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Investigation of Factors Influencing the Use of Wet Strength Resin on Unwashed NSSC Pulp

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Investigation of Factors Influencing the Use of Wet

Strength Resin on Unwashed NSSC Pulp

by

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Abstract

To improve the wet strength of paper, colloidal dispersions of thermosetting wet strength resins are added to the papermaking furnish. However, these resins show low efficiency when applyed to unwashed neutral sulfite semichemical corrugating medium. To determine the reason for this, experiments were made in which corrugating mill stock was made into handsheets using Paramel HE and Kymene 557 wet strength resins.

It was found that Kymene 557 gave poor wet strength when used at levels less than .67%, but that further addition brought increasingly larger gains. The wet strength attained with Paramel HE showed a rapid rise up to a .33% level of addition, but more resin gave smaller gains and the highest wet strength achieved was less than one third that obtained with Kymene. Hydrochloric acid, sulfuric acid and alum were used as pH adjusting agents with Paramel HE. Hydrochloric acid gave the best results and alum caused hard sizing of the sheet. Both Kymene and Paramel were tested on unwashed stock over a range of pH. It was found that Kymene gave best results at pH 8, while Paramel gave gave increasing wet strength with decreasing pH. Through experimentation, it was found that the amount of wood fines in the furnish had little effect on the development of wet strength. Wet strength increased rapidly, however, with washing of the stock. This indicates that the wet strength inhibiting material was part of the residual black liquor carried with the pulp. A list of the materials found in N.S.S.C. spent liquor was compiled, and these materials or representative model compounds were added to washed samples of pulp, which were tested for wet strength development. None of the compounds, except sodium sul-

fite and sodium lignosulfonate, exhibited an effect on wet strength resin efficiency. The sulfite was shown to be slightly detrimental while the lignosulfonate drastically reduced wet strength. As little as 3% sodium lignosulfonate reduced wet strength values by 80%. The lignosulfonate anion could be attracted to, and form a counterion layer around the cationic resin micelles, thus preventing them from being deposited on the fibers. This was believed to be the only major factor inhibiting wet strength on this grade. Wet strength resin was tried on a furnish loaded with calcium chloride in an attempt to change the sodium lignosulfonate into harmless calcium lignosulfonate, but it was found that to form the calcium precipitate, the calcium chloride requirements would be too high to be practical. It appears, that at present, the only way to get practical wet strength on this grade is to use a high level of resin addition or partially wash the pulp or both.

Literature Survey

The uses of paper are often limited by the fact that a typical sheet maintains only about 5% of its dry strength when completely wetted.(1) Early attempts to make paper stand up to water consisted of applying a barrier coating, like polyethylene, or imbedding the fibers in a water resistent material such as asphalt, or sizing the sheet with rosin. However, the first two methods drastically alter the paper and the last only delays the loss of strength. In 1938 a process was patented whereby paper was treated with urea formaldehyde which polymerized under normal drying conditions to form a water insoluble network within the sheet. The application of only about 2% resin to the paper allowed the sheet to maintain 35% of its dry strength when wet.(2) Over the last 25 years a great many new wet strength resins have been produced, and a lot of effort has been expended trying to "wet strength" various grades of paper. One of the grades that has escaped successful and economical wet strengthening is unwashed neutral sulfite semichemical corrugating board.(3)

Until 1962, the urea formaldehyde and melamine formaldehyde resins were the most successful and widely used types.(4) Urea formaldehydes sell for around 22 cents a pound while melamine resins are about 30 cents, so the urea resin is used whenever possible. However, melamine formaldehyde resin maintains its efficiency under a wider range of conditions. It is not as adversely affected by residual black liquor and it cures faster than urea formaldehyde resin under the same conditions.(5) The mechanism of melamine formaldehyde wet strength formation will serve to typify that for many other types of resins, so its action will be discussed in detail.

If melamine and formaldehyde are allowed to react in hydrochloric acid at $100^{\circ}C$.
addition reaction occurs.(6)
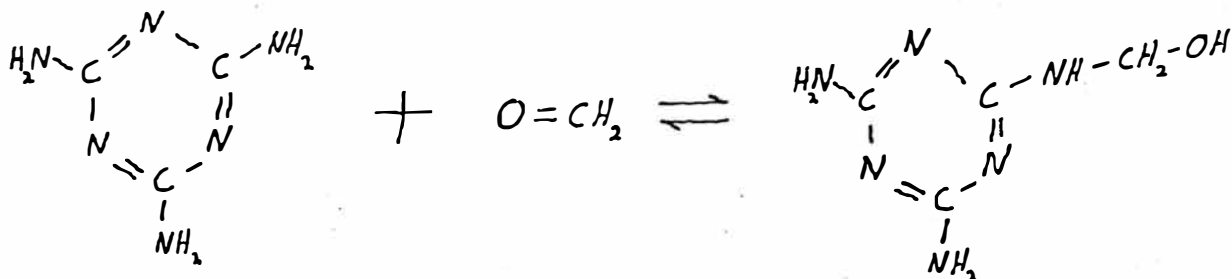
If additional formaldehyde is introduced, the reaction will go further until
hexamethylol melamine is formed, where two methylol groups are attached to each
primary nitrogen atom. In making the first wet strength resins, it was found
that a ratio of one part melamine to three parts formaldehyde gave the best re-
sults. Actually, the melamine had an average of 2.3 methylol groups and existed
in equilibrium with 0.7 parts free formaldehyde. If the melamine formaldehyde
formed is aged in acid solution at a concentration above 12%, at room temper-
ature, a condensation polymerization takes place.(7)
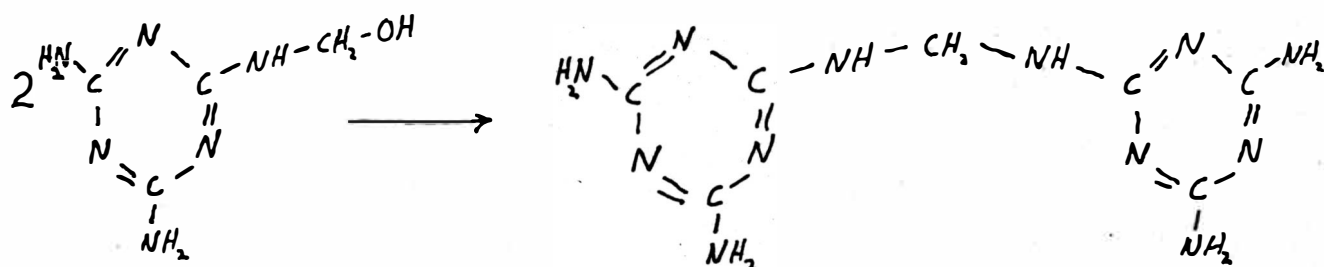
The condensation will proceed through a colloidal stage and then to a gel and
finally form a solid precipitate in about 40 hours, depending on the temperature,
pH, and concentrations. To make the most efficient wet strength resin, the poly-
merization is allowed to proceed to a degree of polymerization of about 20.

A lower D.P. will make the colloid too water soluble and thus give low retention, and a high D.P. will cause the resin to be very susceptible to gel formation, as well as giving poor retention. The melamine formaldehyde is a weak base and accepts a proton in acid solution to form a cation. The like charge repulsion is what makes the colloid stable. However, as the melamine formaldehyde is polymerized, the base strength is decreased and with it the positive charge in the colloidal particles. It is the attraction of this positive charge for the negitive cellulose fibers that holds the resin in the sheet, thus making the weakly cationic high polymer poorly retained.

There are two other practical types of polymer bonding; ether linkage or a self polymerization of the formaldehyde to form a double ether linkage, but these bonds are thought to be of little importance.(8) When the polymer particles are adsorbed on the cellulose fiber and enter the paper machine dryer, they are furthar polymerized to form a highly crosslinked network by the same mechanism. Urea formaldehyde behaves in a similar manner.

It was fairly recently discovered that if one allowed the melamine to age with formaldehyde at a molar ratio of 1:2.5 for several hours, then added more formaldehyde to give a moler ratio around 1:6 the resulting resin gave greater wet strength.(9) These resins are up to 100% more effective in systems with detrimentally high anion concentrations.(10) These are called high efficiency resins.

During the early 1960's, a number of polyamide wet strength resins were introduced. A typical formulation is methylenebisacrylamide copolymerized with ethylenediamine. The polymerization is carried out in water at $85^{\circ}C$. to a D.P. of about 30.(11) Epichlorohydrin is reacted with this polymer to introduce a cationic charge to the resin micelles.

The polyamides are much stronger bases than melamine formaldehyde and thus exist as cationic colloids up to a pH of 11. Thus, they are substantive to fibers in neutral or alkaline stock systems. The polyamides will impart one and a half times the wet-strength per pound, however, their cost is nearly three times that of melamine formaldehyde.(12)

The neutral sulfite semichemical pulping process is a variation of the sulfite pulping which is capable of giving a 90% yield. The cooking chemicals are sodium sulfite buffered with sodium carbonate. The presence of the carbonate gives an initial pH of about 9 so the sodium sulfite exists as sulfite ion.(13) This ion reacts to solubilize the lignin forming sodium lignosulfonate.

$$\begin{array}{c}CH_3 \\ | \\ CHOH \\ | \\ CH_2 \\ | \\ \text{(ring)}-OCH_3 \\ | \\ O \\ | \end{array} \quad + \quad HSO_3^- \quad \longrightarrow \quad \begin{array}{c}CH_3 \\ | \\ CH-SO_3^- \\ | \\ CH_2 \\ | \\ \text{(ring)}-OCH_3 \\ | \\ O \\ | \end{array} \quad + \quad H_2O$$
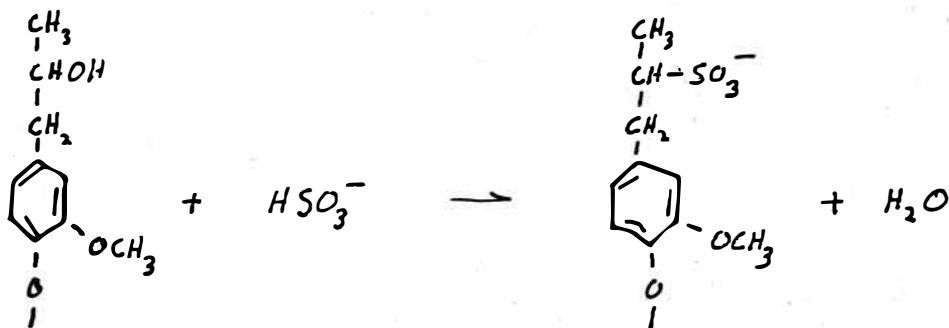
The carbohydrates are partially hydrolyzed during the cooking and saccharic acids are formed that lower the pH to about 7 by the end of the cook. Thus, the cooking liquor may contain about 18% by weight of dissolved solids and 2% suspended solids and contain wood extractives, sugars, sugar acids, ligno-sulfonates, sodium bisulfite, sodium bicarbonate, and wood fines.(14) The pulp itself after refining is only slightly fibrillated and is partially covered with lignin, some of which is sulfonated.

At the Menasha Corporation corrugating mill, the chips are pressed to remove some of the pulping liquor, then diluted with white water, refined, and run over the

Fourdrinier paper machine.

Unbleached neutral sulfite semichemical pulp, that has been washed, is suitable for development of wet strength to a value of about 33% of its dry strength with urea formaldehyde at 1.5% resin addition. Slightly higher results are obtained with melamine and polyamide resins in commercial use when the pulp is partially washed. In addition to the NSSC fibers, there is approximately 18% waste kraft corrugated board in the furnish. Kraft is especially substantive to melamine resin and should assist in developing wet strength. This means that it is probably not some characteristic of the pulp, but the residual black liquor with it, that prevents wet strength development.

As previously mentioned, the residual black liquor has a pH of about 7 and melamine resins are only effective in the range from 3.5 to 5.5. In order for the resin to be used, the pH would have to be reduced. This can be economically done with alum, aluminum chloride or a mineral acid. Because of the buffered state of the system, a large amount might be required. If alum were used the sulfite ion concentration would probably become critically high. Aluminum chloride costs about three times as much as alum and the large amount required might be economically prohibitive. Hydrochloric acid would probably be the most economical chemical to lower the pH and would not introduce wet strength inhibiting ions.

Sodium bisulfite can be made to react with melamine or urea formaldehyde to form a sulfonated anionic molecule. This anionic molecule would not be

substantive to cellulose and the resin would not be retained . This mechanism is unlikely, however, because the reaction only proceeds rapidly at a higher temperature, 100°C., and higher pH, 9.5, than are experienced in the stock system.

The high yield pulp consists of fairly stiff lignin covered fibers which tend to give a large amount of crill during refining. Because this material has a large surface area and is poorly retained, it tends to pick up a disproport- ionate amount of resin and carry it through the wire. The white water system at the Menasha mill is quite closed, so that the fines concentration is about 18 pounds per thousand gallons of white water. It might be possible, however, that since the white water is recirculated, the resin carrying fines would be retained on a subsequent pass over the machine.

The largest single component in the N.S.S.C. black liquor are sodium lignosul- fonates, making up about 60% of the dissolved solids content.(15) These mol- ecules containing the strong sulfonic acid group are ionized at even the lowest pH values used with wet strength resins. The cationic molecules of a synthetic resin would attract the lignosulfonate anions which would surround the resin with a counter ion layer. This would serve to keep the colloid dispersed and unable to deposit itself on the fibers. This is the most likely reason for the failure of the resins in this system.

Therefore, it can be seen that the failure of wet strength resin in this sys- tem would probably be a result of the high fines concentration or the high sod- ium lignosulfonate concentration or a combination of these factors.

In experimental work with wet strength resins, hand sheets are conveniently made on a Noble and Wood sheet mold. Close attention should be paid to the ion concentrations and pH of the water used and a white water recirculating system should be used to reduce the effect of fines loss. The pressing, drying and aging of the hand sheet greatly effects the wet strength obtained. A standard of one pass through a roll press and two minutes on a hot plate at 300°F. followed by two hours in an oven at 105°C. is recommended. The wet tensile test is the most widely used measure of wet strength, but will be reproducible only if the sheets are soaked for a uniform time in water with uniform ion concentration and pH, such as distilled water.

In order to limit the scope of the project, only Hercules Corporation's Kymene 557 polyamide resin and Cyanamid Corporation's Paramel HE resin were used. The pulp for the investigation was all obtained from Menasha Corporation's Otsego board mill. These represent commonly used materials, so the results should be representative of other systems.

Experimental Procedure

The results of the literature search seemed to show that the most critical factors affecting wet strength were; degree of stock washing, pH of the furnish and buffering agent used to adjust it, fines content of the furnish, type of wet strength resin used and resin concentration.

To test the effect on wet strength efficiency of these variables, 4% consistency stock from the machine refiner at Menasha Corperation's Otsego Mill was used. This was diluted to .27% consistency with tap water, then brought to the desired pH and placed in a Noble and Wood stock proportioner. The wet strength resin was added, with stirring, and the furnish allowed to react for 10 minutes with mechanical agitation. Two liters of stock were placed in the Noble and Wood sheet mold, stirred 3 times and the water drained. The wire used was a piece of Menasha Corporation's machine wire of 70 mesh. The wet fiber mat and wire were then run once through a roll press, loaded to 40 pound per linear inch, on a press felt. The sheet was then dried for 2 minutes on a hot plate at about 300 degrees Fahrenheit. It was further dried and cured for 2 hours in a 105 degree Centigrade oven. The sheets were then conditioned at 70 degrees and 50% relative humidity for one day, and tested. Testing was done on the Instrom tensil tester with a jaw width of 13.2 cm. and a pulling speed of 2 cm. per minute. Two 1 inch wide strips were cut, parallel to the wire marks, from each handsheet. One was tested immediatly for dry tensil while the other was soaked for 3 hours in distilled water and tested to give wet tensil. The stock consistency used gave a sheet weight of

about 5.35 grams which corresponds to the 26.5 pounds per thousand square feet of Menasha's corrugating medium. Some of the handsheets were also tested for degree of sizing by the drop test procedure.(16) One drop of distilled water was allowed to fall one centimeter onto the felt side of the handsheet. The time required for the drop to be completly absorbed was recorded.

The first variables investigated were the effect of varying resin concentration and type of buffering agent. Handsheets were prepared and tested according to the previously described procedure using Kymene 557 resin at 0,.33,.67, 1, 2, 4, and 6 percent addition on weight of dry fiber. The pH was 8.5 adjusted with sodium hydroxide. Paramel HE resin was also tested at the same concentrations using three different buffering agents; hydrochloric acid, sulfuric acid and alum. The pH was adjusted to 4.5 in each case.

Next, the effect of varying pH was tested. Because the Paramel buffered with hydrochloric acid and the Kymene with sodium hydroxide proved to be the most effective systems in the first experiment, they were used in the second. Handsheets were made and tested as previously described. Handsheets made with Paramel HE were made at pH 4, 5, 6, and 7 while handsheets using Kymene 557 were made at pH 7, 8, 9, and 10.

The effect of fines was investigated by making handsheets to whose furnish no resin was added. The white water from these handsheets was filtered through Whatman Number 1 filter paper on a Buchner funnel to remove the fines and suspended solids. The filtrate was added to the moist fibers in the mold and

the slurry drained and the filtering process repeated on the white water. The moist fibers were then repulped in the filtered white water, to give a fairly fines free furnish, which was treated with wet strength resins, made into handsheets and tested in the standard manner. The procedure was repeated three times, except in repulping the fibers 33% of the filtered white water was replaced by unfiltered white water in the first case, 67% in the second case and 100% in the third. One percent Paramel HE resin was used at a pH of 4.0 and 2% Kymene 557 was used at a pH of 8.0 to evaluate the effect of fines on both resins.

To determine the effect of residual black liquor on the furnish, Menasha Corperation pulp was given a series of successivly more thorough washings and tested with wet strength resin. To perform the washing, the 4% consistency stock was weighed into 325 gram portions. Each portion was placed in the Noble and Wood sheet mold and the mold filled with tap water to the top mark. The mold was then drained and refilled with water and the process repeated. After the required number of washings, the fiber mats from three portions of stock were combined in a bucket and 13.4 liters of water added. This gave a .27% consistency furnish which was treated with wet strength resin, made into handsheets and tested according to the standard procedure. Paramel at pH 4.0 and Kymene at pH 8.0 were both used in 1% addition on stock that had been washed o, 1, 2, 3, 4, 5, and 6 times.

After carrying out these experiments, one was lead to believe the residual black liquor was the major cause of poor resin efficeincy. Neutral sulfite semichemical black liquor contains numerous closely related chemicals which are nearly

impossible to isolate, but some work has been done in the field and Braun has

a list of common compounds in this mixture.(17) These compounds or related

model compounds were added to washed Menasha pulp and the resulting furnishes

treated with both Kymene 557 and Paramel HE. The stock was washed 4 times as

previously described. Paramel HE was used at pH 4.0 and Kymene 557 at pH 8.0

both at a 1% level of addition using hydrochloric acid and sodium hydroxide

respectivly as buffers.

Sodium lignosulfonate is the major component of neutral sulfite semichemical

black liquor and also the one that was not on hand at Western. This series of

related compounds was isolated from the Menasha Corporation's black liquor by

a modification of the Howard Process.(18) Fifteen liters of spent liquor were

filtered through Whatmann Number 42 filter paper, to remove suspended solids,

then were treated with enough solid calcium hydroxide to bring the pH to 8.5.

The liquor was then heated for 12 hours on a hot plate, at low heat, to allow

the various calcium precipitates to settle. The supernate was then poured off

 and filtered as above and the dregs discarded. The supernate was then treated

with more calcium hydroxide to bring the pH to 11.0 and again left for 12 hours

on the hot plate. The supernate was discarded and the dregs dispersed in enough

saturated calcium hydroxide solution to make an easily pourable slurry. Twenty

milliliters of this slurry were added to each of 6 test tubes in a large cen-

trifuge along with 30 milliliters of saturated calcium hydroxide and the cen-

trifuge run at 1500 revolutions per minute for 30 seconds. The supernate was

discarded and the calcium lignosulfonate particles dispersed in 40 milliliters

of distilled water and then recentrifuged. This water wash was repeated

four more times. The washed solids were then dissolved in 5% hydrochloric acid until only about 20% of the solids remained. The dissolved lignin sulfonic acid was filtered through Whatman Number 1 filter paper on a Buchner funnel. Saturated sodium carbonate was then added to the filtrate until no more precipitate formed upon further addition of carbonate. The slurry was placed in the centrifuge for one minute at 1500 revolutions per minute. The supernate was collected and considered to be a solution of sodium lignosulfonate.

The solids content of this solution was determined by evaporation and the solution added to Menasha pulp washed 4 times as described previously. Furnishes with 0, 2, 4 and 6% sodium lignosulfonate were treated with 1% Paramel HE resin at pH 4.0 and 1% Kymene 557 at pH 8.0 using hydrochloric acid and sodium hydroxide respectivly as buffers. Handsheets were made and tested according to standard procedure.

Although calcium lignosulfonate is not found in the sodium base pulp used, it was also added to washed pulp and tested for wet strength acceptability. This solid calcium lignosulfonate was added at o, 2, 4 and 6% of dry fiber weight, Paramel and Kymene were used and sheets made and tested as above.

Because the calcium lignin sulfonate appeared to be so inert compared to the sodium lignin sulfonate in adversely affecting wet strength development, it was decided to try adding calcium chloride to unwashed pulp to be tested. Calcium chloride was added in 0, 10, and 20% addition to unwashed pulp. Both of the wet strength resins were used on the pulp and handsheets were made and tested.

Discussion

In order to determine which of the possible factors in the unwashed neutral
sulfite semichemical system was responsible for poor wet strength development
it was thought necessary to look at them one at a time, while attempting to
keep other things constant.

Amount of Kymene 557 Resin Used - Kymene 557 wet strength resin was added to
unwashed stock in amounts varying between 0 and 6%, based on weight of fiber.
The data appears on page 14, Table 1, Figure 1. It can be seen from the graph
that it is entirely possible to achieve a high degree of wet strength in this
system. A wet over dry tensil ratio of 30% is desirable but requires an add-
ition of 3% resin. Due to cost considerations, resin addition greater than 1%
is prohibitive. It is interesting to note that up to .67% the sheet gains little
wet strength with additional resin added, but after this, the addition of more
resin gives marked improvement. This might indicate that there is some sort of
chemical reacting with the resin which causes the resin to either be poorly re-
tained or retained in a form which does not contribute to wet strength. As more
resin is added, the interfering species is used up, allowing the additional
resin to function properly. It can be seen from the data that the average
weight of the handsheets tended to vary considerably. The values plotted on
the graph are made up of an average of five individual handsheet values. The
weights of individual handsheets were not closely controlled but this makes
little difference because the sought after variable is a ratio of wet over dry
tensil, which is not affected by sheet weight. Considerable care was taken,
however, to obtain the same overall weight of fiber in each of the batches,

Table 1

% Kymene	Sheet Weight	Dry Tensile	Wet Tensile	% $\frac{Wet}{Dry}$	Sizing
0%	5.46g	15.4kg	.63kg	4.1%	17sec
.33	5.16	14.0	.81	5.8	17
.67	5.30	14.5	.88	6.1	16
1.0	5.54	16.3	1.71	10.5	17
2.0	5.42	15.5	3.57	23.0	17
4.0	5.53	15.7	7.94	50.6	29
6.0	5.34	15.5	9.59	61.9	64

Buffer - - - - - NaOH
pH - - - - - - - 8.5
Stock - - - - - unwashed NSSC

Figure 1   Graph Showing Relation of $\frac{Wet}{Dry}$ Tensile to Percent Kymene
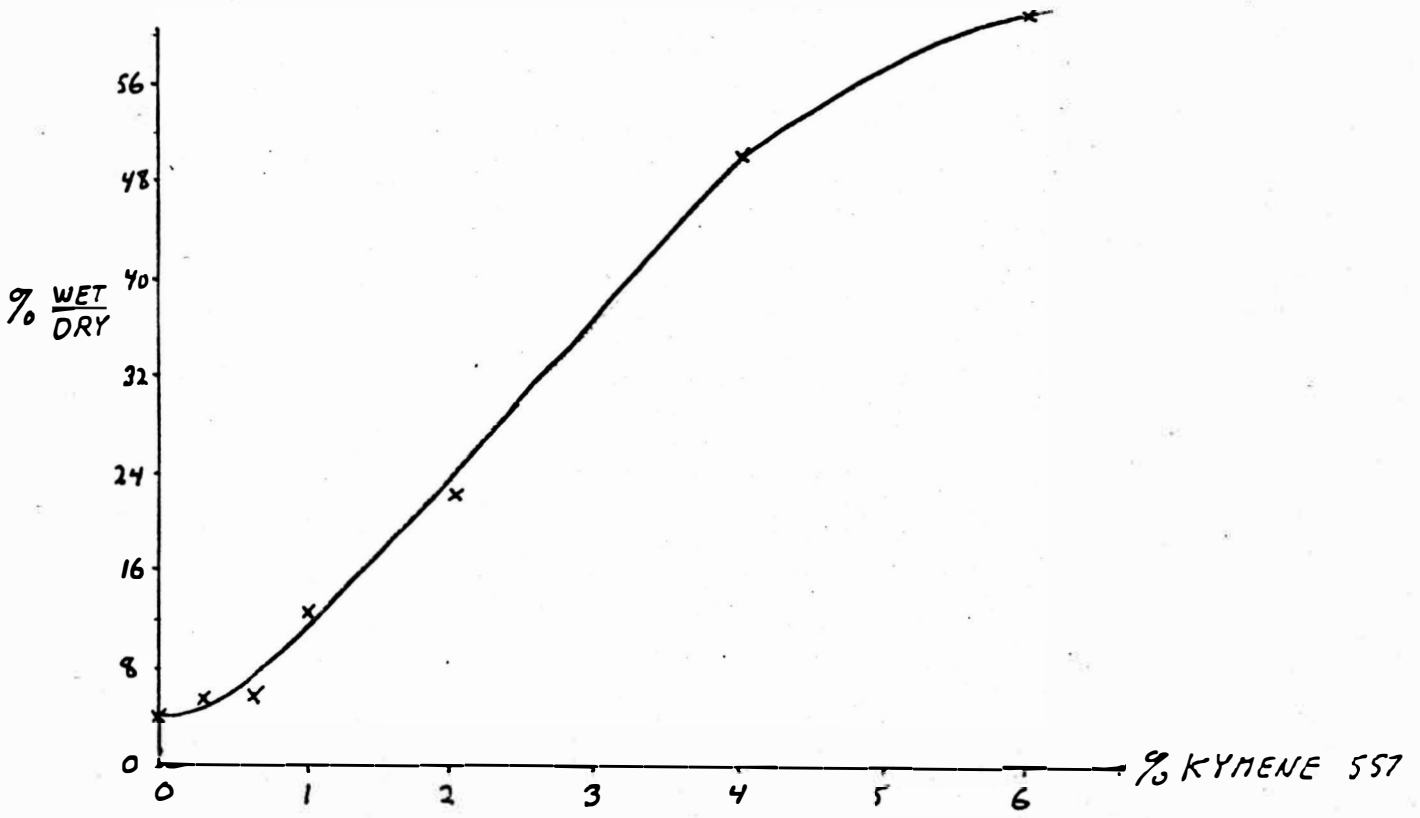
because with a given weight of resin added, a variation in fiber weight would mean a variation in percentage of resin in the sheet. The weight of resin in the sheets should be accurate to plus or minus five percent.

Amount of Paramel HE Resin Used - An experiment to determine the effect of varying amounts of Paramel HE resin on wet strength was carried out in the same manner as with Kymene 557. In the case of the Paramel, three trials were carried out using three different buffering agents to bring the stock from its normal value of 7 to 4.5. The first agent, hydrochloric acid, would be expectd to have little effect on the wet strength, or the sizing of the sheet. The data for varying percentage of Paramel buffered with hydrochloric acid appears on page 16, Table 2 and Figure 2. This curve shows that the first resin added, up to .33% gives some degree of wet strength while additional resin has a reduced effect. This is the opposite of the Kymene 557 curve. It will also be noted that the highest wet over dry tensil ratio is less than one third of the value attained with Kymene. Both Kymene and Paramel when used in the higher concentrations gave considerable foam during sheet making. This is due to the powerful surfactants in the resin formulations used to keep the resin micelles from agglomerating.

The second buffering agent used with Paramel was sulfuric acid. This acid releases sulfate ions, which have an adverse effect on melamine formaldehyde resin retention, so the wet strength obtained would be expected to be lower. One can see that this is the case by looking over the data on page 17, Table 3 and Figure 3. The curve has the same shape as the curve with hydrochloric acid except the wet over dry tensil ratio values are lower. Because this stock con-

Table 2   Varying Level of Paramel HE Addition (HCl)

% Paramel	Sheet Weight	Dry Tensile	Wet Tensile	$\frac{Wet}{Dry}$ %	Sizing
0%	5.42g	14.6kg	.58kg	4.0%	50sec
.33	5.28	14.7	1.18	8.0	53
.67	5.44	14.7	1.36	9.2	63
1.0	5.48	15.6	1.40	9.0	47
2.0	5.65	16.0	1.67	10.4	34
4.0	5.60	16.2	2.54	15.7	38
6.0	5.52	15.5	2.70	17.4	52

Buffer – – – – HCl
pH – – – – – – 4.5
Stock – – – – –Unwashed NSSC

Figure 2   Graph Showing $\frac{Wet}{Dry}$ Tensile Verses Paramel HE Addition

Table Showing Effect of

Table 3   Varying Level of Paramel HE Addition (H_2SO_4)

% Paramel	Sheet Weight	Dry Tensile	Wet Tensile	% $\frac{Wet}{Dry}$	Sizing
0%	5.49g	15.3kg	.55kg	3.6%	34sec
.33	5.43	13.9	1.00	7.2	33
.67	5.48	15.6	.94	6.0	17
1.0	5.57	15.5	1.28	8.3	21
2.0	5.40	14.3	1.33	9.3	24
4.0	5.42	16.6	2.12	12.8	51
6.0	5.55	17.1	2.55	14.9	62

Buffer – – – – H_2SO_4
pH – – – – – – 4.5
Stock – – – – Unwashed NSSC

Figure 3   Graph Showing $\frac{Wet}{Dry}$ Tensile Verses Paramel HE Addition
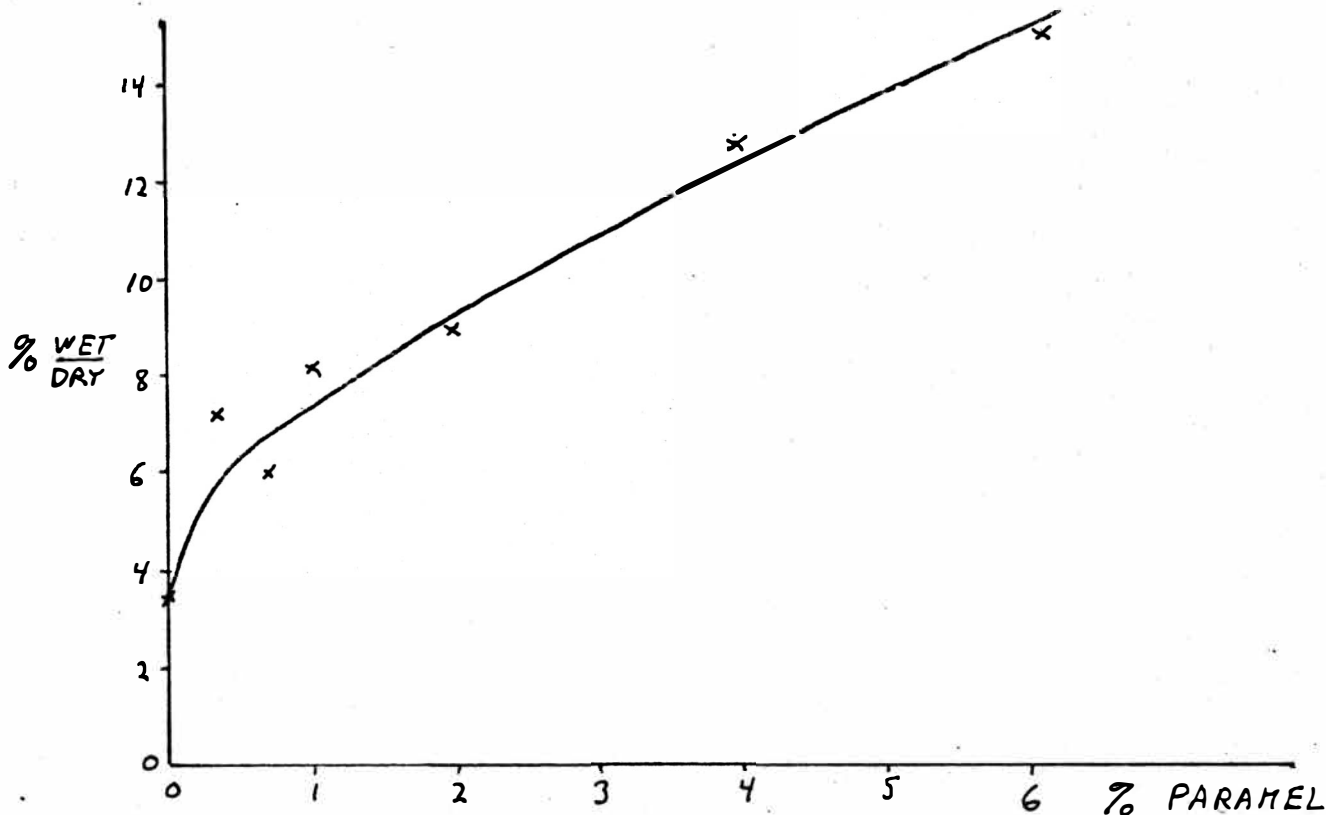
tains residual black liquor, which is buffered to pH 7, it takes much more acid or base to change the stock pH a given amount than would be required in a clean pulp. The bisulfite and bicarbonate ions must be protonated along with some wood and suger acids and organic bases formed from lignin residues. It was observed to require five times more acid to buffer a given amount of unwashed stock than the same amount of clean stock.

The third buffering agent used with Paramel HE resin, was alum. When aluminum sulfate ionizes in water, sulfate ions are released which would adversely effect melamine formaldehyde resin retention. Also the aluminum ions are released which act to bind negitive ionic species to the negitive fibers. It was hoped that the aluminum ions would collect the negitive species in the unwashed stock and make them inactive. Thus, if the species interfering with wet strength resin retention were negitive, the alum might increase the obtainable wet strength. From the data on page 19, Table 4 and Figure 4 it can be seen that this did not happen. The curve maintains the same shape as with the other buffering agents except it is even lower. With 6% resin, the wet over dry tensil ratio is only 9.1%. The fact that alum contains three times as many interfering sulfate ions per mole as sulfuric acid is probably the cause of this low value. There is, however, another problem caused by the alum. The natural wood rosins are sized in the sheet, producing a very water repellant product. The time required for a drop of distilled water to completely penetrate the sheet ran between 17 and 64 seconds with the other systems, but was over 3000 seconds for the system with alum. Actually, the drop evaporated before it penetrated the paper. Because corrugating medium is glued to the
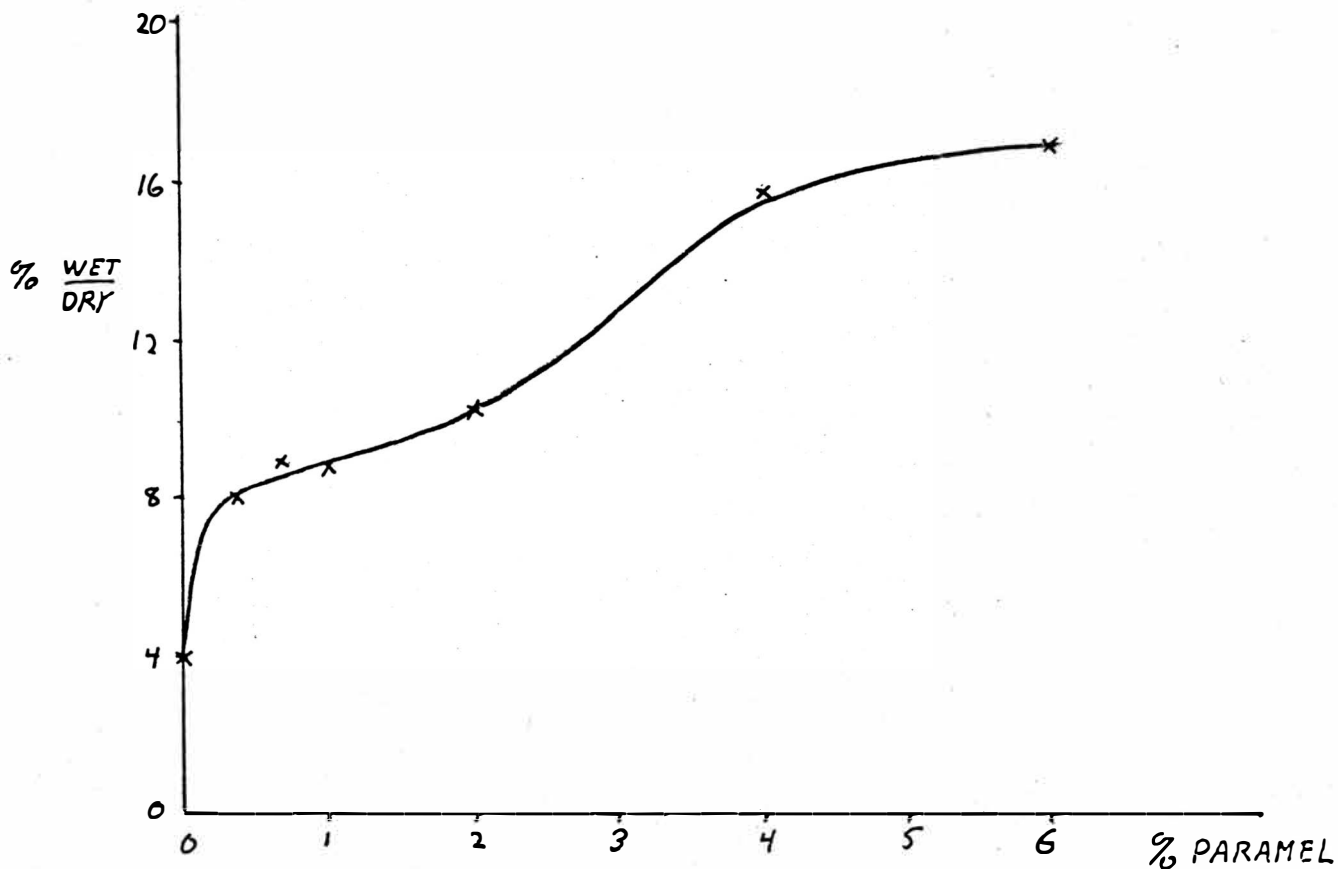
Table Showing Effect of

Table 4   Varying Level of Paramel HE Addition (Alum)

% Paramel	Sheet Weight	Dry Tensile	Wet Tensile	$\%\frac{Wet}{Dry}$	Sizing
0%	5.57g	13.0kg	.64kg	4.9%	3000-sec
.33	5.53	12.1	.74	6.1	3000+
.67	5.35	11.2	.65	5.8	3000+
1.0	5.42	11.4	.77	6.8	3000+
2.0	5.77	11.9	.88	7.4	3000+
4.0	5.58	12.6	1.00	7.9	3000+
6.0	5.52	12.7	1.15	9.1	3000+

Buffer - - - - Alum
Ph - - - - - - 4.5
Stock - - - - Unwashed NSSC

Figure 4   Graph Showing $\frac{Wet}{Dry}$ Tensile Verses Paramel HE Addition
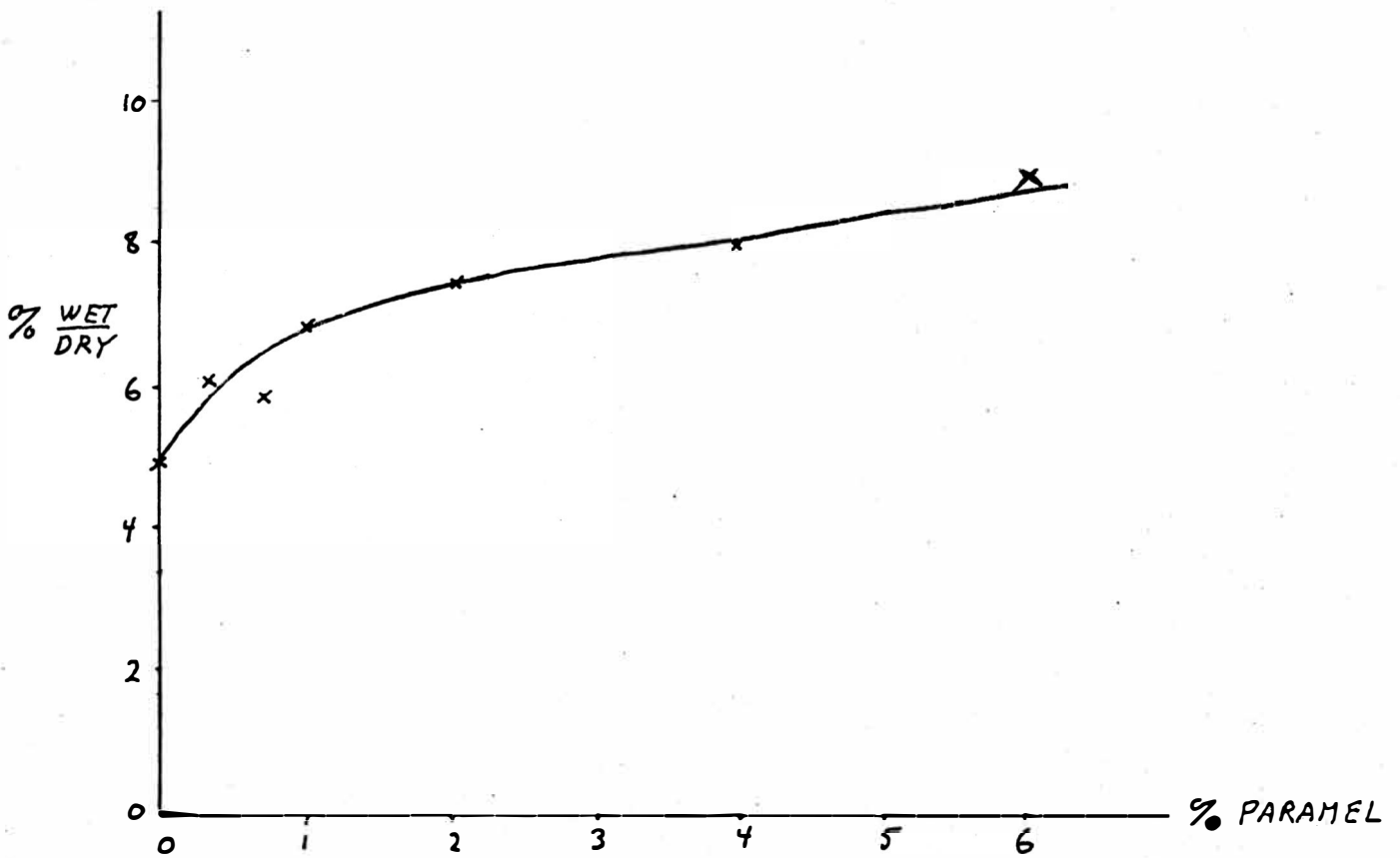
top and bottom liner of box board with water base glue, this hard sizing would make it impossible for glue penetration to take place on a high speed corrugating board machine. The sheets made with alum were soaked for six hours because it took that long for complete wetting.

Range of pH for Kymene 557 and Paramel HE - In order to determine if the low wet strength development in unwashed corrugating stock was caused by some pH dependent factor, the two resins were used over a wide range of pH. The Kymene 557 is designed to be used in basic systems and Paramel HE works well only in acid systems, so each resin was used in its half of the pH range. Since hydrochloric acid appeared to be the most efficient buffering agent for Paramel HE, it was used in these trials. The data appears on page 21, Table 5 and Figure 5. It can be seen that Kymene 557 has a definite peak efficiency at pH 8, so that all Kymene testing done after this point, was done at this pH. The Paramel HE showed a marked increase in efficiency as pH decreased. This resin was not tested at a pH less than 4, though it shows promise in this area. If the wet strength inhibiting factor in the stock was ionized sodium lignosulfonate, as the pH was decreased more of this material would be converted to lignosulfonic acid. This free acid, not being anionic, would probably not interfere with the cationic wet strength resin. Melamine formaldehyde ordinarily does not increase its efficiency at low pH in this way, so it is probable that this is the case. The troubles involved with making paper at a pH less than four would probably be prohibitive and even at pH 4, the wet over dry tensil ratio is only 10.5%. It should be noted that sizing drop test time increases regularly with decreasing pH. This is a major argument for the use of alkaline

Table Showing
Effect of Varying pH

Table 5

pH	Sheet Weight	Dry Tensile	Wet Tensile	%$\frac{Wet}{Dry}$	Sizing
10 Kymene	5.27g	14.2kg	1.25kg	8.3%	15sec
9 Kymene	5.38	15.0	1.40	9.9	16
8 Kymene	5.16	12.9	1.56	11.0	17
7 Kymene	5.41	14.2	1.14	8.8	26
7 Paramel	5.48	13.7	.66	4.8	28
6 Paramel	5.26	13.5	.73	5.4	39
5 Paramel	5.27	14.3	1.11	7.8	51
4 Paramel	5.44	13.6	1.43	10.5	57

Buffers - - - - HCl and NaOH
Resin Addition 1%
Stock - - - - - Unwashed NSSC

Figure 5   Graph Showing $\frac{Wet}{Dry}$ Tensile Verses pH

• KYMENE 557
× PARAMEL HE
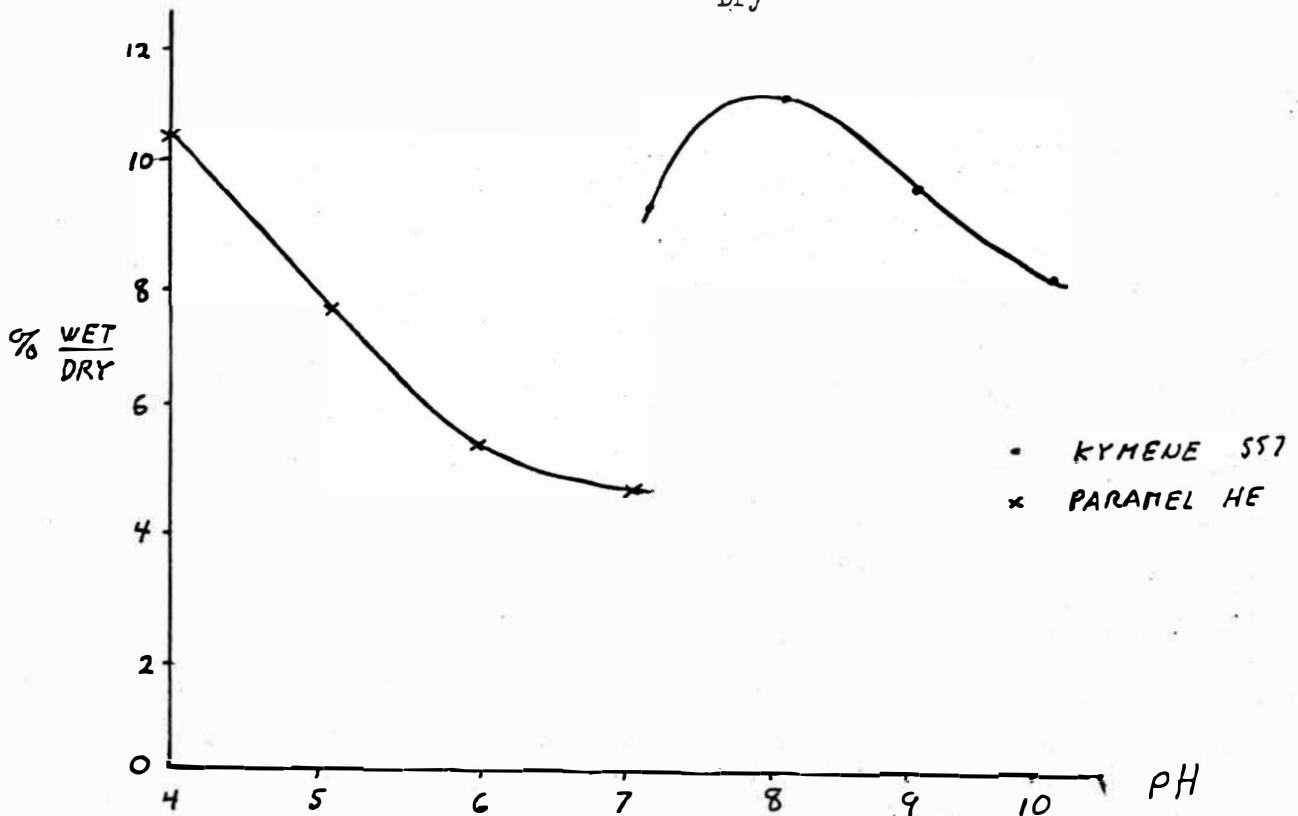
systems and Kymene 557 in the manufacture of absorbant grades. However, in
wet strength corrugating medium it would be best to have a maximum amount
of sizing up to the point where gluing problems developed.

Effect of Fines on Kymene 557 - Because wood fines are smaller particles than
the fibers, they have a larger surface area relitive to their mass than the
fibers. This would mean they could adsorb a disproportionate amount of wet
strength resin and be carried through the wire with the white water. To
investigate this, batches of stock with varying amounts of fines were treated
with 2% Kymene 557. The data appears on page 23, Table 6 and Figure 6. It
can be seen that there is only a slight increase in efficiency in the fines
free system. The fines apparently do not make up a large enough part of the
system to be of significance. Also since part of the fines are caught in the
fiber mat, they do not carry resin away from the sheet.

Effect of Fines on Paramel HE - The same procedure as above was used with Para-
mel HE resin and the results were nearly the same. See page 23, Table 6 and
Figure 6.

Effect of Stock Washing on Kymene 557 - If the factor inhibiting Kymene 557
efficiency is part of the residual black liquor, it should be removed by wash-
ing. Also a well washed system should reveal the inherent wet strength cap-
acity of the pulp. To test this, seven samples of pulp were subjected to suc-
cessivly more complete washings, treated with 1% Kymene 557 and tested for
wet strength. The data appears on page 24, Table 7 and Figure 7. It can be

Table Showing Effect of
Varying Amount of Fines

Table 6

Resin	% Fines	Sheet Weight	Dry Tensile	Wet Tensile	% Wet/Dry
Kymene	0%	5.38g	15.9kg	3.64kg	22.9%
Kymene	33	5.32	15.7	3.45	22.0
Kymene	67	5.40	16.5	3.63	22.0
Kymene	100	5.38	15.5	3.57	21.2
Paramel	0	5.35	16.6	1.84	11.1
Paramel	33	5.33	16.4	1.85	11.3
Paramel	67	5.31	15.8	1.69	10.7
Paramel	100	5.37	16.3	1.78	10.9

Buffers - - - - NaOH and HCl
Resin Addition 2% Kymene and 1% Paramel
Stock - - - - - NSSC Unwashed

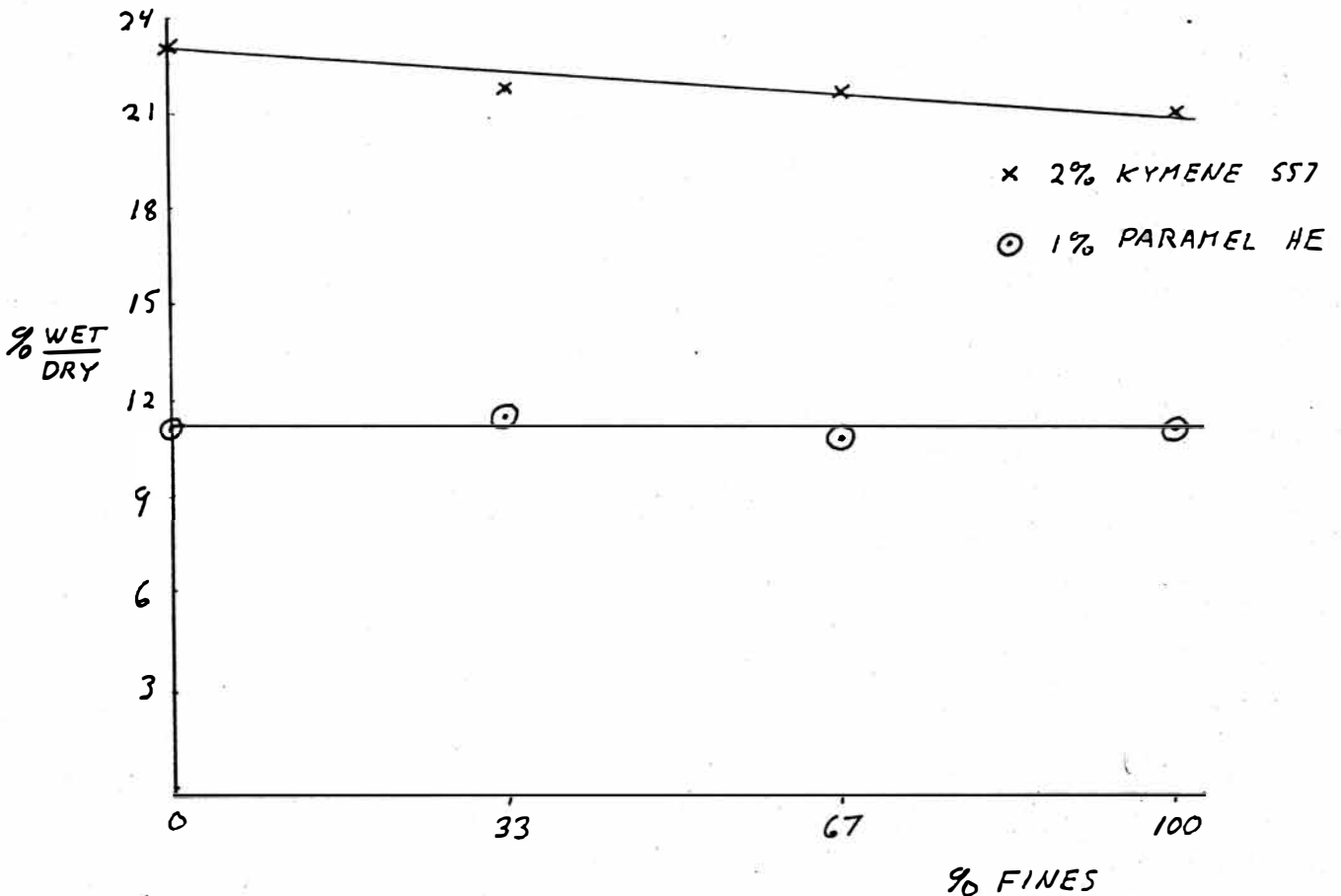Figure 6   Graph Showing Wet/Dry Tensile Verses Percent Fines

× 2% KYMENE 557

⊙ 1% PARAMEL HE

% WET/DRY

% FINES

Table 7   Effect of Stock Washing

Washings	Resin	Sheet Weight	Dry Tensile	Wet Tensile	% $\frac{Wet}{Dry}$
0	Paramel	5.41g	14.8kg	1.28kg	8.65%
1	Paramel	5.09	15.6	2.76	17.7
2	Paramel	5.42	16.7	3.42	20.5
3	Paramel	5.40	16.7	3.41	20.4
4	Paramel	5.45	16.8	3.51	20.9
5	Paramel	5.41	16.5	3.24	19.6
6	Paramel	5.65	17.5	3.64	20.9
0	Kymene	5.45	16.2	1.65	10.2
1	Kymene	5.53	18.6	3.87	20.8
2	Kymene	5.38	18.0	5.24	29.1
3	Kymene	5.51	17.0	5.88	34.6
4	Kymene	6.01	19.4	6.98	36.0
5	Kymene	6.03	21.0	7.43	35.4
6	Kymene	5.91	21.6	7.80	36.1

Buffers - - - - HCl and Naoh
Resin Addition 1%
Stock - - - - - Unwashed NSSC

Figure 7   Graph Showing Wet/Dry Tensile Verses Stock Washing

x KYMENE 557
⊙ PARAMEL HE

% WET/DRY

NUMBER OF WASHINGS
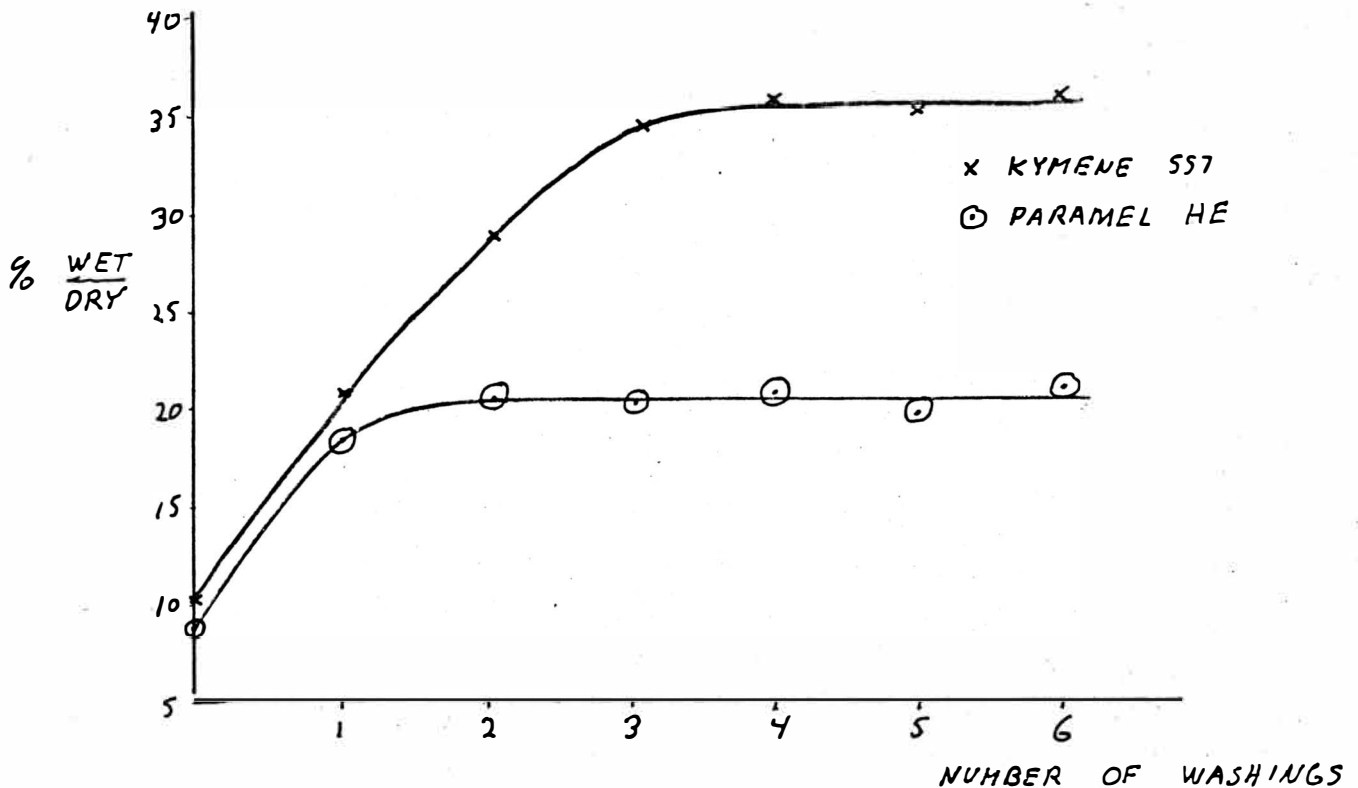
seen that increased washing increases wet strength efficiency, up to a point, after which no more strength is obtained. The most washed stock has a wet over dry ratio of 36.1%. This compares favorably with the value obtained with bleached sulfite pulps.(19) Because high wet over dry strength values are obtained rather quickly in the washing sequence and no further gains are made, it could be concluded that the inhibiting material is easily removed from the stock. This may mean the inhibiting material is not attached to the fibers but is dissolved in the white water.

Effect of Stock Washing on Paramel HE - The same kind of washing sequence was run with Paramel HE wet strength resin and the results were similar except for three points. First, the Paramel shows itself to be less efficient on the fully washed pulp than the Kymene. Secondly, the Paramel loses only 59% of its possible wet strength in the unwashed system, while the Kymene loses 72% of its value. Thirdly, the Paramel requires only one wash to achieve 85% of its potential wet over dry tensil ratio, while the Kymene aquires only 81% of its potential after two washes. The last two factors could be explained by the fact that Kymene 557 has a higher cationic charge density than Paramel HE. (20) If the wet strength inhibiting material is an anionic species that combines with the resin colloidal particles, then the Kymene 557, with its higher positive charge, could be more effective at attracting this species. When the washing lowers the concentration of the inhibiting anion, the Paramel HE, being a weak cation, doesn't react with it to such a large degree. It should be remembered that the sample with zero washing was cleaner than the stock used at the Menasha Mill. Due to the problems of transporting low consistency stock from the Mill to the University, the pulp was brought to the school at 4% consistency and diluted to sheet making consistency with tap water.

Effect of Black Liquor Components on Both Wet Strength Resins - The residual black liquor from the neutral sulfite semichemical pulping process contains numerous chemical compounds. Braun has published a list of the more important constituents.   To determine which ones of these could be detrimental to wet strength development, a series of experiments were run in which batches of well washed Menasha pulp were treated with these compounds. one at a time, and then tested for their ability to accept wet strength resin. The data from these tests appears on page 27, Table 8 and Table 9. It can be seen that none of these compounds seems to have a serious effect on the development of wet strength by either Kymene 557 or Paramel HE. This could be because the compounds were only added at 3% of dry fiber weight and a higher addition is needed to show the detrimental effect. It might also be said that a combination of these compounds would produce an effect that none of them would alone. It will be noticed that sodium sulfite at 3% addition seems to lower the wet over dry tensil ratio somewhat. The lowering is greater in the case of Kymene. At the pH where Kymene was used the sulfite ion would be present and this could have an action similar to the sulfate ion.

Effect of Sodium Lignin Sulfonate on Both Wet Strength Resins - The black liquor constituent present in largest quantity is sodium lignin sulfonate. This is actually a group of many related compounds formed when the wood lignins are sulfonated and broken up during the pulping process. Because the calcium lignosulfonates are water insoluble, it is possible to precipitate them out of the spent liquor by adding calcium ions. This was done as a fractional precipitation using calcium hydroxide and controling the pH of the precip-

Table Showing

Table 8   Effect of Black Liquor Components on Kymene

Components	% Added	Weight	Dry Tensile	Wet Tensile	% Wet/Dry
Control	0 %	5.39g	18.3 Kg	6.32 Kg	34.5%
Ca Lignosulfonate	20	5.29	18.0	5.96	33.1
Glucose	3	5.38	19.1	6.30	33.0
Na Acetate	3	5.28	18.6	6.36	34.2
Lactic Acid	3	5.53	18.2	6.30	34.6
Glycolic Acid	3	5.41	17.7	6.21	35.1
p-Hydroxybenzoic Acid	3	5.38	17.6	6.04	34.3
p-Cresol	3	5.47	18.9	6.31	33.4
o-Phthalic Acid	3	5.49	18.3	6.22	34.0
Succinic Acid	3	5.29	18.8	6.35	33.8
Na Sulfite	3	5.36	17.8	5.67	31.9
Na Carbonate	3	5.31	19.0	6.48	34.1

Table 9   Effect of Black Liquor Components on Paramel HE

Components	% Added	Weight	Dry Tensile	Wet Tensile	% Wet/Dry
Control	0 %	5.39 g	17.7Kg	3.72Kg	21.0%
Ca Lignosulfonate	20	5.31	16.6	3.29	19.8
Glucose	3	5.38	17.9	3.63	20.3
Na Acetate	3	5.48	18.0	3.73	20.7
Glycolic Acid	3	5.32	17.6	3.27	18.6
Lactic Acid	3	5.28	18.2	5.58	19.7
p-Hydroxybenzoic Acid	3	5.51	18.0	3.40	18.9
p-Cresol	3	5.48	16.5	3.45	20.9
o-Phthalic Acid	3	5.41	19.0	4.00	21.1
Succinic Acid	3	5.40	17.8	3.56	20.0
Na Sulfite	3	5.33	18.5	3.16	17.1
Na Carbonate	3	5.45	18.5	3.48	18.8

Resin Addition   1%

Stock   Washed N.S.S.C.

pH   8.0 & 4.0

Buffer   NaOH & HCl

itating solution. After precipitation and washing, a brown granular calcium lignosulfonate was obtained. This was treated with acid to form free ligno-sulfonic acid which was treated with sodium carbonate. Calcium carbonate has a solubility of only 0.0015 grams per 100 ml. so this precipitated out leaving dissolved sodium lignosulfonate as a dark brown solution.(21) This solution was added to washed stock in varying quantities and treated with both of the wet strength resins. Handsheets were made and tested for wet strength and the data appears on page 29, Table 10 and Figure 9. It can be seen that sod-ium lignosulfonate clearly has a detrimental effect on resin efficiency. A lignosulfonate addition of 4 to 5% produces a minumum wet strength only slightly higher than the wet strength of a sheet with no resin at all. It can also be seen that this material lowers the dry strength of the sheet. The percentage of sodium lignosulfonate should not be taken as exact. The sodium lignosul-fonate solution was found to contain 8% dissolved solids by evaporation, but it was not known for certain what the purity of the solution was, so a 6% sodium lignosulfonate concentration was assumed. It is from this assumption that the percentages of addition were plotted.

It seems reasonable that sodium lignosulfonate could inhibit the action of the wet strength resin. Lignosulfonic acid is a fairly strong acid and would be at least partially ionized in the pH range where the wet strength resins are used. The anion consists of a small, highly charged sulfonate group attached to a large organic lignin portion. The electronegative portion would be at-tracted to the positivly charged resin colloid and could either precipitate the resin or could at least form a counter ion cloud

Table Showing Effect of

Table 10   Addition of Sodium Lignin Sulfonate

Resin	% Sod.Lig.Sul.	Weight	Dry Tensile	Wet Tensile	% $\frac{Wet}{Dry}$
Kymene	0%	5.39g	18.3kg	5.32kg	29.1%
Kymene	2	5.49	17.8	3.70	20.8
Kymene	4	5.40	16.9	1.02	6.1
Kymene	6	5.32	16.1	.78	4.8
Paramel	0	5.41	17.1	3.97	23.2
Paramel	2	5.35	16.1	1.75	10.9
Paramel	4	5.40	16.0	.82	5.1
Paramel	6	5.29	16.6	.99	6.3

Buffers - - - - NaOH and HCl
Resin Addition 1%
Stock - - - - - Washed NSSC

Figure 8   Graph Showing $\frac{Wet}{Dry}$ Tensile Verses Na Lignosulfonate Addition

Figure 8 — Graph Showing Wet/Dry Tensile Verses Na Lignosulfonate Addition. Legend: X KYMENE 557, ⊙ PARAMEL HE. Y-axis: % WET/DRY. X-axis: % SODIUM LIGNOSULFONATE
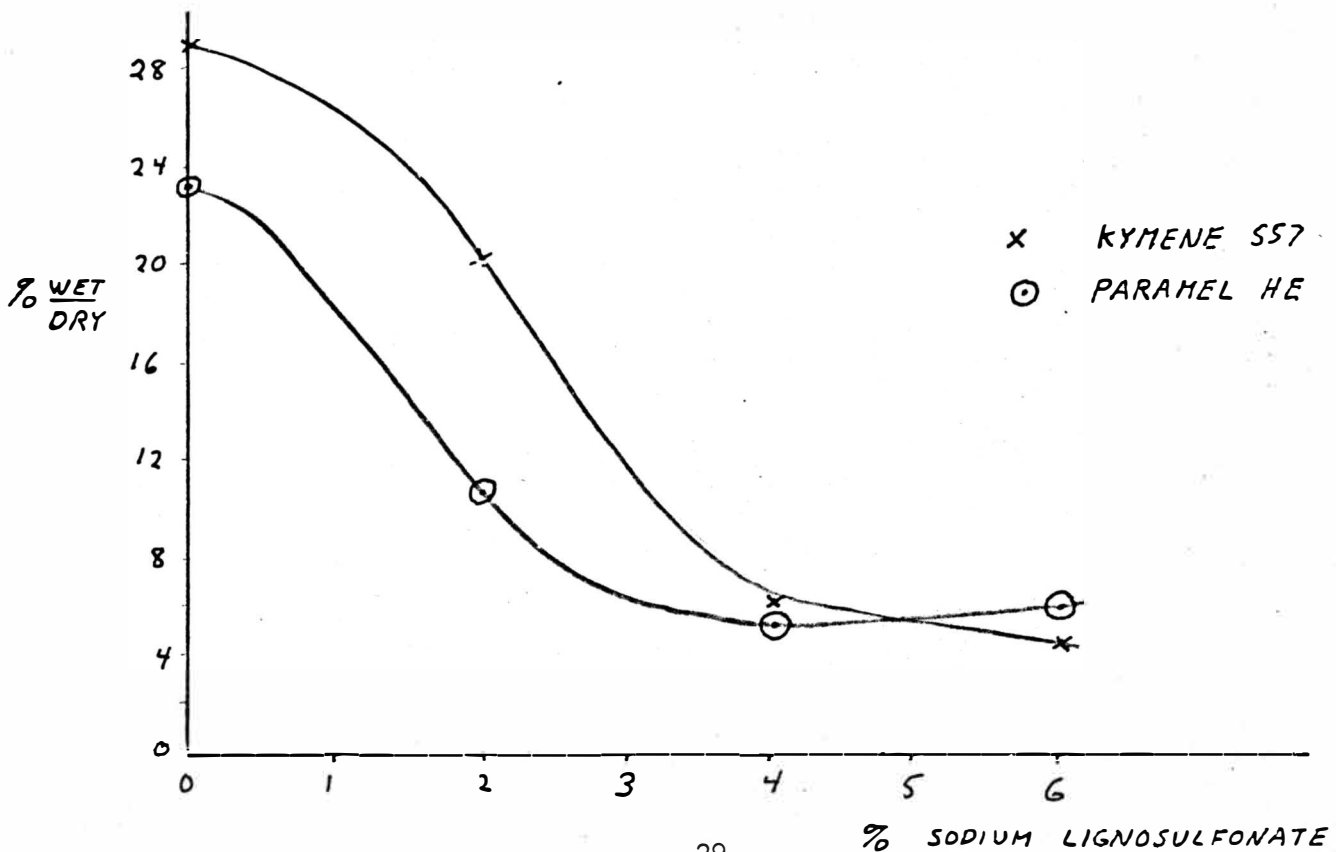
around the resin. This cloud of large negativly charged particles around the resin micells would prevent the resin from being attracted to the negative cellulose fibers. Even if the resin did bond to the fibers, it would be surrounded by a layer of lignin materials and would not be able to form thermosetting bonds with other resin particles or with the fibers. A pictorial representation of this situation is shown below.
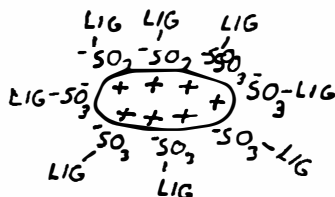
Another piece of data supporting this conclusion is the rapid rise in Paramel HE efficiency as the pH decreases. This could mean that as pH drops more lignin sulfonate groups are being protonated and thus prevented from interfering with the wet strength resin.

Effect of Calcium Lignin Sulfonate on Both Resins - Since calcium lignin sulfonate was obtained as an intermediate in the isolation of sodium lignin sulfonate, it seemed worthwhile to test its effect on wet strength development. This solid, granular material was added to washed stock systems and both types of wet strength resins were tested on the stock. The data appears in Figure 8. It is seen that this material has no noticable effect on either wet or dry strength. It contains the lignin sulfonate group just as the sodium lignin sulfonate did. but it is inert toward wet strength resin. The answer seems to be the lack of a charge on the calcium precipitate, which means it is not attracted to the resin. The calcium lignin sulfonate was added in large quantities and much of it stayed in the sheet as evidenced

by the grainy feel of the paper. This indicates that Paramel HE or Kymene 557 can produce wet strength in a sheet even when a considerable amount of lignin sulfonate material is trapped among the fibers. The fact that this lignin sulfonate did not seem to lower the dry strength, as would be the case with a filler like clay, may mean that the lignin portion is contributing to sheet strength. Calcium lignin sulfonate has thermoplastic properties that make it useful as a plastics extender and these may play a part in holding the sheet together.

Effect of Adding Calcium Chloride to Unwashed Stock - Since sodium lignin sulfonate has a detrimental effect on wet strength development and calcium lignin sulfonate does not, it seemed that the lignin sulfonate could be tied up by adding a large number of calcium ions to the furnish. To test this, varying amounts of calcium chloride were added to batches of unwashed stock which were then treated with samples of both wet strength resins. The data appears in Table 11. It is seen that the only consistent effect is a lowering of the dry strength by increasing amounts of salt. Apparently the stock system is too dilute for any calcium lignin sulfonate precipitation to occur. In order for precipitation to take place, the requirements for calcium chloride added would be immense.

Table 11

Table Showing
Effect of Calcium Chloride on
Unwashed Pulp Wet Strength

Resin	% CaCl	Weight	Dry Tensile	Wet Tensile	% Wet/Dry
Kymene	0%	5.35 g	15.9 Kg	1.78 Kg	11.2%
"	10	5.23	15.2	1.81	11.9
"	20	5.43	14.7	1.62	11.0
Paramel	0%	5.34	16.3	1.55	9.5
"	10	5.27	15.7	1.52	9.7
"	20	5.35	15.0	1.44	9.6

Conclusions

This investigation brought to light a number of facts about the use of wet strength resins on unwashed N.S.S.C. pulp as well as a comparison of Kymene 557 and Paramel HE. It is found that Kymene 557 is capable of developing a very high wet strength value on the unwashed pulp while Paramel HE is not. However, the quantity of resin needed for this high wet strength is prohibitive from a cost standpoint. It was found that hydrochloric acid is a better pH adjusting agent for Paramel HE than sulfuric acid or alum. The sulfuric acid introduces sulfate ions into the system which are detrimental to wet strength development. The alum does the same but has the additional disadvantage that is reacts with the natural wood rosins in the stock to give a hard sized sheet. This sizing prevents the water base glue from soaking into the corrugating medium when it is made into board.

It was found that both Kymene 557 and Paramel HE are pH dependant with Kymene 557 having a peak efficiency at pH 8 while Paramel HE increases its efficiency with decreasing pH. It is believed the latter phenomenon is caused by protonation of ligninsulfonate anions at low pH. Since these ions are believed to inhibit wet strength resin efficiency, as they are protonated, their effect is decreased.

A number of factors in the system were found to have little effect on the development of wet strength. One of these was the quantity of wood fines in the system. The removal of most of these fines gives only a slight increase in efficiency for either wet strength resin.

It was shown that as the residual black liquor is washed from the pulp, the

wet strength attainable is dramatically increased. This would indicate that it is some component in this cooking liquor that is responsible for the poor wet strength development in the unwashed stock. Furthermore, the wet strength increases rapidly with only slight washing which means this inhibiting compound is easily removed and is probably not attached to the fibers, but is in solution. When the stock is fully washed, the resins are capable of imparting as good a wet strength as is obtained with bleached sulfite pulps, so that one can not say the pulp itself is not compatable with Kymene 557 or Paramel HE. resins. Comparing the two resins, it is seen that at one percent addition. Kymene 557 imparts a wet strength almost twice that of Paramel HE at the same level of addition with completely washed stock.

A number of black liquor components were tested to see if they had an effect on the ability of the two resins to impart wet strength. It was discovered that at a 3% level of addition only sodium sulfite and sodium lignin sulfonate had an adverse effect. The effect of sodium sulfite was to reduce the percentage wet over dry tensil by 6% with Kymene 557 and by 13% with Paramel HE at the 3% level of addition. The effect of sodium lignin sulfonate was much greater. At 3% addition this material reduced the wet strength attainable with either Kymene or Paramel by 68% and at 6% addition this sulfonate completely prevents the resins from acting. It is felt that sodium lignin sulfonate is the only important reason for the failure of Paramel and Kymene resins to work satisfactorily on this type of stock.

In the experimental work, it was shown that lignin sulfonate can be precipitated as a calcium salt and that this water insoluble material has no detrimental

effect on wet strength resin efficiency. It was hoped that by adding calcium chloride to the pulp, the lignin sulfonates could be prevented from destroying the wet strength resin's action. This proved unfeasable because at reasonable levels of addition of calcium chloride the solution was not concentrated enough to precipitate the sulfonate.

If wet strength corrugating medium were to be produced in a commercial operation either the stock would have to be given some washing or the level of resin addition would have to be made higher than for clean pulps, or both. If little or no washing could be tolerated, perhaps because of lack of waste disposal facilities for the washings, and a high wet strength is desired, then Kymene 557 at high addition would give wet strength at a high cost. If washing is feasable, then the same results could be obtained with washed stock and Paramel HE because the Paramel resin is less expensive. More of the money would be spent on the washing and less on the resin in this second case. If the wet strength requirements were low and cost was paramount, then a slight washing followed by treatment with Paramel HE would probably be best. The Paramel HE costs less and loses less of its efficiency but it has a lower possible efficiency and has less gain in wet strength at higher additions.

Suggestions for Further Work

Since this paper is believed to show that sodium lignosulfonate is the component in N.S.S.C. pulp that inhibits wet strength, it would be worthwhile to investigate the reaction between this material and wet strength resin. Also this paper makes no attempt to discover whether the failure of these resins is due to their lack of retention in the sheet or whether the resin is retained in a form that does not contribute to wet strength. The most profitable endeavor in this area would be an attempt to discover a wet end additive that would reduce the activity of sodium lignin sulfonate so that a wet strength resin could work effectivly in the system.

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