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The Effect of pH on Alkaline Sizing of Kraft and Sulfite Softwoods

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THE EFFECT OF pH ON ALKALINE SIZING OF KRAFT AND SULFITE SOFTWOODS

by

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ABSTRACT

Alkaline sizing has many inherrent advantages over conventional sizing with rosin and alum. The presence of alum alone in the papermaking system can be a detrimental factor to some characteristics of the process and the final sheet. By sizing under alkaline conditions not only is alum eliminated from the system but also a superior grade of sizing is achieved.

For the sizing of softwoods with Aquapel, an alkyl ketene dimer, it was found desirable to size in the pH range 8.0 to 8.3 and Canadian Standard Freeness 500 to 530. The kraft softwood was found slightly more susceptible to alkaline sizing reactions than the sulfite softwood. Significant effects of pH were observed on the rate of development of reaction between the sizing agent and the fiber and on the extent of reaction.

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Introduction

The intention of this study is to determine the effects of pH, one of many important variables of the papermaking process, on alkaline sizing of bleached sulfite and bleached kraft softwoods. For over a century most paper and paperboard has been made under acid conditions primarily because of the necessity to use alum to effect rosin sizing. Alum has other desirable functions, notably pitch control in some unsized groundwood grades, filler retention, and improved drainage. Alum is often called the papermaker's "cure-all". An acid papermaking system also has some disadvantages, such as increased corrosion of equipment, loss of paper strength, less permanence and poorer adsorbency.

Within the last few years it has become possible to make wet-strengthed and hard sized paper and paperboard at neutral and slightly alkaline pH with polyamide wet strength resins and a chemical size called Aquapel*. Aquapel is a ketene dimer made from fatty acids, primarily C_{16} and C_{18}. The ketene dimer sizes by attaching a hydrophobic hydrocarbon chain to the fiber surface by a chemical bond. In this reaction the ketene forms an ester with a hydroxyl on the fiber surface. Aquapel is

* A registered trademark with Hercules Incorporated.

usually added to the stock near the wire at pH 7.0 to 8.5 using a cationic retention aid to retain the Aquapel in the sheet. Sizing develops on drying and further on aging in the rolls. Although pH is not as critical for alkaline papers, it does have some affect on the reactions involved and should be controlled.

Advantages of Alkaline Sizing

Conventional sizing of paper under acidic conditions involves reacting a sizing agent, such as partially saponified rosin size, modified rosin, or a mixed emulsion of rosin and wax, with aluminum sulfate in the presence of the pulp. The usual procedure is to add the alum after the rosin is thoroughly mixed. The best sizing results are obtained at pH 4.5-5.0.

A basic difference in the acid and alkaline sizing is the manner in which each reagent achieves the sizing. The reaction of rosin and alum form a size precipitate which is not attached or evenly distributed over the surface of the fiber in the final sheet, but is retained in the form of small particles within the surface. The dimensions of the particles and their retention and distribution on the unbonded surfaces cause variations in sizing efficiency. This sizing is often effected by the

intense heat of the summer months, sometimes resulting in fugitive sizing.

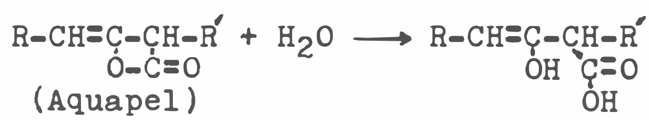
The inert hydrophobic material formed upon reaction of the ketene dimer with cellulose produces a sheet with uniform and evenly distributed sizing characteristics. Heat has no detrimental effects as it only increases the extent of reaction.

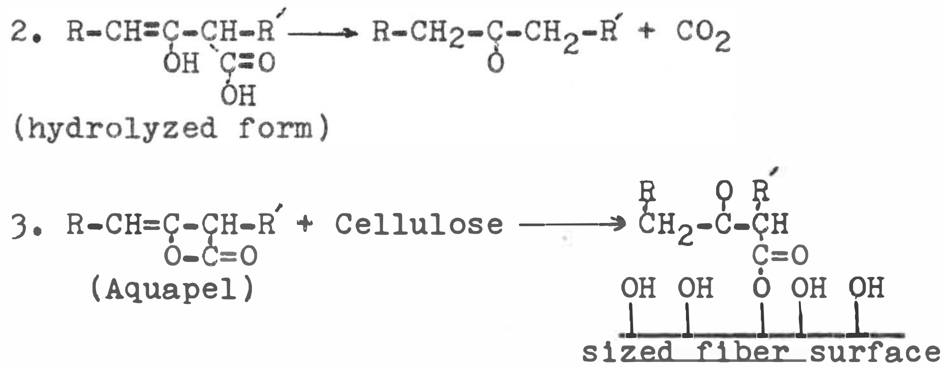
Some of the lesser noted advantages inherrent with alkaline sizing are longer wire life due to less corrosion, sometimes improved drainage rates due to the elimination of the alum floc, better optical properties, and improved aging characteristics[17].

Reactions of Aquapel

Aquapel will react with any material that has an active hydrogen. It is believed to react chemically to form a B-keto ester, an inert material creating superior sizing characteristics to conventional acid medium sizing. The reactions are as follows and are a function of time and temperature, the initial rate of which dependent upon pH.

1.





In reactions 1 and 2 Aquapel is hydrolyzed by water and then further decarboxylates to form a ketone dimer. The reaction with cellulose and the mechanism of attachment to the fiber surface is shown in step 3. It is obvious that the efficiency of sizing is dependent upon a minimal amount of hydrolysis of the ketene dimer.

As in most chemical reactions, the reaction between Aquapel and cellulose increases with temperature. Adequate sizing may be developed ahead of the size press by increasing the steam pressure in the first dryer section. Many machines making alkaline sized paper operate at the full extent of their drying capacity[18].

Alum has an adverse effect on the rate of reaction between Aquapel and cellulose but not on the extent[19].

Experimental Procedure

The apparatus used was as follows.

Noble and Wood Cycle Beater

Noble and Wood Papermaking System

Hercules Sizing Tester

pH meter

titration equipment

The materials and reagents used were as follows.

Aquapel 360X emulsion

Kymene 557 solution (2%)

calcium carbonate

sulfuric acid

pulp (kraft and sulfite bleached softwoods)

Hercules size test solution #2

Hercules standard hard water

In order to determine the freeness at which to conduct the testing of pH, freeness versus sizing curves were established. The handsheets were sized with one pound per ton Aquapel with one pound per ton Kymene 557 as a retention agent at vatious intervals of beating.

The solids content of the Aquapel emulsion was determined by drying one gram at 105 degrees Centigrade for ten minutes. The emulsion used was found to be 8.1 percent. Tens grams of the Aquapel emulsion were diluted to 311 grams with demineralized water to yield a 0.26 percent solution. One pound per ton is the equivalent

of 0.48 milliliters of the prepaired solution per handsheet. The Aquapel additions were made with a graduated hypodermic like needle.

A stock 2 percent solution of Kymene 557 was used as a retention agent for the Aquapel. One pound per ton was used by adding 0.13 grams solution to the proportioner (based on 50 grams dry fiber in proportioner).

The handsheet making procedure was carried out in accordance with the Hercules standard method for the Aquapel sizing of handsheets. A general description of the procedure is as follows: The water tank is filled with Hercules standard hard water (100 parts per million hardness and 50 parts per million alkalinity) and adjusted to 150 parts per million alkalinity and the desired pH using carbonate and caustic soda respectivly; a sufficient amount is drained into the machine tank and proportioner and the entire system rinsed thoroughly; fifty grams dry fiber (two 980 milliliter aliquots of 2.6 percent consistency) are added to the proportioner and diluted to 18.8 liters with the prepaired water; the Kymene is added to the proportioner and allowed to agitate with the stock; the Aquapel is added to each individual aliquot as it is taken from the proportioner; the formed sheet is pressed to a solids content of 33 percent and

dried at 232 degrees Fahrenheit to 4% moisture, which is regulated by controlling the speed of the dryer; the pH of the proportioner and deckle box are recorded; finally the sheets are conditioned and tested. The "Hercules Sizing of Aquapel" procedure can be consulted for a more detailed description of the procedure.

The water adjustment consists of adding a specific amount of calcium carbonate to raise to alkalinity to 150 parts per million and then analyzing by titration against 0.02N sulfuric acid using methyl purple indicator. The volume of acid required to neutralize 50 milliliters of water multiplied by twenty is the alkalinity in parts per million calcium carbonate. The water temperature is maintained at 25 plus or minus 2 degrees Centigrade.

The efficiency of sizing at different pH levels was determined by testing on the Hercules Sizing Tester immediately off the dryer and after one week natural aging. The penetrant used was Hercules size test solution #2, 1.25 percent special purified dye and 1.0 percent formic acid. The sizing test was reported as the time for the reflectance of the wire side of the sample to decrease 20 percent, i.e., the time to reach 80 percent of the original reflectance. Approxiamately ten milli-

liters of the solution was applied to the felt side of each sample.

To study the effect of pH on the rate of curing of the alkaline size, handsheets were sized at pH levels of 7.0, 8.0, and 9.0 and allowed to dry at room temperature with sizing tests performed at the various time intervals of 0 hours (off machine), 4, 12, 24, and 168 hours.

Optimum Freeness

The results of sizing the softwoods at various intervals of Canadian Standard Freeness are tabulated below with off-machine and one week natural aging tests.

Table I. Freeness vs. Sizing of Kraft

CSF	Basis Weight	pH	Moisture	Sizing O.M.	Sizing 1 week
700	39.8	8.0	4.5%	2	117
620	40.0	8.0	4.5%	4	248
530	40.2	8.0	4.9%	5	305
480	40.0	8.0	4.7%	5	288

Table II. Freeness vs. Sizing of Sulfite

CSF	Basis Weight	pH	Moisture	Sizing O.M.	Sizing 1 week
605	39.4	8.1	4.2%	32	101
507	39.7	8.1	4.6%	46	294
450	39.7	8.1	4.2%	40	271
410	39.9	8.1	4.8%	35	274
375	39.9	8.1	5.1%	31	273

From the data it is evident the optimum sizing is

achieved in the freeness range of 500 to 530 for each pulp.

Effect of pH

The sizing results at various pH levels in the optimum freeness range are as follows.

Table III. Sizing vs. pH of Sulfite

pH	CSF	Basis Weight	Sizing O.M.	Sizing 1 week
6.9	525	39.8	0	29
7.6	525	40.1	2	131
8.3	531	39.8	4	339
9.1	531	39.6	2	290

Table IV. Sizng vs. pH of Kraft

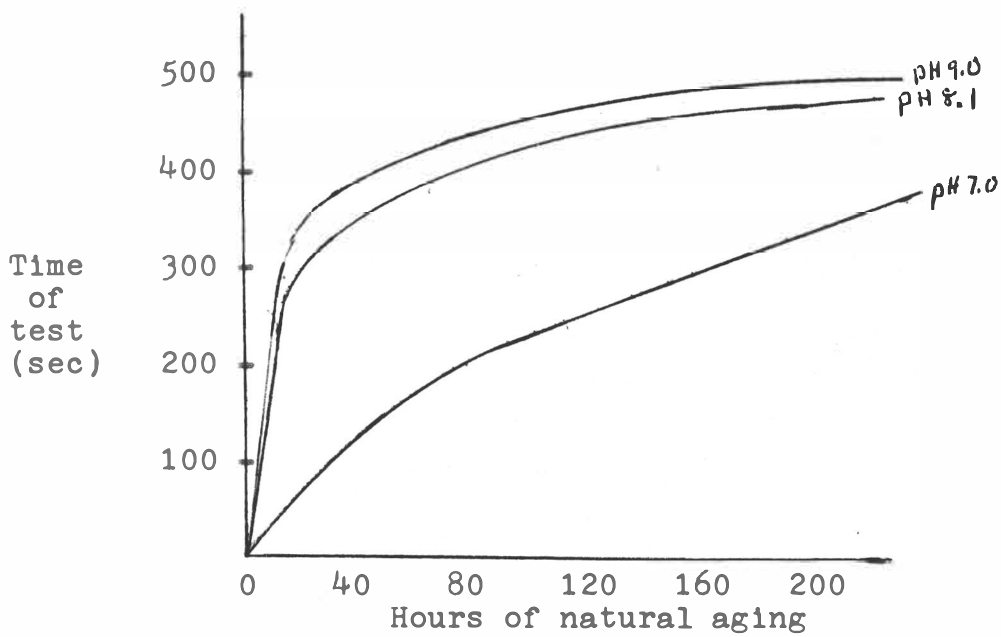
pH	CSF	Basis Weight	Sizing O.M.	Sizing 1 week
7.0	510	38.9	11	120
7.8	510	40.2	30	231
8.1	510	40.0	83	415
9.2	510	40.2	78	402

The optimum sizing is found near pH 8.2. Below pH 8.0 a significant decrease in sizing efficiency occurs and above 8.5 a leveling off tendency is noted. If the pH is too low the protonation of the R-CH group of the cellulose chain is made more difficult, inhibiting the reaction, and if the pH is too high, extensive hydrolysis of the ketene dimer takes place, limiting the available amount of size to react with the fiber. Also plac-

ing an upper limit on the pH is the fact that cationic starches lose their effectiveness at higher pH levels.

The pH was also found to have a considerable affect on the rate of cure of the sized sheet. As can be seen from Fig. 1 below, the higher the pH the higher the rate of development of the reaction between Aquapel and the fiber. However, as the pH gets much above 8.0, the difference in rates is very slight as the cationic starches begin to lose their effectiveness[19].

Figure 1. pH vs. Rate of Cure



From the graph it is apparent the ultimate value at each pH level will not show as much difference as the

initial rate of cure.

Comparison of Kraft and Sulfite

Only slight differences are to be noted in the alkaline sizing of kraft and sulfite softwoods. The properties obtained from alkaline cooked fibers make them more advantageous for alkaline sizing than when cooked in an acid medium. The kraft fiber tends to be less brittle, more difficult to hydrate, and capable of developing higher strength properties. Kraft pulps normally have greater pentosan, greater alpha-cellulose, and higher lignin contents than acid cooked pulps. This is especially true with softwoods.

That the best sizing is achieved with kraft pulps over sulfite is confirmed in the preceding tables. The initial off-machine sizing of the sulfite is relatively zero while reaching a higher value almost equal to that of the kraft after one week natural aging. The development of sizing in the kraft sheet coming off the dryer is about ten percent of the ultimate value, indicating a faster rate of curing than with the sulfite, although very little difference upon aging.

The difference in curing rates may be due to the higher accessibility of the hydroxyl groups of the cell-

ulose chains to the alkyl ketene dimer, while the lower accessibility of hydroxyls of the sulfite is probably overcome with aging. Another factor having bearing on the rate of cure is the higher alpha-cellulose content in the kraft pulp. Together with a higher alpha-cellulose content and more available hydroxyl groups, the alkaline cooked pulp is found more susceptible to alkaline sizing than the sulfite pulp.

Conclusions

The major difference between acid and alkaline sizing is the reaction of the alkaline size with the cellulose chain, where as in sizing with rosin, no chemical reaction occurs between the sizing agent and the fiber. This accounts for the superior sizing characteristics obtained in a sheet sized under alkaline conditions.

The effect of pH on alkaline sizing is noted both in the curing rate and the ultimate sizing. The highest efficiency is attained in the pH range 8.0-8.5 with optimum characteristics at 8.2. Below pH 7.5 the reaction is retarded due to the hindrance of the protonation of the ketene dimer, and above pH 8.5 extensive acid hydrolysis of the ketene occurs, minimizing the amount of size available for reaction with the cellulose.

Increasing the rate of cure is promoted by increasing the pH. A large difference in the rates is observed between pH 7.0 and 8.5, while above 8.5 the difference diminishes. Thus, an upper limit of 8.5 is placed on the pH for alkaline sizing due to the ineffectiveness of the retention aids at higher levels. By keeping the pH as high as possible, while retaining the size in the sheet, the heat required for drying can be kept at a minimum and the off machine sizing at a maximum.

The factor of pH is not as critical in alkaline sizing as in sizing with rosin and alum. The range of pH can vary from 7.0 to 9.0 and still retain sufficient sizing characteristics in the sheet, as the extent of sizing is primarily dependent upon time for completeness of reaction between the sizing agent and the cellulose. To maintain optimum machine operating conditions, although, the pH should be controlled as accurately as possible.

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