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The Effects of pH on Alkaline Sizing of Bleached Hardwood Pulps with Aquapel

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THE EFFECTS OF pH ON ALKALINE SIZING OF BLEACHED HARDWOOD PULPS WITH AQUAPEL

by

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ABSTRACT

The effects of pH on alkaline sizing of two bleached hardwood pulps, kraft and sulfite, was investigated. The pulps were refined in a Noble and Wood cycle beater and handsheets were made with a Noble and Wood handsheet making system. The handsheets were internally sized with 0.15 percent Aquapel using 0.05 percent Kymene 557 as a retention aid. Upon varying the pH of sizing of bleached hardwood sulfite pulp the Hercules Ink Photometer measurements of 258, 636, and 563 seconds were observed at pH's of 7.0, 8.5, and 9.5 respectively. The sizing increased with pH up to a certain pH value and then decreased with a further increase in pH. The Ink Photometer measurements were higher for bleached hardwood kraft pulp, 291 seconds at 7.0 pH and 846 at 8.5 pH, indicating a higher alkaline sizing efficiency for the bleached kraft pulp over this pH range.

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THEORY AND HISTORICAL BACKGROUND

In the early history of papermaking, when the product was used only for writing and printing, the need to limit the spreading of ink resulted in sizing the paper with gelatinous vegetable materials which had the effect of sealing or filling the surface pores. Later, the term sizing was applied to the treatment of paper stock prior to the formation of the sheet with water-repellant materials such as rosin or wax; this is known as internal sizing. The use of paper for wrapping and packaging brought additional requirements in protecting the contents from fluid transfer through the paper. In some cases this has resulted in the demand for complete resistance to fluid penetration.

By nature, cellulose fibers are hydrophilic. So depending upon the amount of beating and sheet porosity paper can be quite absorbent toward water and other low viscosity liquids. More viscous liquids such as oil are also absorbed by paper,however, there is doubt as to whether oil penetration is dependent upon the porosity of paper. The mechanism by which sizing brings about resistance to penetration by liquids is explained by the following relationship

$$1)\quad R = \frac{\gamma r \cos\theta}{4 \eta l}$$

where γ is the surface tension of the penetrating liquid,

r is the radius of the capillary involved, η is the viscosity of the liquid, λ is the length of the capillary and θ is the contact angle which forms between the solid fiber surface and the liquid (1). This indicates that decreasing r by beating the pulp and thereby making a denser paper should improve sizing or decrease penetration.

Hydrophobic, inert sizing agents have a decreasing effect on liquid penetration by increasing the contact angle between the liquid and the fiber surface. The penetration rate is related to the contact angle in that if a low contact exists, capillary attraction causes spontaneous entrance of the liquid into the capillary. However, if the contact angle is greater than 90°, the value of cos θ becomes negative, and a resisting pressure develops which prevents penetration (2).

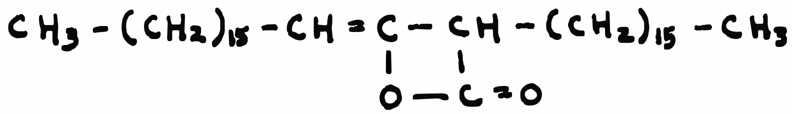
Of the sizing agents presently used for internal sizing, rosin size is the most common. Several mechanisms for rosin sizing have been proposed, but none have been proven. The basic principle is that the negative charge of the rosin particle in solution with cellulose fibers is changed to positive by a sufficient amount of alum which enables it to precipitate onto the negatively charged cellulose fibers.

Addition of the alum decreases the pH of a pulp slurry. Rosin sizing is impossible under alkaline conditions, with a pH of 5.0-5.5 contributing the most

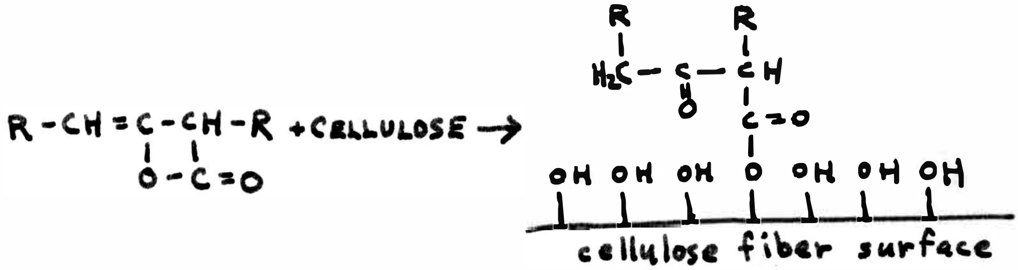
effective sizing conditions (3). With the advent of closed white water systems, excessive build-up of sulfate ion tends to occur if alum alone is used to control the pH, resulting in equipment corrosion and the production of paper having poor aging properties. If alum is reduced to take care of this situation, poor sizing will take place. Automatic addition of an alkaline material other than carbonate, while alum is added in the normal manner, is used to combat the sulfate ion build-up in some mills. The pH at which the rosin sizing is done, greatly influences the aging properties of the paper. The acid content of the sheet increases as the sizing pH decreases and fiber deterioration increases with the acid content. This presents a problem when paper is sized with rosin in the most efficient pH range. The pH can be increased to reduce the strength loss with aging, however, a hard rosin size must be used if good sizing is desired. This presents additional problems . Paper sized with rosin in the higher pH range yellows on exposure to sunlight. A loss of sizing with aging occurs resulting in an absorbent paper (4). So one can see the difficulties encountered in attempting to produce a permanent paper and one that won't yellow on exposure to sunlight while sizing under acidic pH conditions.

These problems in acid sizing are greatly responsible for the development of polyamide wet strength

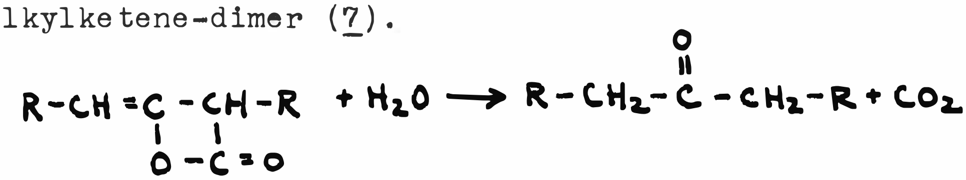
resins and Aquapel, which permit sizing under alkaline conditions. Aquapel, a product of Hercules Powder Company, is an alkylketene dimer prepared from long-chain fatty acids. Palmitic ($C_{16}H_{32}O_2$) and stearic ($C_{18}H_{36}O_2$) acids are the ones generally used to develop maximum water resistance. When made from stearic acid, Aquapel has the following structure (5):

2) 

Under neutral or alkaline conditions, the lactone ring of the alkylketene dimer will open and react with materials containing free hydroxyl groups or amide groups. Aquapel's sizing effect results from its reaction with free hydroxyl groups on cellulose fibers to form an ester, which is water repellant and chemically inert. The reaction of Aquapel with cellulose is

3) 

where R is an alkyl group (6). An undesired side reaction in this alkaline sizing process is hydrolysis of the alkylketene-dimer (7).

4) 

Aquapel can also react with water to form a ketone,

which is of no value in sizing.

EXPERIMENTAL SECTION

Experimental Objectives

The objectives of this investigation were as follows:

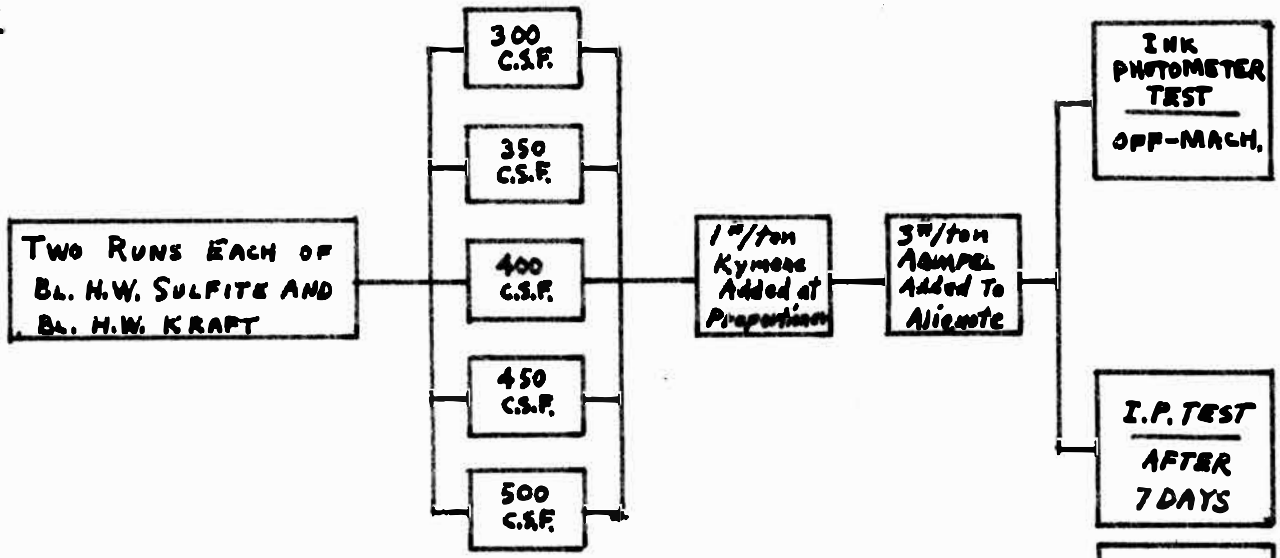
1) Determine the optimum sizing freeness for two bleached hardwood pulps, kraft and sulfite.
2) Determine the effect of the pH of the pulp slurry on alkaline sizing efficiency for bleached hardwood pulps.
3) Compare the efficiency of alkaline sizing of the two pulps.

Experimental Design (See Flow Diagram on Next Page)

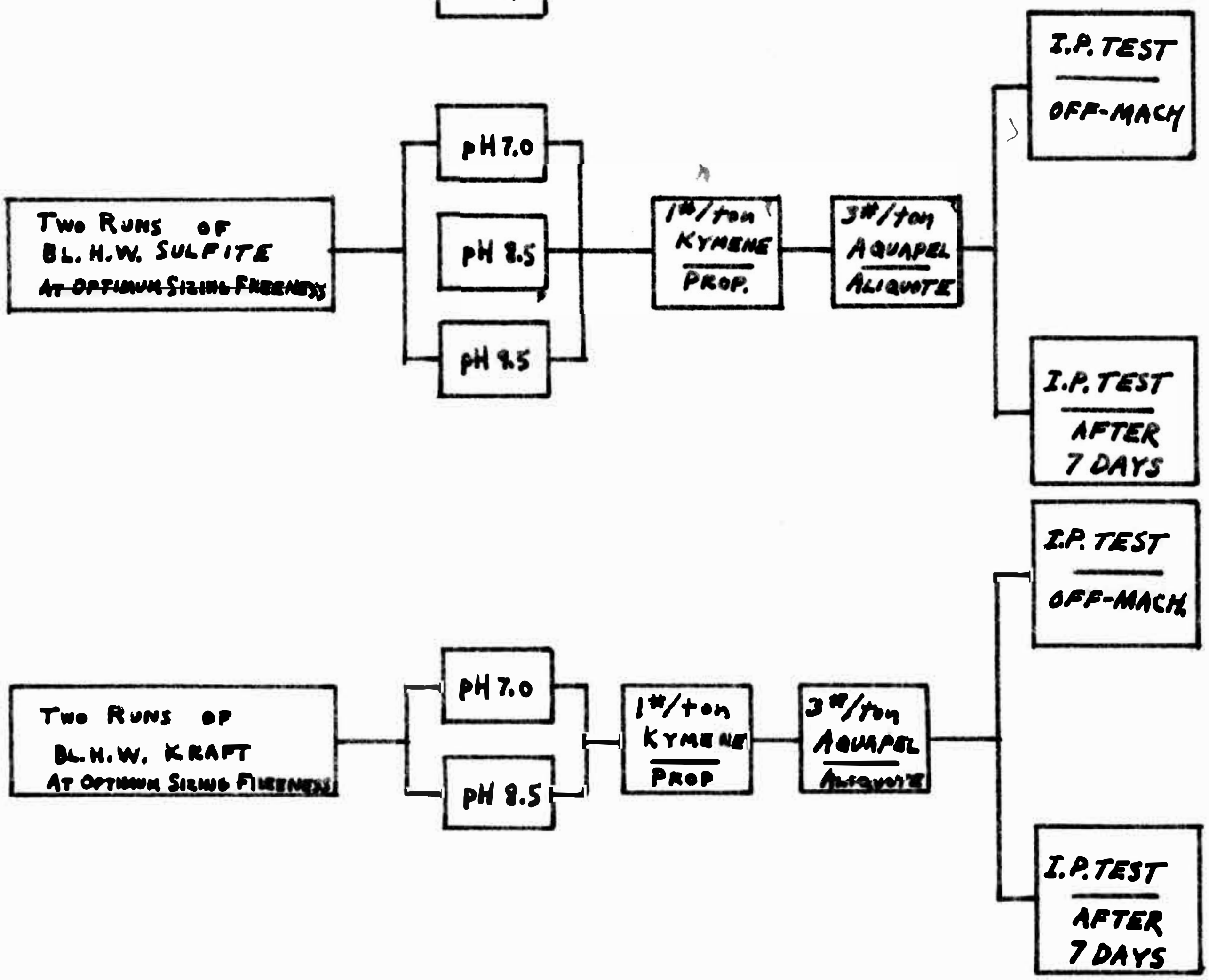
The experimental work was separated into two parts. First, the optimum freeness (C.S.F.) for alkaline sizing was determined for both bleached hardwood pulps (See Graph I). And second, the results from the first part, the effect of the pH of the pulp slurry on Aquapel sizing efficiency was determined. This was accomplished by sizing the bleached sulfite pulp at three pH values, 7.0, 8.5, and 9.5, and then testing the sizing of the handsheets on the Hercules Ink Photometer. Also the bleached kraft pulp was sized at two pH levels, 7.0 and 8.5. These two levels were sufficient for observing whether the two pulps differed in their ease of alkaline sizing with alkylketene-dimers. Careful control of conditions is of utmost importance in this experiment. All sizing in the second part of the experiment was performed at the optimum sizing freeness.

FLOW DIAGRAM OF EXPERIMENTAL PROCEDURE

PART I



PART II



Experimental Procedure

The water used in the experiment contained 50 PPM alkalinity and 100 PPM hardness. For convenience the total alkalinity was considered to be PPM $CaCO_3$. Before the beater and the proportioner were filled, the alkalinity was carefully adjusted to 150 PPM with addition of $CaCO_3$. Adjustments of pH were made with NaOH and H_2SO_4. The pulp was diluted to .26 percent consistency in the proportioner using the prepared water and Kymene 557 was added in the amount of one pound per ton of dry pulp with gentle agitation. Before addition to the proportioner the Kymene was diluted to a 2 percent solution. Aquapel was added to each aliquote in the amount of three pounds per ton of dry pulp. Since the Aquapel used was in an emulsion form, it was necessary to determine solids. The percent solids of the Aquapel - water emulsion was determined as follows:

1) a 1 gram sample was weighed onto a 50 mm. drying dish,

2) the sample was dried at 150°C for 15 minutes,

3) the dish was reweighed to determine the solids.

Since Aquapel reacts immediately with water and does not react with cellulose until the bulk of the water has been removed, the best sizing is achieved by adding the Aquapel to the aliquote just prior to formation of the handsheet. Using Kymene 557 for retention, about 65-85 percent of the

Aquapel is retained by the paper when used on the paper machine . Approximately 65 percent of the retained quantity reacts with the fibers and the other 35 percent is lost by hydrolysis with the water in the wet sheet (8). Time delays between forming, pressing, and drying are detimental to good sizing because of the reaction of the alkylketene - dimer with water in the sheet. The water should be removed as quickly as possible.

The handsheets were pressed to approximately 33 percent solids and dried to approximately 4.5 percent moisture. The dryer temperature was maintained at 232°F and its speed was 1.1 revolutions per minute for all drying.

Size tests were made as soon as possible (off-machine) following drying on each handsheet and then again seven days later after the Aquapel-cellulose reaction was complete. Differences in the time lapse between sheet formation and testing can substantially effect the off-machine tests. Uniformity of this time lapse is critical because the rate of the sizing reaction is highest during the initial stage. No attempt will be made to correlate the off-machine tests in the discussion of the results, since the time lapses may have varied by as much as 15 minutes for some of the runs. The amount of sizing as the reaction rate approaches zero is much more meaningful and will be of prime concern when reference is made to the experimental results.

All sizing tests were made in a constant humidity room at a temperature of 74±1°F, using three Hercules Ink Photometers. The Photometers were calibrated prior to each test to insure correlation of the results. The Hercules Ink Photometer measures the time in seconds required for a special ink solution in contact with the felt side of the paper to penetrate enough to reduce the reflectance of the wire side to 80 percent of its original value. The ink solution is 1.0 percent formic acid and 1.25 percent of a .45 optical density dye by weight composition.

DISCUSSION

Optimum Sizing Freeness

Results comparing the sizing of bleached hardwood sulfite and bleached hardwood kraft pulps at various Canadien Standard Freenesses are given by the following table.

TABLE I.

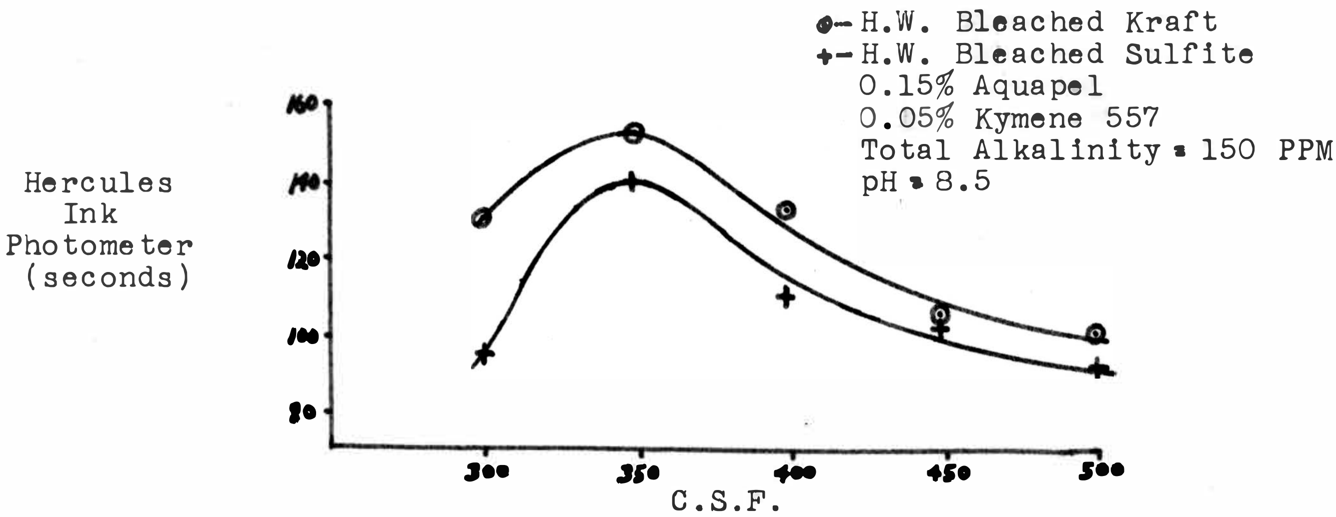
The Effect of Freeness on Alkaline Sizing (pH 8.5)

C.S.F.	300	350	400	450	500
BLEACHED SULFITE	94.2	139	109	101	90.4
BLEACHED KRAFT	129	152	131	103	99.2

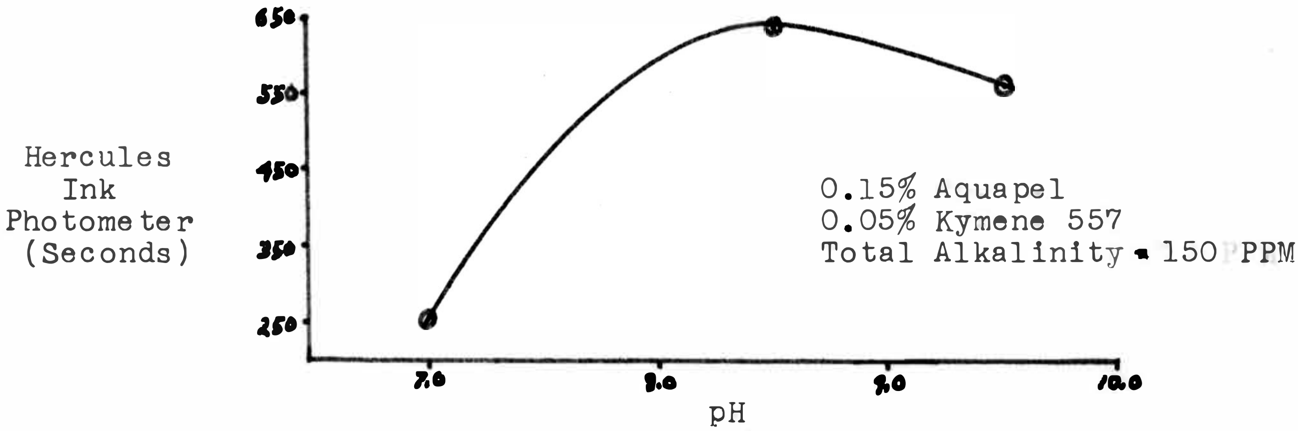
note: values in table are Hercules Ink Photometer measurements in seconds obtained immediately after the handsheets were dried.

The optimum sizing freeness was 350 C.S.F. for both pulps. The sizing effieciency was observed to increase with beating, reaching a maximum at 350 C.S.F. Further beating to 300 C.S.F. caused the sizing efficiency of both pulps to decrease (See Graph I). Since Aquapel's sizing effects result from its reaction with free hydroxyl groups on cellulose, the simplest explaination might be ~~that the number of hydroxyl groups on the cellulose which are free to react with the alkylketene-dimer increase with beating reaching a peak and then decreasing with further beating. Looking at the cell-ulose polymer structure, there are three free hydroxyl groups on cellulose, the simplest explaination might be~~

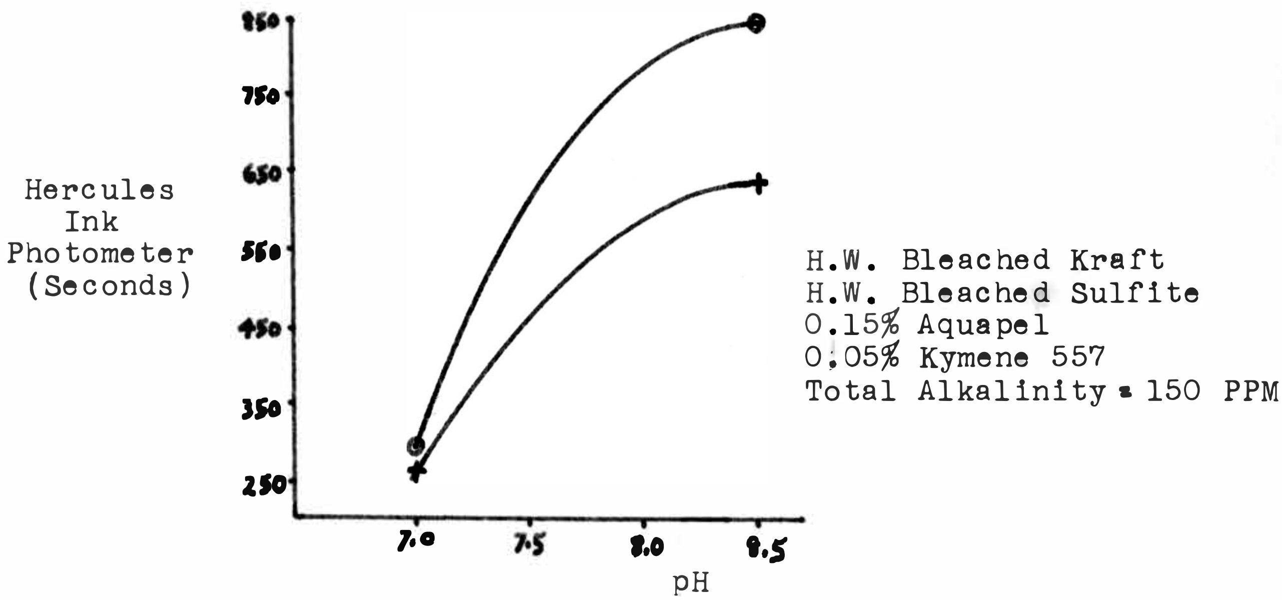
GRAPH I The Effect of Freeness on Alkaline Sizing



GRAPH II The Effect of pH on Alkaline Sizing of H.W. Bleached Sulfite



GRAPH III A Comparison of the Ease of Alkaline Sizing of Two Hardwood Pulps



that the number of hydroxyl groups on the cellulose which are free to react with the alkylketene-dimer increase with beating reaching a peak and then decreasing with further beating. Looking at the cellulose polymer structure, there are three free hydroxyl groups per unit in the 2- 3- and 6- positions. But in the unbeaten cellulose pulp only a small portion of these hydroxyl groups are free to react with chemicals. The hydroxyl groups of the cellulose molecule tend to form hydrogen bonds with hydroxyls of adjacent chains, giving the cellulose a "super structure" of lateral area (9). Because this superstructure is mostly crystalline, only a limited fraction of its hydroxyl groups are available for interaction with chemical reagents. Beating opens up the crystalline structure allowing more hydroxyl groups to react with the alkylketene-dimer. As mentioned earlier, Aquapel does not react with the cellulose until after the sheet has been formed and most of the water removed. So the decrease in sizing efficiency with beating beyond 350 C.S.F. could be attributed to the fact that the sheet density may increase to a point where, although hydroxyl groups were freed during beating, the formation of such a tight fiber mat results in less hydroxyl groups being available to react with the alkyl-ketene dimer than at 350 C.S.F.

Another explaination may come from the fact that

the moisture content of the pulp increases with beating to a certain freeness and then begins to decrease (10). Since the alkylketene-dimer is in solution in the water, the amount of alkylketene-dimer in the pulp should be proportioned to the amount of water present. Thus the retention of Aquapel in the pulp would increase to a certain freeness and then decrease yielding the type of results observed in Graph I.

pH Effect on Alkaline Sizing of Bleached Hardwood Pulps

Graph II illustrates that pH definitely effects the Aquapel sizing efficiency of bleached hardwood sulfite pulp. The Hercules Ink Photometer measurements for handsheets of both pulps sized at various pH values are compiled in the following Table.

TABLE II.

Alkaline Sizing of Bleached H.W. Pulps at Various pH Values

pH	7.0	8.5	9.5
SULFITE (OFF-MACH.)	78.5	134	137
SULFITE (AFTER 7 DAYS)	258	636	563
KRAFT (OFF-MACH.)	91.0	165	——
KRAFT (AFTER 7 DAYS)	290	846	——

After allowing sufficient time for the complete sizing reaction to take place Ink Photometer measurements of 258 seconds, 636 seconds, and 563 seconds were observed at 7.0, 8.5, and 9.5 pH values respectively. Increasing the sodium hydroxide concentration in a fiber suspension activates more cellulose kydroxyl groups allowing more alkylketene-dimer to react with the cellulose. The result is an increase in sizing efficiency between pH 7.0 and pH 8.5. Besides its esterification reaction with cellulose, it was mentioned earlier that the alkyketene-dimer can be hydrolized to a ketone. An explaination of the decreased sizing efficiency at

pH 9.5 is that the hydrolysis of the alkylketene-dimer becomes excessive at that pH (11). This probably occurs after the sodium hydroxide concentration becomes higher than that required to activate the cellulose hydroxyl groups. Any further increase of the sodium hydroxide concentration probably results in a signi-ficant increase of the alkylketene-dimer hydrolysis, since the excess hydroxyl ions can not activate any more cellulose hydroxyl groups. The net result is a decrease in the amount of Aquapel reacting with cell-ulose and, therefore, a decrease in sizing efficiency.

Comparison of the Ease of Alkaline Sizing of Two Bleached Hardwood Pulps

Comparison of the Ink Photometer measurements on the bleached hardwood sulfite and the bleached hardwood kraft pulps sized at the same pH values, with the amounts of Aquapel, Kymene 557, and total alkalinity constant, show better sizing results for the Kraft pulp at both pH8.5 and pH 7.0 (See Graph III). The sizing measurements at pH 8.5 were 636 seconds and 846 seconds for the sulfite and Kraft pulps respectively. This difference was verified by reruns on both pulps. The difference was large enough to indicate that the kraft pulp is easier to size with Aquapel than is the sulfite pulp in the 7.0 - 8.5 pH range.

With rosin and alum sizing different pulps vary in the ease with which they can be sized. So it would not be surprising if different pulps varied in the ease with which they can be alkaline sized. Unbleached pulps are easiest sized with rosin sizeability decreasing with increasing pulp purity. Part of the reason is that the acidic impurities in various pulps interact with both rosin size and alum to form exchange compounds. Under proper pH conditions and ionic composition, these compounds improve the retention of the rosin size precipitate because of differences in electrical charges (12).

Taking a look at the compositions of the bleached sulfite pulp, the following table is given by Sutermeister (13).

TABLE III.

Composition of Bleached Sulfite Pulp

TOTAL CELLULOSE	-CELLULOSE	LIGNIN	PENTOSANS	EXTRACTIVES	ASH
98.1%	85.5%	0.5%	3.4%	0.9%	0.5%

Grant (14) says that about 16 percent of a highly bleached kraft pulp is hemicellulose. Assumimg nearly equal amounts of total cellulose in the two pulps, by these figures the kraft pulp would be lower in alpha cellulose. Another source (15) ~~content of a pulp~~ states that the higher the alpha cellulose content of a pulp the more difficult it is to size with rosin. This same source listing pulps by ease of rosin sizing ranks bleached kraft 3rd and bleached sulfite 5th. These facts all seem to indicate that alpha-cellulose accounts for a larger fraction of the total cellulose in bleached sulfite pulp than in bleached kraft pulp.

Since the sulfite pulp has the higher crystalline cellulose (alpha) - amorphous cellulose ratio, less of the hydroxyl groups in the sulfite pulp are available for reaction with the alkyl-ketene dimer than in the kraft pulp. The expected result when sizing the two pulps at the same pH would be better sizing with the kraft pulp which contains more accessible free hydroxyl groups.

CONCLUSIONS

The freeness of a bleached hardwood pulp has a significant effect on sizing efficiency under neutral and alkaline conditions. There is an optimum freeness with respect to Aquapel sizing with a decrease in efficiency both above and below this freeness.

Increasing the pH at which a bleached hardwood sulfite pulp is sized with Aquapel improves the amount of sizing developed over the pH range, 7.0 - 8.5. Above this pH range, between 8.5 and 9.5, the sizing efficiency decreases due to excessive hydrolysis of the alkylketene-dimer.

Finally, bleached hardwood kraft pulp can be sized to higher Hercules Ink Photometer values than bleached hardwood sulfite pulp with Aquapel over the pH range, 7.0-8.5., when other variables are held constant.

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