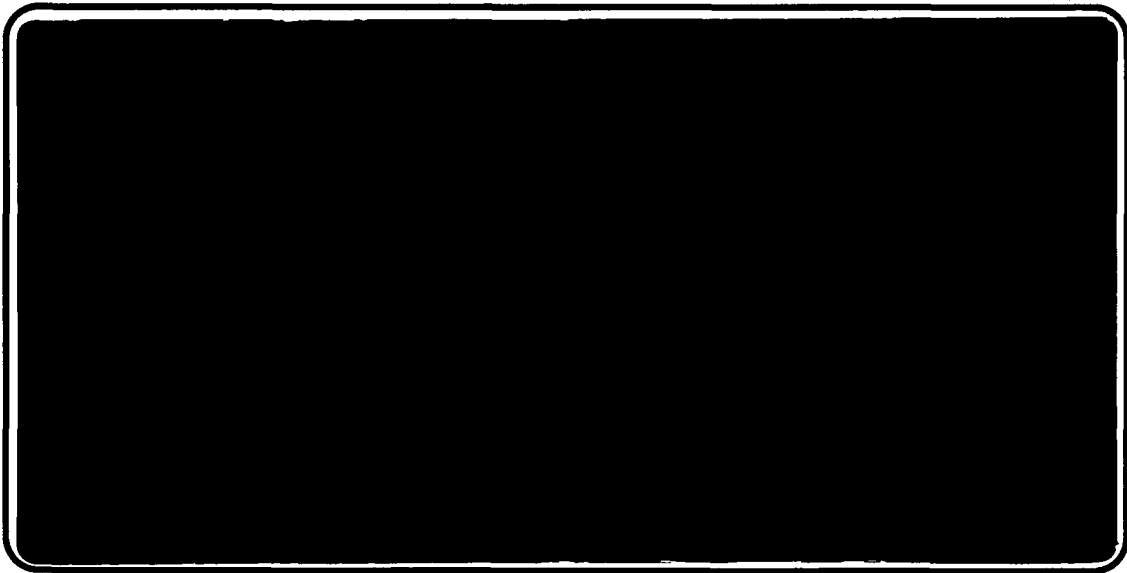




Property of
GEORGIA-PACIFIC CORPORATION
Technical Information Center
Atlanta, Georgia

*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST TECHNICAL PAPER SERIES



NUMBER 361

ALKALINE PAPERMAKING: AN OVERVIEW

B. CROUSE AND D. WIMER

SEPTEMBER, 1990

Property of
GEORGIA-PACIFIC CORPORATION
Technical Information Center
Atlanta, Georgia

Alkaline Papermaking: An Overview

B. Crouse and D. Wimer

Submitted for TAPPI Alkaline Papermaking Short Course
Orlando, Florida
October 16, 1990

Copyright© 1990 by The Institute of Paper Science and Technology

For Members Only

NOTICE & DISCLAIMER

The Institute of Paper Science and Technology (IPST) has provided a high standard of professional service and has put forth its best efforts within the time and funds available for this project. The information and conclusions are advisory and are intended only for internal use by any company who may receive this report. Each company must decide for itself the best approach to solving any problems it may have and how, or whether, this reported information should be considered in its approach.

IPST does not recommend particular products, procedures, materials, or service. These are included only in the interest of completeness within a laboratory context and budgetary constraint. Actual products, procedures, materials, and services used may differ and are peculiar to the operations of each company.

In no event shall IPST or its employees and agents have any obligation or liability for damages including, but not limited to, consequential damages arising out of or in connection with any company's use of or inability to use the reported information. IPST provides no warranty or guaranty of results.

INTRODUCTION

At present, alkaline processes are used to produce 20% of the paper and paperboard made in the United States. In Europe, this figure is 50-60%. It is expected that alkaline papermaking in the U.S. will grow throughout the 1990's. The driving forces for this growth are process advantages and product improvements, which translate into cost advantages, as well as environmental considerations and possible government regulation. One example, the uncoated free sheet grade, is predicted to increase from 26% made by the alkaline process to 52% by 1993 (1). This study provides a general overview of this process and outlines the materials used and their impact on some of the paper properties.

CLASSES OF SIZING AGENTS

The three most common neutral/alkaline sizing agents currently being used are alkenyl succinic anhydrides (ASA), alkyl ketene dimers (AKD), and neutral rosin systems. Some of their advantages versus acid papermaking are shown below (2, 3, 4). Many of these advantages are interrelated. Optimum conditions should be developed based on each mill or grade and its needs.

Advantages of Alkaline/Neutral Systems Versus Acid Systems

Improved Sheet Strength

Substitution of Calcium Carbonate for Titanium Dioxide

Improved Paper Stability on Aging

Reduction in Energy Consumption

Increased Productivity

Reduced Corrosion

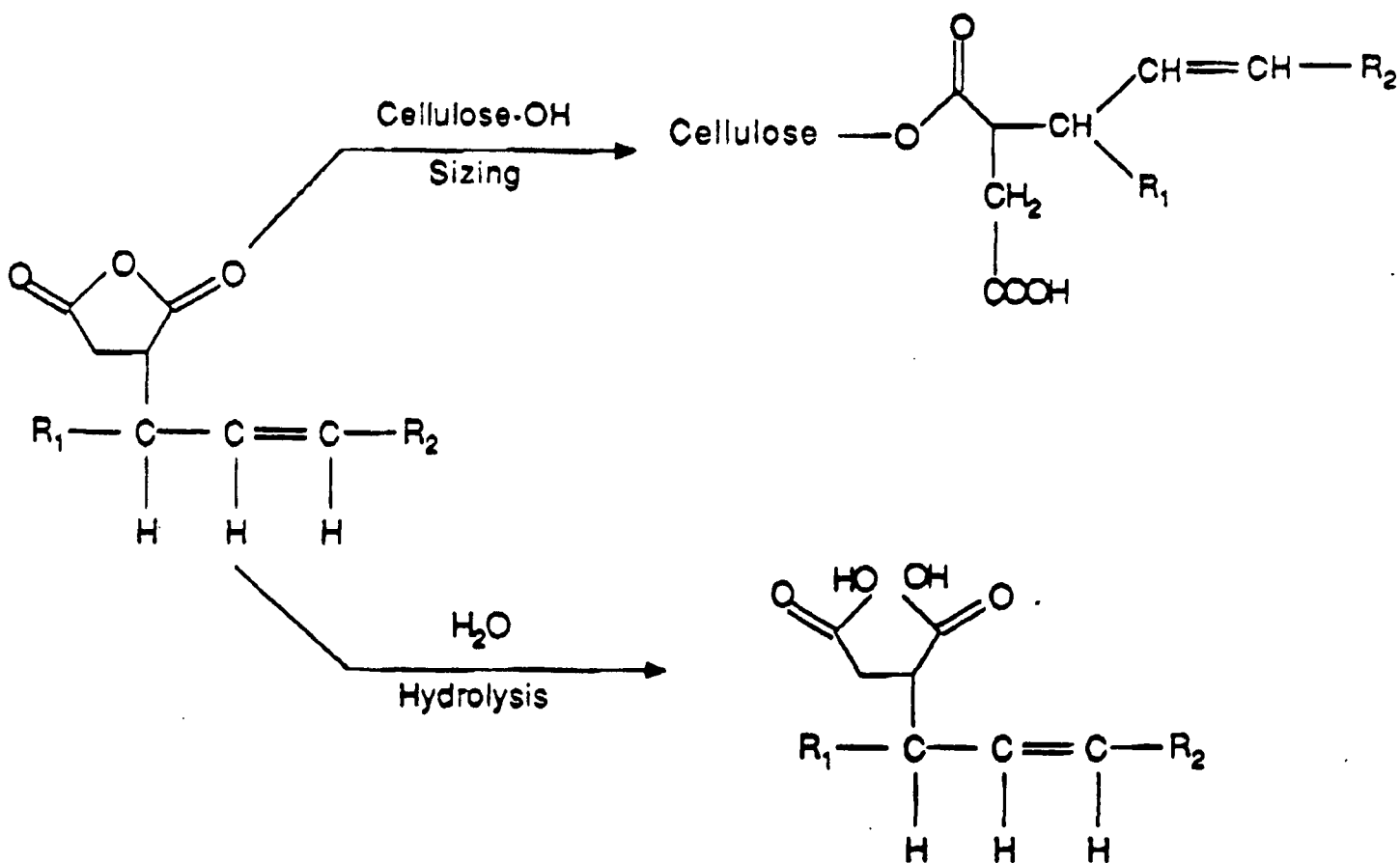
Increased System Closure

ASA is an unsaturated fatty acid anhydride. It is depicted in Figure 1 with its reactions for sizing and hydrolysis. ASA is the most reactive of the three sizing agents discussed here. For this reason it must be emulsified on-site and used shortly after make-up. In addition, first pass retention must be maximized to prevent recirculation of the size in the wet end. This is often accomplished with a cationic polymer or cationic starch addition. All these steps will minimize hydrolysis, which can result in poor sizing (5, 6, 7). The hydrolyzate can also cause press picking problems due to its tackiness, but its effects can be minimized by employing sufficient aluminum ion at a pH greater than 7 as detailed by Scalforotto (8). An advantage of ASA sizing is that due to its reactivity 80 to 100% of the ultimate sizing is achieved while on-machine (5, 6). This allows for good size press solution hold-out (5).

AKD is a ketene dimer with two alkyl chains produced from two fatty acid molecules by dimerization of their acid chlorides (9). It is depicted in Figure 2 with the reactions for sizing and hydrolysis. AKD tends to be less reactive than ASA. It does not hydrolyze as rapidly and the sizing reaction does not proceed as rapidly as with ASA. It has been reported that newer

Figure 1

Reactions of Alkenyl Succinic Anhydride (2,5)
(where $R_1 = C_1$ or C_2 , $R_2 = C_{12}$ to $C_{16}(2.)$)



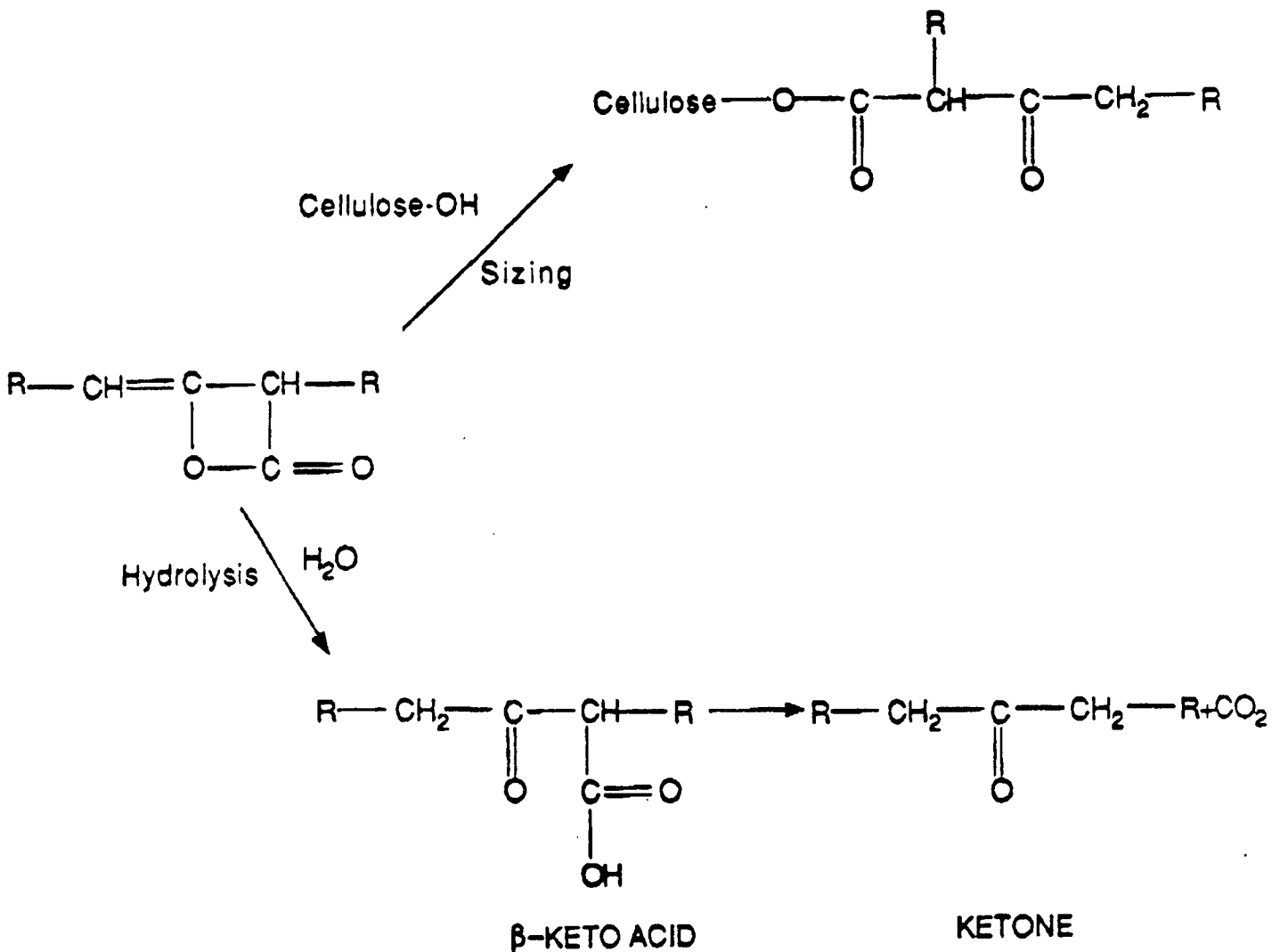
cationic emulsions have shown increased reactivity with cellulose while not showing increased hydrolysis (10). The AKD emulsions are prepared by the supplier and shipped to the mill at solids ranging from approximately 5 to 15%. These emulsions tend to be stable for periods of several weeks to several months depending on storage conditions.

Evidence in the literature shows that the beta ketoester formation shown in Figure 2 may not occur (11, 12, 13). More recent evidence, however, supports the reaction between AKD and cellulose (14, 15, 16, 17, 18, 19). At present, the covalent bond mechanism for sizing is reasonably well accepted. This leads to some of the practical considerations for use of AKD. The rate of sizing development increases as pH increases from 6.5 to 8.5; however, the ultimate degree of sizing begins to level off at pH 7.5 (9). The effect of system alkalinity is important in improving the reaction between AKD and cellulose up to levels of 100-150 ppm as CaCO_3 . This is probably due to a catalytic effect of the bicarbonate anion which complexes with the cellulose and AKD to accept the hydroxyl proton and to provide a proton to the AKD molecule (15). Others suggest that the improved reactivity is due to swelling of the fiber to provide an additional and more reactive surface (9). Alum use is less prevalent in AKD systems as its benefits and detriments are still unclear. At higher pH and alkalinity it is unlikely alum would be helpful, but at a pH around 7.0 with low alkalinity some mills have seen runnability improvements (20).

AKD sizing tends to develop more slowly than ASA sizing, due to the lower reactivity with more of the sizing developed upon aging. This effect is less pronounced with the newer emulsions and proper control of pH, alkalinity, and drying. AKD seems to be especially effective for controlling the edge penetration of fluids in grades such as liquid-processed imaging products and

Figure 2

Reactions of Alkyl Ketene Dimer (2,9,10)
 (where R= C12 to C20)



milk carton board. It may also be applied at the size press to further increase sizing. However, care must be taken to prevent hydrolysis and increased paper slipperiness.

Neutral rosin systems are just beginning to develop in North America. They employ dispersed rosin acid size emulsions which may be either cationic or anionic. Cationic material such as a polyaluminum chloride or synthetic polymer is used to retain the size (3, 21, 22, 23). Systems operate around pH 7 or lower but can go as high as about 7.5 depending on carbonate content and degree of sizing required (24). With systems employing polymers to retain the rosin emulsion, alum must still be used to provide aluminum on the fiber surface to orient and bond the rosin in the dryer section. Marton states that these systems should give good on-machine sizing with fewer control problems than the reactive sizes and should be more cost effective (25). In general, these systems cannot provide high levels of sizing, especially as carbonate level and pH increase.

Comparison of Acid and Alkaline Sizing Systems

Two of the more detailed comparisons of acid and alkaline sizing systems were written by Muller and Dumas (26, 27). The key words from these publications, and our own experience, are summarized in Table I and Figure 3.

As the names of the systems imply, one requires an acidic environment while the other requires an alkaline environment. In a similar manner, the rosin acid systems tolerate and require aluminum salts while aluminum salts in alkaline systems are generally reserved for neutral rosin. The Dumas

description (27) is worth reading as it carefully describes the step-by-step sequence of events in the alkaline sizing process and its greater fragility or sensitivity to other papermaking environmental factors. The rosin alum system is different because the size precipitate and retention conditions are largely controlled in the wet end, and the balance of the process performance is signaled by its wet end history.

A significant performance difference between the two systems may be found in their comparative resistance to a range of penetrants. The strongly held covalent bonds of the alkaline system provide a fuller range of sizing protection, especially against alkaline penetrants. This may be significant with certain aqueous coating preparations, liquid packaging, and developing systems common to some imaging products. The more tenuous aluminum oleate bridge between the rosin and cellulose surface functional groups is prone to alkaline hydrolysis under these environments. This results in unacceptable sizing performance.

Another interesting difference between the two methods of sizing is in the sizing response curves and the rate of sizing development. As depicted in Figure 3, the rosin alum system shows improved sizing response against an acid penetrant as the size concentration is increased. Some sizing protection is provided with the lowest concentration of size, and the improvement continues to size concentrations as high as 1.5% of 2%. This system responds as a bulk sizing effect would be observed (e.g., as the pore size of the paper structure is reduced the rate of wetting is reduced). Conversely, the alkaline systems show no such resiliency but instead show a rather steep sizing response curve with a clearly defined minimum critical concentration of size.

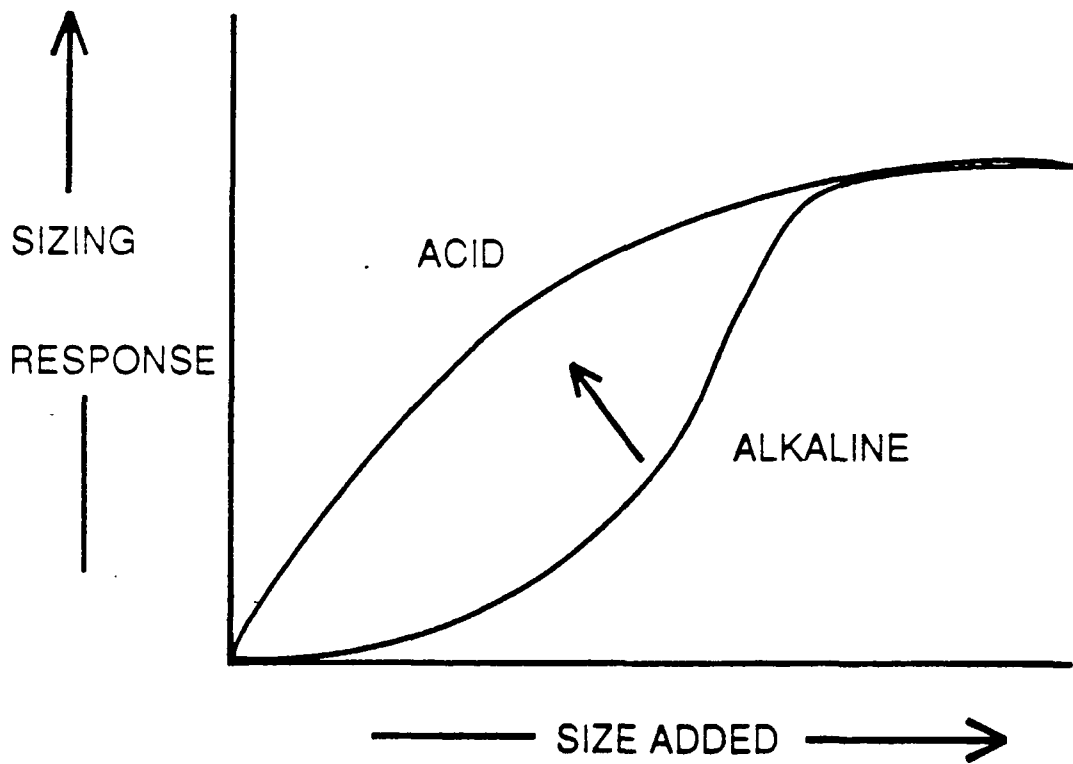
In another analogy, the acid system could be considered more forgiving while the alkaline system shows a greater tendency toward an "all or nothing" behavior. A practical result of the sharp minimum critical concentration phenomenon of the alkaline system is that papermakers run the risk of losing all sizing if they venture too close to the low end of the response curve. The acid system is much more forgiving in this respect and shows more resiliency.

Walkden has explained that the shape of the sizing response curve is in part due to the cationic charge density of the sizing emulsion protective colloid (10). This explanation is based upon the principle that dimer retention is positively correlated with increasing cationic charge density of the sizing emulsion. Lindstrom, et al., have demonstrated a similar positive correlation between retention aid charge density and AKD retention (15). Still another factor which influences the sizing response curve shape is the dimer concentration in the AKD size system and the purity of the fatty acid content. All of these factors have the tendency to change the sigmoid sizing response curve shape toward a smooth normal and positive curve. These explanations may be suitable for both the observed rate and concentration effects. Therefore, as the dimer retention increases, the sizing addition minimum critical concentration becomes less and the response curve changes in the direction of the arrow shown in Figure 3. The rate of the alkaline sizing reaction, for example, reaction with cellulose functional groups, is positively influenced by increasing drying temperature and pH (28). The higher pH and alkalinity are believed to increase the rate of reaction in the dryers (29).

Figure 3

SIZING RESPONSE

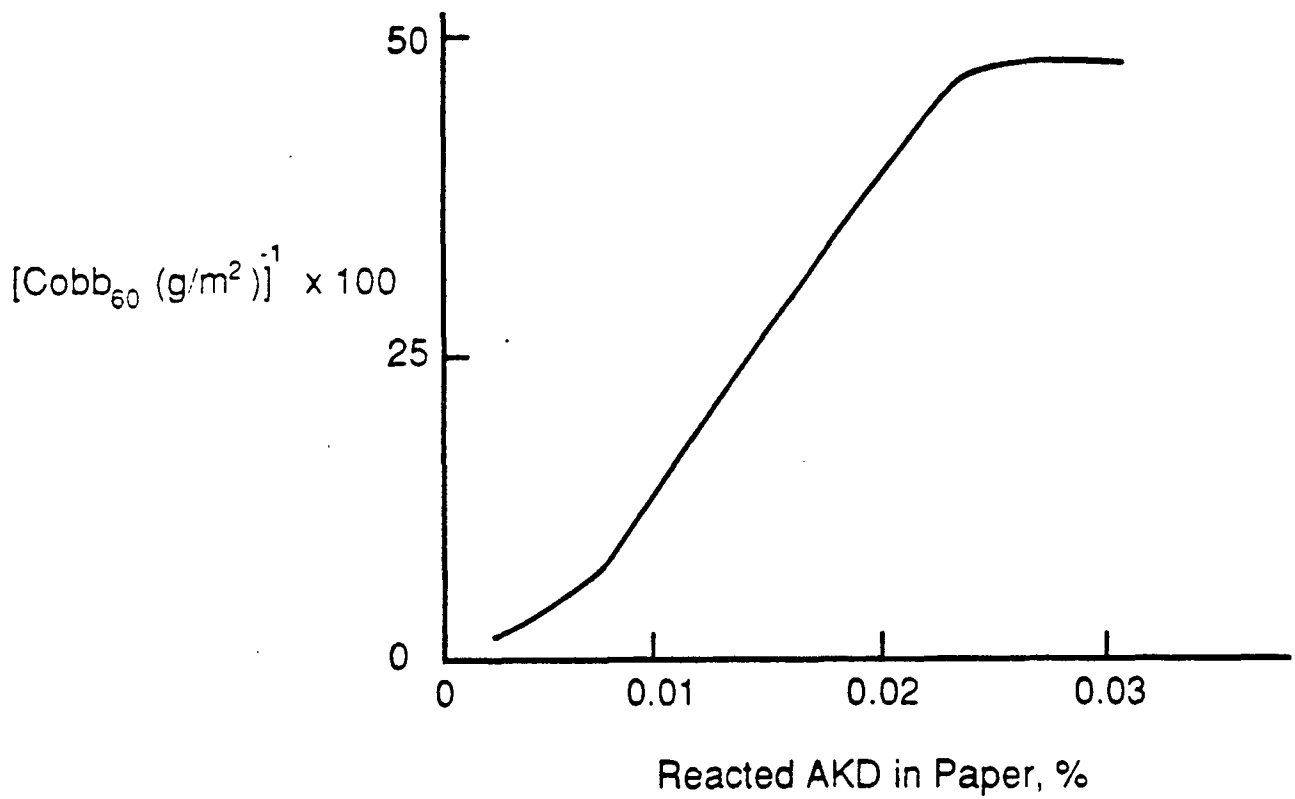
ACID VS. ALKALINE SIZING



Sizing response curve moves in the direction of the arrow as:
(1.) Cationic charge density of size protective colloid increases
(2.) Dimer: Size ratio & fatty acid purity increases

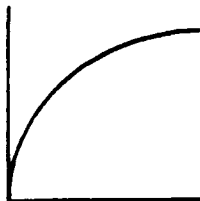
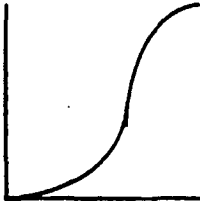
Figure 4

SIZING RESPONSE CURVE
% REACTED AKD IN PAPER VS. COBB₆₀



After: Lindstrom, T., and Soderberg, G.
"On The Mechanism of Sizing With AKD, Part 1"
Nordic Pulp and Paper Research J., No. 1
1986, p. 29

**Table 1
COMPARISON
OF ACID AND ALKALINE
SIZING SYSTEMS**

	ACID ROSIN SIZING	ALKALINE SIZING (ASA, AKD)
1. Effective wet end pH range	3.5 to 6.0	7.0 to 10.0
2. Compatible with alum	Yes	No
3. May be used as both wet end & surface size	No	Varies
4. Resistance to penetrants of varying pH	Not resistant to alkaline penetrants	Resistant to a range of acid & alkaline penetrants
5. Size storage life	Months/Years	Hours/Days/Weeks
6. Time to full sizing development	Seconds/Minutes	Hours/Days
7. Effect on paper coefficient of friction	0 to ↑	↓
8. Sizing response vs. size concentration profile	Progressive increase in sizing performance with ↑ concentration 	Rather steep minimum critical concentration response 
9. Typical size doses, wt. % based on fiber	0.25 to 1.5	0.1 to 0.4
10. Robustness of size retention mechanism	Robust	More fragile
11. Dependence on drying environment for sizing performance	High	High
12. Robustness of entire sizing system	Robust	More sensitive

The Role of Calcium Carbonate

One of the primary driving forces for converting to alkaline papermaking is the desire to employ calcium carbonate, especially in the place of titanium dioxide. In general, the cost of calcium carbonate is approximately one-tenth that of titanium dioxide. For many applications, two parts or less of calcium carbonate can give similar optical properties when substituted for one part of titanium dioxide. This represents a substantial savings. Due to the higher strength potential of alkaline systems, this additional filler may displace some fiber, yielding more savings.

Calcium carbonate is available in several forms. The use of precipitated calcium carbonate (PCC) is expanding rapidly with the availability of on-site generating plants able to tailor the particle size and crystal form for optimum optical, sizing, and strength properties (30). When the PCC is dispersed for shipping by an anionic polyelectrolyte, the subsequent filler and fines retention will be reduced in similar systems (31). For this reason the electrokinetics will have to be adjusted differently for on-site versus off-site use of PCC generated at a single plant. Standard anionic ground limestone shows advantages over PCC in strength and sizing properties due to its larger particle size; however, it tends to be more abrasive and exhibits poorer optical properties and bulking characteristics (30). Cationic ground limestone can show improvements in sizing response retention and strength over the anionic form (32, 33) and can show optical properties equivalent to PCC (33). Newer, modified PCC fillers which are adjusted to various levels of cationic charge show improved sizing versus unmodified PCC (34).

Permanence of Alkaline Papers

Acidic paper is the villain. Alkaline paper is the good guy in the white calcium carbonate hat. That is essentially the way The New York Times contrasted their permanence (35). It has long been recognized that the papermaker's alum contributes sulfate ions to the process in addition to the desired aluminum ions. In the aqueous system, the sulfate and aluminum ions are free to react with available protons to produce weak acids. Acid hydrolysis is believed to be one chemical reaction resulting in the loss of paper permanence (36). The presence of other urban airborne sulfur compounds such as sulfur dioxide further hastens the process. Coupled with the attractive cost of calcium carbonates, the prediction that 70% of all U.S. white papers will be acid free by the end of the 20th century seems perfectly conceivable (37).

Alkaline papers have been defined as "A paper containing calcium carbonate. Such a paper is alkaline (extract pH usually in the range from 7.5 to 9.5) and contains a reserve buffering capacity that can neutralize acidic gases sorbed from the atmosphere" (38). They have also been defined as alkaline reserve papers: "The presence of a compound (e.g., calcium carbonate) put in the paper at a level sufficient to neutralize acid that might in the future be generated from aging of the paper or from atmospheric pollution. A minimum alkaline reserve equivalent to 2% calcium carbonate based upon oven dry weight of paper is required" (39). These standards for permanence define the term as being "a function of the chemical stability of the paper and its ability to maintain initial properties over a long period of time" (38). ASTM D 3458 also provides a Type Numbers measure of degrees of permanence which

correlate directly with paper extract pH. Type I covers the extract pH range of 7.5 to 9.5 while Type III requires a minimum extract pH of 5.5. The well known Barrow studies (40) were among the best documented studies which correlated paper extract pH with permanence. This appears to hold for both physical and optical properties (41).

Other commonly accepted measures of permanence include the characteristic of papers toward color reversion -- the general loss of brightness and whiteness and the retention of original strength, such as fold and tear -- after some period of aging (42). Alkaline papers are believed to be superior to acid papers in all of these keeping properties. In fact, as early as 1936, the alkalinity provided by calcium carbonate was cited as contributing to increased paper permanence (43).

Mill Conversions: Experiences and Concerns

Planning

One element of continuity in published papers dealing with mill conversions from acid to alkaline papermaking is the need for an organized, major commitment on the part of the site management. The conversion to alkaline papermaking may be as eventful as starting up a new machine or at least manufacturing a new grade.

Since each paper machine is unique, the experience and requirements for a successful conversion are as varied as the machines. In the following section, bear in mind that most authors of papers about mill conversion experiences are relating individual experiences on individual machines, experiences which may not always translate to all machines.

Observed Differences, Acid versus Alkaline

Sizing

A significant difference between these two methods of papermaking lies in the sizing response. Although the size level required to obtain equal performance is generally lower for an alkaline system than for an acid system (44), the sizing response curve for the alkaline system is entirely different.

Figure 3 shows a typical sizing response curve for the two systems. Note that for acid systems, such as a classic rosin - alum system, progressive improvement in sizing response may be observed with increasing concentration of size. The neutral systems have a much sharper inflection point on the sizing response curve and a steep region of rapidly increasing sizing response with concentration. This characteristic response curve is responsible for the sharp minimum critical concentration for alkaline sizing agents against many penetrants. In other words, the acid-sizing system tends to provide a higher degree of resilience over a wide range of size concentration. The neutral system is much less forgiving and, should the size concentration drop below the minimum critical concentration, sizing response may become zero (27).

The rate of sizing development is also lower for the alkaline systems (45). The time and temperature factors that regulate this rate have been perceived as both assets and liabilities. If the papermaker is interested in maximizing on-machine sizing, press pick-up or coating strike-in, it is an asset. If coating hold-out is necessary, it becomes a liability.

Alkaline sizing systems have been demonstrated to be superior to acid sizing systems over a wide range of penetrants. This is in largely believed to be a function of the irreversible nature of their size-to-cellulose bonding (45).

Other sizing related differences may be found in the hydrolysis sensitivity of the alkaline size. This is both temperature and time dependent and results in a significant loss in sizing performance.

Another element of emulsion sensitivity is the shear stability of the emulsion. In many mills where first pass retention is less than optimum and where systems were closed, the constant recycling of a fraction of make-up size is detrimental due to repeated exposure to shear fields created by the many pumps in machine transport systems (27). One mill also reported that alkaline-sized sheets provided more even and higher size pickup.

Strength

Papers produced with alkaline sizing systems reportedly tend to be stronger than their acid counterparts (46) since, generally, the cellulose in the alkaline environment will swell and wet at a faster rate than it would in an acid environment (47). The more hydrated cellulose is then easier to refine. In other words, for an equal amount of energy in the refining process, the cellulose in the alkaline environment receives more work and is more highly fibrillated than it would have been in an acid environment.

Another way of looking at this difference is in terms of energy conservation. Since the more hydrated fiber requires less energy to refine to a specific surface area, it would be possible to develop a paper of equal strength using less mechanical energy.

Coefficient of Friction

The popular alkaline sizing agents, especially AKD and ASA, are known to produce papers with a lower apparent coefficient of friction than seen on rosin-alum papers. This slipperiness has caused problems in roll building and sheet tracking (48). In mills with alkaline systems, these concerns have generally been addressed by modifying the mechanical conditions in the roll winding and rewinding operation and in the sheet slitting and cutting operations. Other solutions have included chemical and mechanical fixes such as adding a small percentage of filler to the size press solution. Precipitated CaCO_3 is desirable for this purpose, since its crystal geometry can be used to increase the paper surface coefficient of friction.

Picking and Emulsion Stability

Wet press picking is one of the major operating issues in alkaline papermaking. Contributing factors to wet press picking are the hydrolysis products of the ASA or AKD emulsions (8, 46). Since both of these systems have varying degrees of thermal and mechanical instabilities, they have a tendency to hydrolyze as a function of time, temperature, and shear forces.

Solutions to the hydrolysis concern have included altering the point of addition of the emulsion to a location as close as possible to the headbox. This minimizes shearing instability due to the action of various transport pumps. Other solutions include the use of cooled storage tanks for the sizing emulsion, operating the machine at a lower stock temperature, and maximizing first pass retention.

By minimizing retention losses, the amount of recirculated size is also minimized, and the concentration of hydrolyzate is reduced. Since the sizing emulsions are slightly cationic, it is also beneficial to strategically enter them into the stock system at a comfortable distance from the anionic additives addition point.

Emulsions which are characterized as having fine and uniform particle size distributions are considered optimum for emulsion stability (8). These conditions are regulated by the emulsification process and therefore require careful monitoring of the emulsification conditions and quality of the emulsified size.

Deposits

Paper mills making the acid to alkaline conversion commonly experience a breakout of deposits and associated housekeeping problems. This is generally attributed to the significant pH shock to the paper machine's transport system and the associated solubility and release of chemical deposits from previous acidic papermaking (27). These concerns can be minimized in most cases by conducting a thorough alkaline boilout prior to the conversion.

Most papermakers have also found it advantageous to dedicate a machine and its support system to all alkaline grades rather than continuing to convert back and forth. If shifting occurs between alkaline and acid grades on the same machines, papermakers need to conduct appropriate boilouts between each conversion.

Drying and Energy Considerations

If there is an enigma in alkaline papermaking, it probably lies in drying and energy. As previously stated, the alkaline environment increases cellulose hydration which, in turn, makes the refining process more energy efficient. On the Fourdrinier, the dry line on an alkaline grade appears farther down the wire than it does on its acid counterpart. Despite the fact that the sheet on the wire appears wetter, many practitioners claim that moisture in the press section is similar to that of the acid counterparts and steam requirements for drying are no different than for acid grades. This topic clearly should be left to individual experimentation and interpretation. It certainly does not lend itself to generalization and is undoubtedly highly specific to machine configuration, stock preparation, and paper grade design.

Corrosion

An apparent advantage of an alkaline system is that its environment is not nearly as corrosive to metallic surfaces as is the acidic environment (4).

The abrasion effects, however, associated with the use of calcium carbonate, may offset any longevity advantages attributable to the higher pH. Others have shown that the corrosive effects from the microbiological, size hydrolysis products and electrochemical reactions may be additional concerns for alkaline systems (52). This is another area for speculation, and tangible scientific evidence appears to be lacking in the literature.

Complexity

To some papermakers, an alkaline system is less complex than a standard acid system (49). When they compare rosin plus alum against a single component self-reacting size, they conclude that the latter system is half as complicated as the former. Most complex alkaline systems, however, also use polymeric retention aids, slimicides, higher levels of filler, and other addenda. It seems unfair to generalize about a system's degree of complexity.

Retention

Size retention is usually more difficult to achieve and is more important in an alkaline system than it is in an acid system. The importance reiterates the difference in the sizing response curve demonstrated earlier. Satisfactory high retention requires careful use of a retention aid (50).

Cationic potato starch has a higher molecular weight than corn starch and some of the synthetic polymers -- a quality believed to be responsible for their superior size retention performance (4). Since both the sizing compound and the retention aid generally are ionic materials, the system becomes more sensitive to ionic balancing, unwanted precipitates, and gradual accumulation of miscellaneous anionic particles (49).

Closure and Effluent Control

When properly balanced, alkaline sizing systems provide higher retention and cleaner effluent (44). Some practitioners have stated that alkaline

systems are more amenable when run under closed conditions because they demonstrate less ionic buildup in the system. The proper balancing of system components, including broke and recovered fiber, is critical in achieving high retention and the associated clean effluent.

Breaks and Production Rate

Early in the conversion process, mills which have not obtained a chemically balanced wet end have observed an increase in web breaks. In most cases, these are attributable to the emulsion hydrolyzate and acid deposits from earlier machine history. After this initial period of trial and adjustment has passed, most mills report improved machine productivity. This is generally attributed to two factors: (1) In mills which were previously refiner limited, increased strengths obtained from alkaline refining generally permit high machine speeds. (2) Since the wet web strength is also increased, draw tensions may be run higher and wet web breaks are more controlled.

Machine Wear

Synthetic wires and vacuum box covers wear faster with calcium carbonate filler paper. The filler's abrasiveness is generally believed to be responsible. It is well documented that some of the earlier calcium carbonate fillers are harder than the clay pigments that they replaced in alkaline papermaking.

Optical Properties and Permanence

Although alkaline sized papers generally have lower opacity than their acid sized equivalent, the optical permanence and mechanical durability of these products is superior to their acid counterparts (50). The higher degree of hydration is largely responsible for the opacity reduction when compared with acid papers of equal filler content. Archivists and other groups interested in paper preservation have for some time recognized and specified the use of alkaline papers in applications where keeping and durability are of interest. The Library of Congress, the National Institute of Standards and Technology, The Society of American Archivists, and ANSI have all published specifications which describe the use of alkaline paper materials for their preferred keeping characteristics.

Microbiological Concerns

The older rosin-alum systems were generally free of microbiological contamination owing to the use of healthy doses of alum. Alkaline environments, on the other hand, are prone to slime formation of the fungal type (51). It is therefore essential for good housekeeping practices to formulate alkaline paper systems with appropriate fungicides or microbicides.

Cost

It is apparent in all of the literature that the major driving force for converting from acid to alkaline is to take advantage of the economies of

calcium carbonate as a filler (45). Current market prices show calcium carbonate to be priced at 60-70% of the cost of clay. The alkaline papermaker is also more inclined to produce products in the filler range to 18-25% as opposed to the classic range of 7-12% in the rosin-alum systems (4). This driving force will continue to be the major incentive for further conversion from acid to alkaline papermaking.

Patent Trend Analysis of Alkaline Sizing Activity

Introduction

One indication of the amount of activity in the area of alkaline sizing is that mentioned in the patent literature. A number of convenient data bases exist which contain patent documentation. For this analysis, the Derwent Data Base was searched from 1970-1989. It was key worded for neutral and alkaline sizing and other related but narrower terms. The data base obtained from the Derwent search was down loaded into a patent analysis software program known as PATSTAT PLUS, which can generate statistical data analyses, graphics, and spreadsheets from the patent literature. PATSTAT PLUS has a variety of other uses including technological forecasting. The following PATSTAT analysis was conducted November 29, 1989:

Patent Trend Analysis

The trend search revealed 652 patent documents issued around the world between 1970-1989. Figure 5 shows the trend of this activity with time. Understand that many patent documents require several years of processing before they are issued; consequently, the more recent years in the search

should be considered incomplete. Also, the Derwent search covered the world patent literature and therefore includes issued patents as well as other patent documents such as unexamined applications. Note that in some countries such as Japan and West Germany, there is an abundance of unexamined patent applications due to the nature of their patent process.

Figure 5, which summarizes the total patent activity, shows a steady increase through the most current period. Of the total patent documents included in this analysis, 37% were dated in the 1970's and 63% were dated in the 80's. The patent trend analysis displays a listing of patents and their numerical contribution to the patent literature. If we differentiate between supplier patents and user patents, it can be seen by examining Tables II and III that the majority of the activity has been in the supplier and chemical manufacturing sector. If we examine user activity in the technology, the majority of the activity is centered in Japanese manufacturing.

In Japan, the numerical evaluation showed concentrations of activity at the Mitsubishi Paper Mill and Fuji Photo Film. Of the North American paper manufacturers, Westvaco and Weyerhaeuser were most active. The European activity was concentrated with Felix Schoeller and Wiggins Teape. From the supplier rankings, Arakawa and Mitsubishi were the most active Japanese manufacturers while BASF, Bayer, and Ciba Geigy were most active in Europe. In North America, Hercules led the activity, followed by Dow Chemical, National Starch, and Monsanto. In a ranking by patent country, Japan dominates the activity with 40% total. West Germany follows with 16%. The United States patent activity amounted to 15% of the total and all of the other remaining patent countries and patent codes accounted for less than 7% of the remaining activity on an individual basis.

This partial analysis of the patent literature in alkaline papermaking has shown a rapid increase in patent activity from 1970 to the present. Recently, it was estimated that nearly 30% of the U.S. paper production is converted to alkaline, with nearly twice that level in Europe (53). Technological forecasters would extrapolate the patent trend data here to suggest that technology-focused activities in alkaline papermaking will continue well into the 1990's since the technology has not matured.

ACKNOWLEDGEMENT

Thanks to Mary Dugan for her skill in conducting the patent search and PATSTAT PLUS analysis. Thanks also to Diane Arnold for her professional and timely assistance with the manuscript preparation.

Figure 5

PATENT ACTIVITY BY YEAR

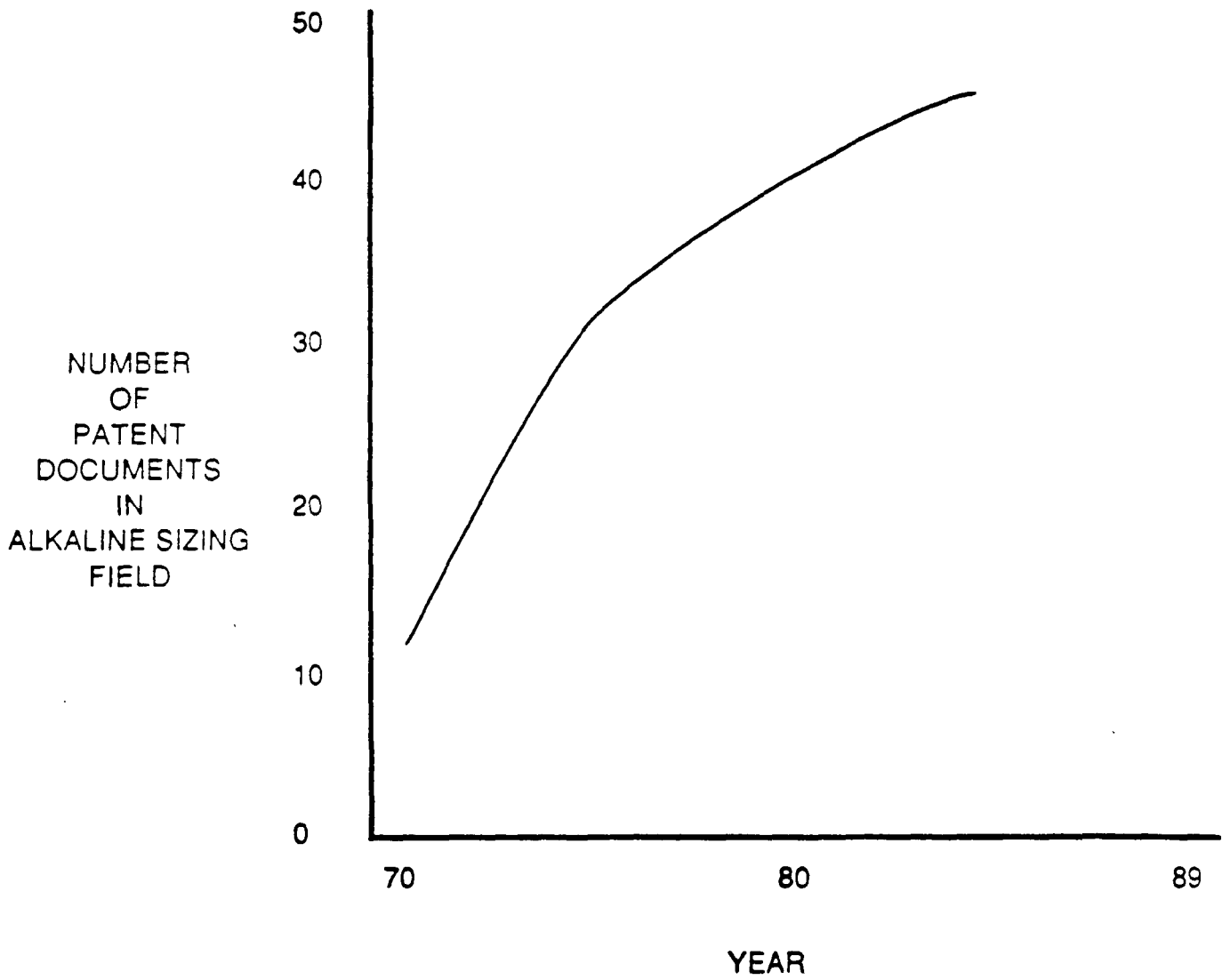


Table 2
PATENT DOCUMENTS
BY COUNTRY

JAPAN	424	40%
WEST GERMANY	174	16%
UNITED STATES	163	15%
CANADA	78	7%
FRANCE	68	6%
FENLAND	57	6%
U.S.S.R.	52	5%
NORWAY	51	5%
	<hr/>	<hr/>
	1,067	100%

TABLE 3

WEST GERMANY

BASF	21
BAYER	20
CIBA-GEIGY	13
CHEMISCHE WERKE HULS	9
GERR GIULINI	6
HOECHST	5
RHONE-POULENC	4
AKZO	3
FELIX SCHOELLER	3
VEB ZELLSTOFF PAPIER	3
ATOCHEM	2
DEGUSSA	2
HENKEL	2

U.K.

ENGLISH CLAYS	4
ALLIED COLLOIDS	1
ANGLO-AMERICAN CLAY	1
IMPERIAL CHEM. IND.	1
WIGGINS TEAPE	1

Table 4

<u>JAPAN</u>		<u>U.S</u>	
ARAKAWA	35	HERCULES	11
MITSUBISHI PAPER MILL	22	DOW CHEMICAL	7
KAO	16	NATIONAL STARCH & CHEM.	6
SEIKO CHEMICAL INDUSTRY	15	MONSANTO	5
SANYO CHEMICAL INDUSTRY	13	U.S. GYPSUM	4
SUMITOMO CHEMICAL INDUSTRY	9	AMERICAN CYANAMID	3
KINDAI KAGAKU	8	PENICK & FORD	3
KURARY	8	WESTVACO	3
mitsui	8	AIR PRODUCTS & CHEM.	2
OJI PAPER	8	AMERICAN COLOR & CHEM.	2
FUJI PHOTO FILM	7	DUPONT	2
HARIMA KASEI KOGYO	6	MARDON FLEXIBLE PACKAGING	2
DENKI KAGAKU KOGYO	5	MERCK	2
JAPAN CARLIT	5	MOBIL	2
NICHIDEN KAGAKU	5	NALCO	2
NIPPON PETROCHEM	5	STALEY	2
TOMOESANA PAPER	5		

1. Walkden, S. A., New Momentum for Alkaline Papermakers, Tappi J., Vol. 72, No. 11, November 1989, pg. 8.
2. Dumas, D. H., An Overview of Cellulose-Reactive Sizes, TAPPI Sizing Short Course, 1980, pp. 47-54.
3. Abell, S., Alkaline Papermaking and Rosin Size, TAPPI 1985 Alkaline Papermaking Conference, TAPPI Press, pp. 31-36.
4. Wiley, T., Converting to Alkaline: U.S. Fine Paper and Board Mills Step Up Pace, Pulp and Paper, Vol. 62, No. 12, 1989, pp. 43-45.
5. Farley, C. E., Wasser, R. B., Sizing with Alkenyl Succinic Anydride, The Sizing of Paper, 2nd Edition, TAPPI Press, 1989.
6. Proverb, R. J. and Dauplaise, D. L., Chemical Optimization of the ASA Sizing System, TAPPI Papermakers Conference, 1989, pp. 91-93.
7. Maher, J. E., The Role of Retention in Alkaline Sizing Systems, Alkaline Papermaking Conference, TAPPI Press 1985, pp. 89-92.
8. Scalfarotto, R. E., Remedies for Press Picking Boost Efficiency of ASA Synthetic Sizing, Pulp and Paper, April 1985, pp. 126-129.
9. Evans, D. Bruce, Alkyl Ketene Dimer Sizes, The Sizing of Paper, 2nd Edition, TAPPI Press, 1989.
10. Walkden, S. A., Alkaline Sizing Today with Ketene Dimer Emulsions, TAPPI Annual Meeting 1989, pp. 1-2.
11. Lund, R. C., Studies on the Mechanism of AKD Sizing, Alkaline Papermaking Conference, TAPPI Press, 1985, pp. 1-5.
12. Rohringer, P., Are So-Called Reactive Sizes Really Cellulose Reactive, Tappi J., Vol. 68, No. 1, January 1985, pp. 83-86.
13. Roberts, J. D. and Garner, D. N., The Mechanism of Alkyl Ketene Dimer Sizing of Paper, Part 1, Tappi J., Vol. 68, No. 4, April 1985, pp. 118-121.
14. Lindstrom, T. and Soderberg, G., On the Mechanism of Sizing with Alkyl Ketene Dimers, Parts 1-2, Nordic Pulp and Paper Research Journal, No. 1, 1986, pp. 26-42.
15. Lindstrom, T. and Soderberg, G., On the Mechanism of Sizing with Alkyl Ketene Dimers, Parts 3-4, Nordic Pulp and Paper Research Journal, No. 2, 1986, pp. 31-45.
16. Kamutzki, W. and Krause, T., Mechanisms During the Neutral Sizing with Alkyldiketenes, Wochenblatt fur Papierfabrikation, Vol. 111, April 1983, pp. 215-222.
17. Odberg, L., et al., Evidence for B-Ketoester Formation During the Sizing of Paper with Alkyl Ketene Dimers, Tappi Journal, Volume 70, No. 4, April 1987, pp. 135-139.

18. Nahm, S. H., Evidence for Covalent Bonding Between Ketene Dimer Sizing Agents and Cellulose, *J. Wood Chem. Tech.*, 6, 1, 1986.
19. Dumas, D. H. and Evans, D. B., AKD-Cellulose Reactivity in Papermaking Systems, TAPPI Papermakers Conference, 1986, pp. 31-35.
20. Cates, Robert, Personal Correspondence, 1989.
21. Wortley, B., Advances in Neutral pH Sizing Help Solve Operating Problems, PIMA, February 1989, pp. 44-45.
22. Wortley, B., The Role of Alum in Acid, Neutral and Alkaline Papermaking, TAPPI 1987 Advanced Topics in Wet End Chemistry Seminar, pp. 55-61.
23. Ehrhardt, S., Sizing with Rosin Under Neutral Papermaking Conditions, 1990 Papermakers Conference, pg. 171, April 1990.
24. Wortley, B., General Chemical Seminar, 1990 Papermakers Conference, April 1990.
25. Marton, J., Published Interview, PIMA, July 1989, pp. 56-57.
26. Muller, F., "Sizing of Paper with Synthetic Products", *Farben Revue*, No. 21, 1972, p. 53, published by FARBENFABRIKEN BAYER G MBTT, Leverkusen, West Germany.
27. Dumas, D. H., "An Overview of Cellulose-Reactive Sizes", TAPPI, 64(1), January 1981, p. 43.
28. McCarthy, W. R., and Stratton, R. A., "Effects of Drying on ASA Esterification and Sizing", *Tappi Journal*, 70(12), December 1987, p. 117.
29. Swanson, J. W. (ed.), "Internal Sizing of Paper and Paperboard", TAPPI Monograph, No. 33, 1971, p. 164.
30. Gill, R. A., Satellite PCC-The Behavior of Various Calcium Carbonate Fillers and Blends on Paper Properties, TAPPI Papermakers Conference, 1988, pp. 39-51.
31. Sanders, N. D. and Schaefer, J. H., Zeta Potential Distributions in Pulp/PCC Mixtures, TAPPI Papermakers Conference, 1989, pp. 69-74.
32. Penniman, J. G. and Olson, C. R., The Chemistry of the Neutral/Alkaline Process, TAPPI 1985 Alkaline Papermaking Conference, TAPPI Press, pp. 113-133.
33. Goodwin, L., Benefits of Cationic Ground Calcium Carbonate, TAPPI Papermaker's Conference, 1989, pp. 257-260.
34. Gill, Robert A., Modified PCC Fillers to Reduce Sizing Demand and Improve Runnability, 1990 TAPPI Papermakers Conference, pp. 255-267, April 1990.
35. The New York Times, March 8, 1989, p. B1.
36. Luner, P., "Paper Permanence", TAPPI, 52(5), May 1969, p. 796.

37. Morris, G.D.L., "Alkaline: Paper Mighty as the Pen", Chemicalweek, March 22, 1989 p. 18.
38. ASTM Standard D3458-85, Standard Specification for Copies From Office Copying Machines for Permanent Records.
39. ANSI Z39 48 - 1984, Permanence of Paper for Printed Library Materials.
40. Barrow, W. J., "Deterioration of Book Stock; Causes and Remedies", The Virginia State Library, Richmond, VA, 1959.
41. Dahl, S., "Evaluation of Condition of Manifold Papers in File", National Bureau of Standards Report 10429, June 1971.
42. Bureau, W. H., "How Long Will it Last?", Graphic Arts Monthly, 50(7), July 1978, p. 68.
43. Jarrell, T. and Ueitch, F., U.S.D.A. Technical Bulletin 541T, 1936.
44. Brink, H. G. and Gasper, L. A., "ASA Sizing in Alkaline Papermaking", TAPPI Alkaline Papermaking Seminar (Portland), p. 15-25, April 27-29, 1983.
45. Dumas, D. H., "Alkaline Sizing - The Papermaker's New Friend?", TAPPI Papermakers Conference Proceedings, April 9-11, 1979, p. 67.
46. Beatty, J. E., "Alkaline Papermaking: Appleton's Decade of Problem Solving, Success", Pulp and Paper, December 1983, p. 86.
47. Beach, E. M., "Alkaline Papermaking - Wet End Operation", TAPPI Journal, 67(4), p. 92-94, April 1984.
48. Chen, G. C., Belgard, W. E. and Olson, C. R., "Overcoming Alkaline Papers' Slipping Problem", TAPPI Papermakers Conference Proceedings, p. 133-135, April 6-8, 1987.
49. Riddell, M. C., "A Decade of Experience with Alkaline Papermaking", TAPPI Papermaker's Conference Proceedings, April 9-11, 1979, p. 87.
50. Hennessy, T. J., "Conversion to Alkaline System Requires Extensive Testing", Southern Pulp & Paper, April 1983, p. 18.
51. Bryson, H. R., "Alkaline Papermaking: Scottish Mill Now Has 15 Years Experience", Pulp and Paper, 57(7), July 1983, p. 74.
52. Bowers, D. F., "Corrosion Considerations for Alkaline Papermaking", Tappi J., 69(1), January 1986, p. 62.
53. Bottiglier, J., "Will the 1990's be the Alkaline Decade?", PIMA, December 1989, p. 18.