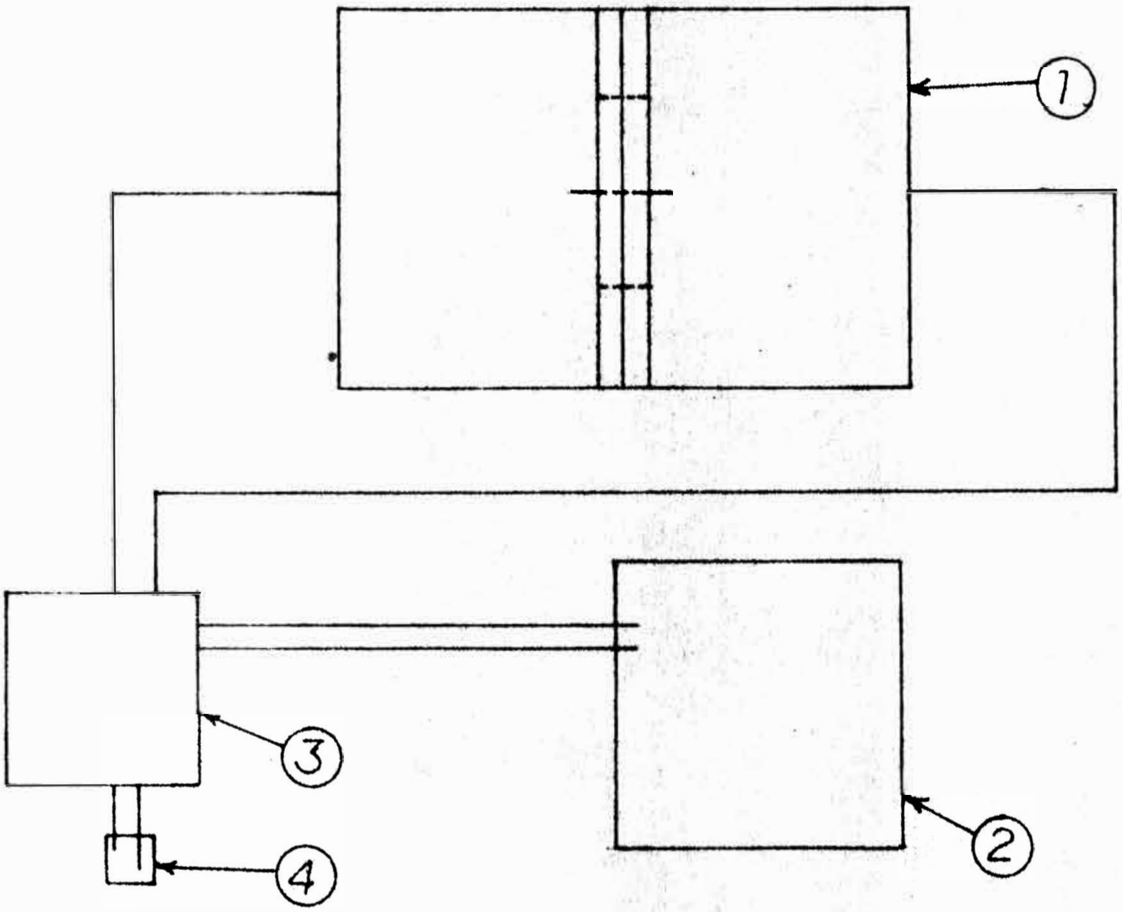
## Design of Water Retention Cell

A modified version of the Thomin, Heuten and Anic (18) electrical conductivity cell was chosen to best meet the requirements of the test. A strip chart recorder was substituted for the current meter and timer. Also a constant current power source was replaced with a current limiting device. The water retention testing device consisted of a measuring cell, power source, current limiting device, and a strip chart recorder, shown in Figures 1-3. The measuring cell has two coating chambers made of thermally and electrically non-conductive material. A sheet of standard test paper is placed between the two coating chambers. A round hole is cut out of the contacting sides of the two chambers to permit the coating to simultaneously penetrate the test paper from both sides. The two insulating plates are used to restrain the coating until the start of the test. The two chambers are bolted together with a paper sample in between, and a copper electrode in each chamber. The water penetrating into the sheet from the coating reduces the resistance of the paper and increases the current through the cell. A Sargent Welch model XKR recorder is utilized to measure current against time.

## Sources of Error

Preliminary work with the test device showed the cell electrodes to be a major source of error. It was found that variations in coating level changed the effective surface areas of the electrodes. A difference in the wetted surface area of the electrodes produced an electro potential

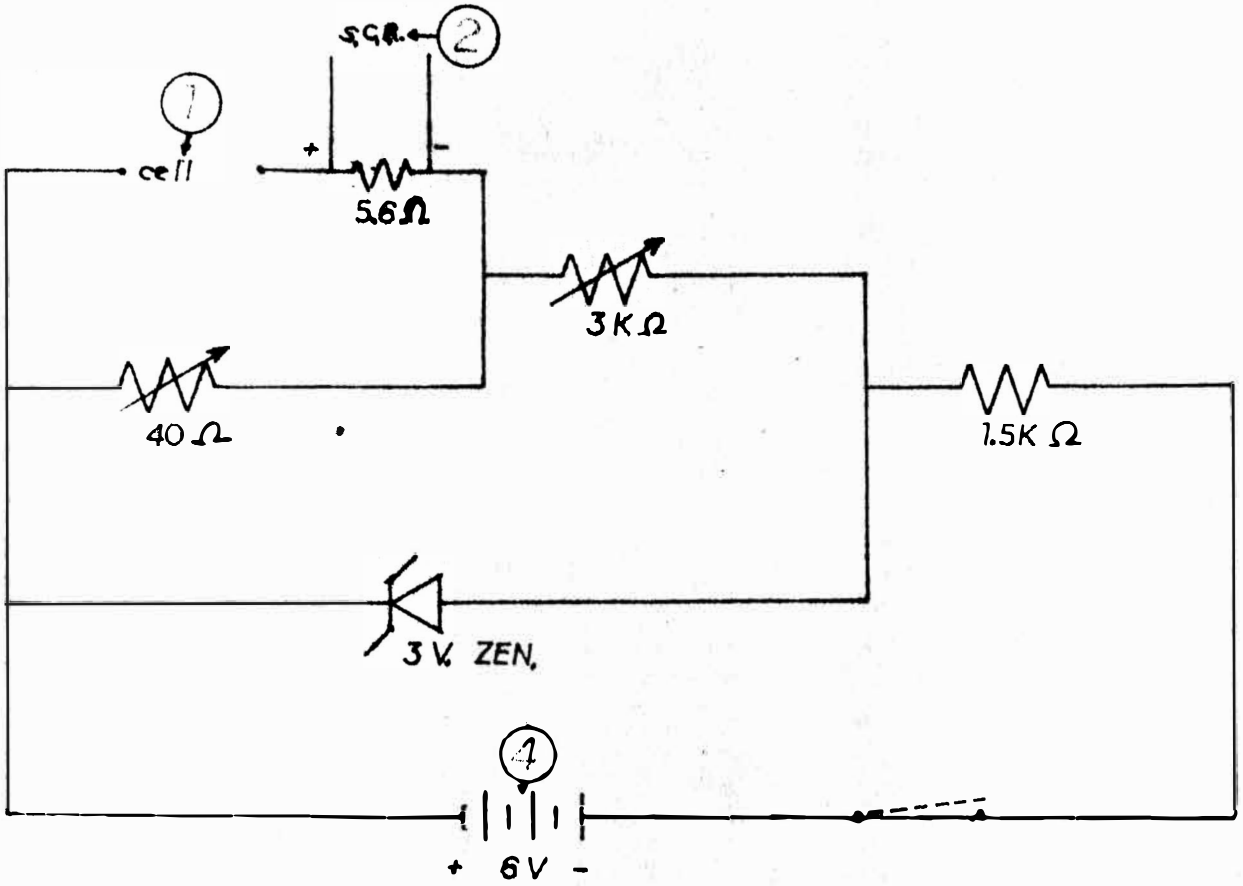
# TEST ASSEMBLY



| NO. | ASSEMBLY | REQ'D |
|---|---|---|
| 1 | WATER MIGRATION CELL | 1 |
| 2 | STRIP CHART RECORDER X-AXIS CHART RATE>10cm/min | 1 |
| 3 | CURRENT LIMITING CIRCUIT | 1 |
| 4 | 6 V LANTERN BATTERY | 1 |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

D. H.

FIG. 1



CURRENT LIMITING CIRCUIT
(ASSEMBLY NO.3)

| DESCRIPTION |
|---|
| 3 VOLTS 1/4 W. ZENER DIODE |
| 5.6Ω 1/4 W. RESISTOR |
| 1.5KΩ 1/4 W. " |
| 40Ω VAR. 2W. " |
| 3KΩ VAR. 2W. " |
| TOGGLE SWITCH ON/OFF |
| OPROX. TOTAL COST |
| |
| |

FIG. 2

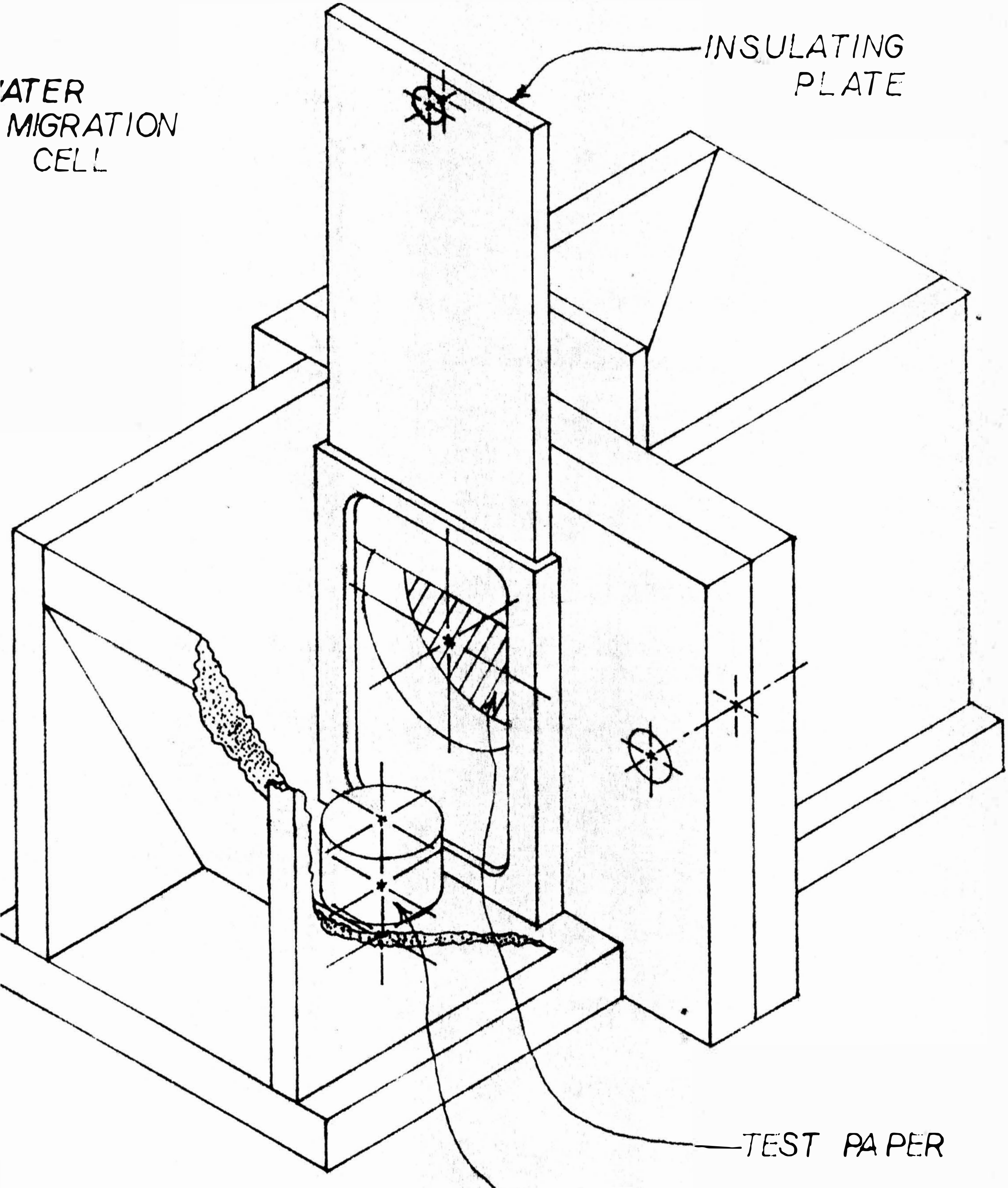

ATER
MIGRATION
CELL
INSULATING
PLATE
TEST PAPER
ELECTRODE

FIG.3

which caused the cell to act as a battery. The problem was corrected by using electrodes of equal size and placing them in the drains of the cells. The electrode remains completely covered and is not influenced by changes in level.

At the initial filling of the cells, the system experiences a decaying voltage. After a period of five minutes the coating of electrodes is completed and the voltage becomes constant. Because of this problem a holding period of five minutes is required beford calibration.

The conductivity of the coating was found to be important. A coating containing no copper sulfate experienced a lower water retention value, than the same coating containing copper sulfate. It is important to compare coatings of equal conductivity.

## Water Retention Procedure

I. Calibration of Tester

- A. Assemble test cell with a sheet of base stock between the two cells.
- B. Place electrodes in bottoms of test cells.
- C. Fill chambers with coating to rim.
- D. Remove insulating plates to start coating flow.
- E. Allow to set for five minutes.
- F. Turn on power source and strip chart recorder.
- G. Set strip chart recorder calibration.
  1. 20 cm/sec speed
  2. 0-10 mv scale
  3. turn off gain
  4. short circuit and adjust zero
  5. use variable resistor in current limiting device to set voltage at .6 millivolts and .6 cm on strip chart recorder.
  6. increase gain to maximum
  7. system is now calibrated

II. Running of Test

- A. Close insulating plates to stop coating flow.
- B. Unbolt test cell leaving electrodes and pool of coating in place.
- C. Clean outside of cell and replace base paper.

D. Reassemble test cell

E. Start chart motor and recorder on strip chart recorder.

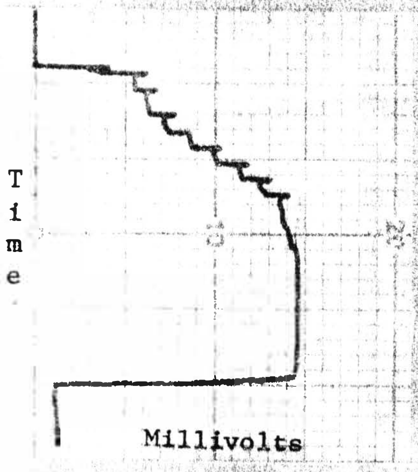
F. Start test by removing insulating plates.

G. Test is completed when voltage equals maximum voltage.

H. Repeat test by starting with No. 1

III. Calculation of Water Retention

A. The water retention value is calculated by taking one half of the maximum voltage drop from the chart paper and finding the number of centimeters that the test ran to reach this value. The millivolts are hortizontal and time vertical on the strip chart paper. The centimeters on the vertical axis are converted to seconds by multiplying by 3 sec/cm.



## Coating Preparation Procedure

I. Clay Dispersion

- A. Add 980 grams of distilled water to a stainless steel container.
- B. Weigh out 1400 grams of predispersed Engelhart HT, a number two coating clay.
- C. Using the bench size Cowles dissolver blend clay into water to produce a good smooth dispersion at 58% solids.

II. Starch Cooking Procedure

- A. Add 733 g of distilled water to stainless steel container.
- B. Weigh out 220 grams of Penford gum 230 at 10% moisture, this will be 200 grams of oven dry starch.
- C. Mix starch into water and agitate for five minutes.
- D. Adjust pH to 6.5 to 7.5 if needed.
- E. Begin heating with indirect steam and slow agitation for 10 minutes to a maximum temperature of 180°F. Gelatinization point will be reached in about 2.5 minutes at 147°F.

III. Enzyme Conversion

- A. Add premeasured 22.5 ml of enzyme solution containing .2 grams of enzyme (.1% based on starch).
- B. Converted starch at 180°F maximum temperature under low agitation for required time period.
- C. After elapsed conversion time, adding 22.5 ml copper sulfate solution containing .2 grams $CuSO_4$ (equal to weight of enzyme).

- D. Turn off steam
- E. Allow to agitate for two minutes to terminate enzyme conversion

IV. Brookfield Viscosity

- A. Place sample of converted starch in testing container.
- B. Allow starch to cool to 150°F for measurement.
- C. Take viscosity at 100 rpm and applicable spindle.

V. Coating Preparation

- A. Weight out 560 grams of convert starch at 20%.
- B. Use dissolver to blend starch into prepared clay slurry at low agitation.

VI. Brookfield Viscosity

- A. Place sample of coating in sample container.
- B. Allow to cool at 120°F.
- C. Take viscosity at 100 rpm with applicable spindle.

## Starch Preparation

222g starch at 10% moisture (200 grams dry)

| | |
|---|---|
| 733 g | $H_2O$ |
| 22.5g | $CuSO_4$ solution (.2 g $CuSO_4$( |
| 22.5g | Enzyme solution (.2 g enzyme) |
| 1000 g | Starch at 20% solids |

## Coating Preparation (10 parts starch to 100 parts clay)

50% solids

| Total | Dry Weight | $H_2O$ | Material |
|---|---|---|---|
| 1400 | 1400 | 0 | Clay |
| 700 | 140 | 560 | Starch |
| 980 | 0 | 980 | Water |
| 3080 | 1540 | 1540 | |

# DISCUSSION OF RESULTS

A comparison of water retention values of clay slips at different solids levels was conducted as a check for reproductivity and accuracy of the testing device. Englehart HT, a number two coating clay, was dispersed in distilled water. The clay slips containing no adhesive were measured for Brookfield viscosity and water retention. Table I below, indicates the close agreement with the evaluation done by Thomin, Heuten, Anic. A reduction in solids and viscosity had a corresponding decline in water retention. Because of the difference in clays, base stocks, and temperature a small variation in values would be expected.

## TABLE I

## EFFECTS OF SOLIDS ON WATER RETENTION

| Solids, % | Viscosity[a] | Water Retention secs. |
|---|---|---|
| 70 | 950 | 4.4 |
| 68 | 450 | 3.7 |
| 61 | 150 | 2.8 |
| 59 | 70 | 2.4 |

DATA OF THOMIN, HEUTEN, ANIC (16)

| Solids, % | Viscosity[b] | Water Retention secs. |
|---|---|---|
| 69 | 347 | 5.3 |
| 65 | 120 | 3.8 |
| 60 | 72 | 2.5 |
| 55 | 49 | 1.9 |
| 50 | 35 | 1.7 |

a) Brookfield, cp, 100 rpm, 25°C  b) Brookfield, cp, 100 rpm, 30°C

Starch coating with a range of viscosities were evaluated to see the relationship between conversion time, viscosity and water retention. A high viscosity hydroxyethyl ether starch (Penford Gum 230) was enzyme converted for 0, 5, 10, and 15 minutes to produce a range of starch viscosities. The unconverted starch exhibited the highest viscosity with decreasing viscosities with longer conversion times. The reaction of enzyme with starch reduces molecular size with time. Starch was the adhesive in a 10 parts adhesive to 100 parts clay pigmented coating. Brookfield viscosities of the converted starches and respective coating were measured.

A 54 lb. Mead base stock was used as the standard test paper in this evaluation. Water retention measurements of the coatings at equal solids and adhesive levels demonstrated the effects of starch modification. As can be seen by Table II, five minutes of conversion time reduced the viscosity from 3640 to 1640 centiposes and also produced a 35 percent drop in water retention. Water retention seconds continue to decrease with increased conversion times and reduced viscosities. This agrees with the 50 percent loss of water retention, Frost experienced with a five minute dextrinization of starch, (see figure 4). Frost indicated no measurements of viscosity (17). But Schoch stated it was desirable to fragment the starch molecule only enough to produce the required viscosity and that smaller molecules had less ability to bind water (18). Frost was able to correlate wax pick test and water retention with the amount of enxyme used in conversions of equal time, (figure 5).

## TABLE II

| Enzyme Conversion in Minutes | Brookfield 150°F Starch Viscosity, cp | Viscosities 100°F Coating Viscosity, cp | Solids | Secs to 1/2 max. |
|---|---|---|---|---|
| 0 | 5000 | 3640 | 53% | 4.8 |
| 5 | 270 | 1640 | 53% | 3.1 |
| 10 | 250 | 1400 | 51% | 2.8 |
| 15 | 150 | 760 | 52% | 2.3 |

## TABLE III

| | Basis Weight lb/25x38x500 | Bulk $ft^3/lb$ | Porosity Sheffield | Sizing HST 20% R | Water Retention sec. |
|---|---|---|---|---|---|
| Base Stock A | 46.7 | .0224 | 11.3 | 262 | 4.2 |
| Base Stock B | 36.0 | .0267 | 10.3 | 252 | 4.0 |
| Base Stock C | 53.6 | .0195 | 7.0 | 219 | 3.2 |
| Base Stock D | 48.0 | .0229 | 7.6 | 8 | 2.6 |

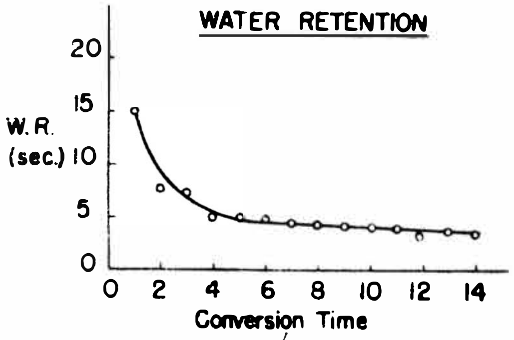


Fig. 4

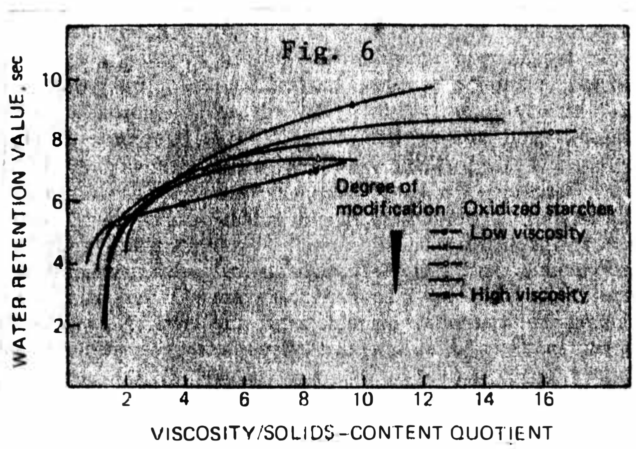


Fig. 6

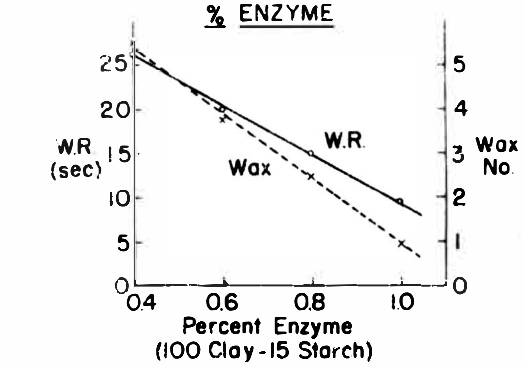


Fig. 5

The work done by Thomin, Heuten, Anic with a viscosity range of oxidized starches doesn't agree very well with Frost's findings or results of this study. Figure 6 shows Thomin, Heuten, Anic water retention values of a clay pigmented coating containing eight parts of styrene acrylate dispersion and six parts of oxidized starch. Only at the lowest viscosity solids quotient does the high viscosity, least modified starch, have the highest water retention. The highest viscosity, least modified, starch would be expected to have the highest water retention at all levels of solids and viscosity. The least modified starch was determined to have the highest water retention in Frost's and this study. See Table II and figure 5. Total adhesive was the main difference between Thomin, Heuten, Anic study and this study. Thomin, Heuten, Anic used styrene acrylate and starch, in this evaluation and Frost's study only starch was used.

The water retention of four coating base stocks, A and D containing low groundwood, B groundwood, and C no groundwood was tested. Looking at Table III, it appears that the bulk of the base stock is not related to water retention. A base stock has the highest water retention but next to the least bulk. The samples with the highest bulk would be expected to be the most porous, having the lowest Sheffield values. Surface sizing could be responsible for the A paper being the least porous sheet. The A paper also has the longest sizing seconds and water retention. The D sheet displayed the lowest water retention and had a higher Sheffield than the C paper. Sizing level appears to have the greatest influence on water retention. Beazley, Windle, and Climpson found that increases in sizing correlated with increases in water retention to a point, then had only slight increases in water retention at higher sizing levels (19). The D base stock was determined in an independent coating evaluation to experience dusting problems during supercalendering (20). While the two other base stocks, A and B, showed little or no dusting. It would appear that there may be some relationship between water retention and dusting. The results of an investigation by Dappen suggest that the adhesive in a coating may be redistributed as a result of the penetration of the fluid phase of the coating into the raw stock (21). This redistribution of adhesive could be responsible for the dusting problem.

# CONCLUSIONS

The water retention cell was found to be valuable device for predicting water holdout properties for base stocks and water retention of coatings. Enzyme conversion time was inversely related to viscosity and water retention. Water retention may be a function of starch molecular size and indirectly related to Brookfield viscosity. The sizing level in base papers appeared to have the greatest influence on water holdout. Data from the four base stocks was not sufficient to draw any conclusions relating bulk or porosity to water holdout.

## LITERATURE CITED

1. Taylor and Dill, Tappi 50 (11): 536 (1967).
2. TAPPI Monograph Series 36, Protein Binders in Paper and Paperboard Coatings, p. 94.
3. TAPPI Monograph Series 17; Starch and Starch Products in Paper Coating, p. 147.
4. Ibid, p. 146.
5. Dappen, J.W. Tappi 34, No. 17: 324-334, (July, 1951).
6. Soemers, W.H., Tappi, 53 (4): 640, (1970).
7. Windle, W., Beazley, K.M., and Climpson, M, Tappi (12): 2227, (1970).
8. TAPPI Monograph Series 17, p. 39.
9. TAPPI Monograph Series 17, pp. 134 and 135.
10. Frost, F.H., Tappi 35 (7)16A, (1952).
11. Soemers, W.H., Tappi 53(4): 640, (1970).
12. Stinchfield, J.C., Clift, R.A. and Thomas, J.J., Tappi 41 (2); 77 (1958).
13. Mark, W.R., Tappi 52 (1): 70, (1969).
14. Taylor, D.L. and Dill, D., Tappi 50 (11): 536, (1967).
15. Ibid
16. Thomin, W.H. Heuten, G., and Anic, J., Tappi 57 (10), (1974).
17. Frost, F.H., Tappi 35 (7): 16A, (1952).
18. Schoch, T.J., Tappi 35 (7): 22A, (1952).
19. Windle, Beazyley, Climpson, Tappi 53 (12):2227 (1970).
20. Personal Contact with Professor James Kline, WMU. Department of Paper Science and Engineering.
21. Dappen, J.S., Tappi 34, No. 17: 324-334, (July, 1951).