

AN ABSTRACT OF THESIS OF

Mankui (David) Chen for the degree of Doctor of Philosophy in Forest Products Presented on September 17, 1996

Title: INVESTIGATING THE MECHANISM OF PAPER SIZING THROUGH A DESIZING APPROACH AND A NEW APPROACH TO ROSIN SIZING WITHOUT MORDANTS

Abstract approved: \_\_\_\_\_

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Christopher James Biermann

A series of chemical penetrants are employed to investigate the chemical characteristics of size bonds in different sizing systems. The bonding strength has been proved to be determined by the type of bonding. In rosin-alum size the size bond is an indirect coordinate bond, which is vulnerable to the attack by acid, alkaline and especially by aluminum-affinited ligands, in which ligand substitutions take place and determine the rate of ink penetration in the Hercules Size Test (HST) test. Alkyl Ketene Dimer (AKD) can react with cellulose to form a direct  $\beta$ -keto ester bond. This covalent bond is strong enough to resist the attack of acid or alkaline and is almost inert to these chemicals. However, if a small amount of alum is used in AKD sizing, there will be two types of size bond existed in the acid condition. Therefore, different HST values will be observed depending on what ink is used. A hypothesized mechanism about ligand substitution has been proposed and verified indirectly. This simple desizing approach provides

important information on sizing mechanisms and will benefit new sizing agent research.

As a new approach to rosin soap sizing, it was found that dipping handsheets in the rosin soap solution and drying the sheets at elevated temperatures could induce effective sizing on different pulps. No mordant (alum) is needed in this process. The pH of the dipping solution seems to have little effect on the sizing result. Some desizing inks with strong effects on conventional rosin soap sized paper were found to have little desizing effect on these type of handsheets. These facts strongly indicate that covalent ester linkages could be the bonds that form between rosin molecules and fibers in this process. The dry schedule, heat temperature, and the concentration of dipping solution have shown various effects on the sizing results depending on the types of pulp used. Completely understanding the sizing mechanism and making this process commercial is well worth additional research work. This method, however, suffers from its speed of fugitiveness.

INVESTIGATING THE MECHANISM OF PAPER SIZING THROUGH A  
DESIZING APPROACH AND  
A NEW APPROACH TO ROSIN SIZING WITHOUT MORDANTS

by

Mankui (David) Chen

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APPROVED:

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Major Professor, representing Forest Products

Signature redacted for privacy.

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Head of Department of Forest Products

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Dean of Graduate School

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Mankui (David) Chen

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INVESTIGATING THE MECHANISM OF PAPER SIZING THROUGH  
A DESIZING APPROACH AND A NEW  
APPROACH TO THE USE OF ROSIN SIZING WITHOUT MORDANTS

Chapter 1

INTRODUCTION

Paper has become an inseparable part of our life. We use paper for writing, printing, wrapping and many other purposes every day. Sizing is one of the important properties for many types of paper. The chemistry involved in the sizing process is very complex and represents the major aspect of the wet end process of papermaking. This subject has been studied by paper scientists for more than one hundred years. Some important developments have been achieved. However, in past research, some investigations were based on unrealistic papermaking conditions or the experimental techniques were inadequate for producing meaningful results. Some important aspects have been overlooked. Some erroneous assumptions have been repeated many times without verification, and some problems which have been confusing us for many years still remain unsolved. This paper is designed to clear up some issues in the sizing mechanism and provide some useful and reliable information for both papermakers and paper scientists to improve sizing efficacy and search for new sizing agents.

### 1.1 What is sizing?

Sizing is the paper's property to resist liquid wetting and penetration. The liquids are usually water or aqueous solutions such as ink, milk, coffee, blood, citrus juice, and other fluids. This property is basically required by the end use properties of most paper products for writing, printing, wrapping, packing and construction applications. It is often required by papermaking operations to control aqueous pickup and penetration in a subsequent coating or size-press operation. Since paper is a cellulosic fiber material, many hydroxyl groups from cellulose and carboxyl groups from hemicellulose actually are water-loving groups. They naturally attract water molecules through hydrogen bonding. Therefore, without special treatment, paper has no such ability to resist liquid wetting and penetration. Sizing has to be achieved through sizing treatment, in which a sizing agent is used to convert the original hydrophilic fiber surface to a hydrophobic surface.

### 1.2 Sizing agents

Davison (1) describes a sizing agent as a material that gives the fiber surfaces a relatively low-energy surface coating so that high-surface energy aqueous liquids will form a high contact angle and thus be discouraged from moving extensively laterally or transversely on the sized surface. Sizing agents are normally amphipathic materials, which have two different parts in their structures -- the

hydrophilic polar end and hydrophobic nonpolar end. In the sizing process, the hydrophilic part should bind to the fiber surfaces and leave the hydrophobic part extending outward to cover the fiber surfaces. When sufficient surface coverage is reached, the paper will have suitable water repellency. Many types of organic chemicals have this structure, but only a few types of chemicals are commercially used as sizing agents in the paper industry. They are rosin, fatty acids, alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD).

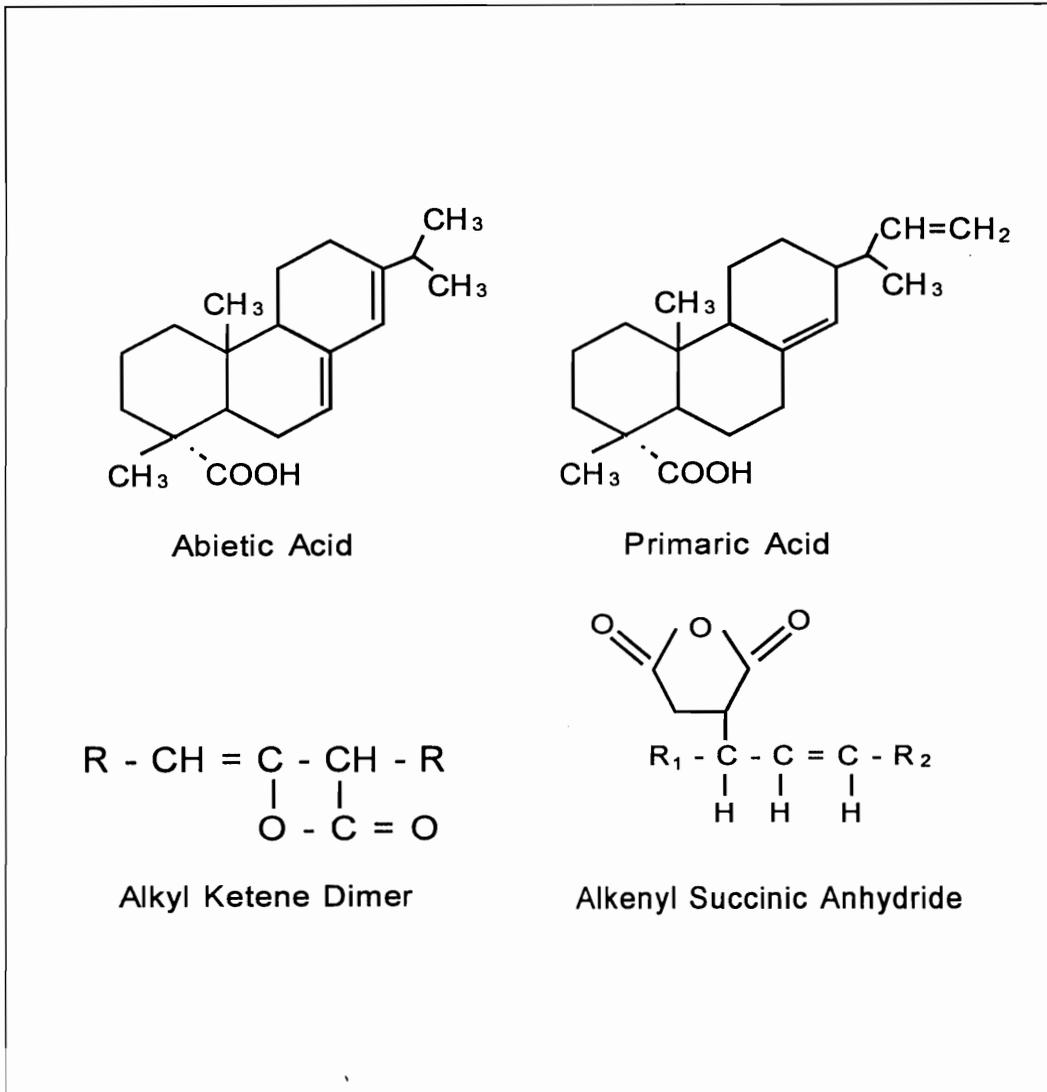
#### 1.2.1 Rosin

Rosin is a traditional sizing agent used in the paper industry for more than a hundred years. It is an alkylated, tricyclic, unsaturated organic acid derived from a variety of natural sources (tall oil, wood rosin, gum rosin). The two main components of rosin are abietic acid and primaric acid (**Figure 1.1**). The smaller carboxyl group is the polar and hydrophilic end. The large hydrocarbon portion is hydrophobic. In the sizing process, the polar end is oriented toward the surface of the fiber with its nonpolar hydrophobic end outward.

#### 1.2.2 AKD and ASA

Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) (**Figure 1.1**) are two types of synthetic sizing agents

Figure 1.1 Commonly used sizing agents



widely used in the last thirty years in the paper industry. Both are amphipathic materials attached with about 16 carbon hydrocarbon chains. The polar ends (ketene or anhydride) are capable of reacting with the hydroxyl groups on the cellulose to form covalent ester linkages with fibers.

Although rosin and synthetic size agents have different structures, especially different hydrophilic groups, they all function by decreasing the wettability of the fiber surface through the introduction of the hydrophobic groups on a fiber sheet. However, the size hydrophobicity is not enough for effective sizing. A useful sizing agent must meet following requirements (1-5):

1. It must produce fiber surface having a low degree of wettability by aqueous liquids.
2. It must be well distributed over all the fiber surfaces, to insure adequate water repellency throughout the paper structure.
3. Its molecules must eventually be well bonded to the fiber surfaces.
4. It must have a high degree of chemical inertness toward the impinged liquid.

All sizes must meet the same requirements to be effective. However, each size carries a different approach to meet these requirements and this results in some different sizing properties.

### 1.3 Rosin size and alum chemistry

#### 1.3.1 Rosin sizing

Rosin, since its discovery in 1804, has been used as an important internal sizing agent in the papermaking process. It is inexpensive, stable and easy to handle. The sizing process has several additional advantages (6):

1. The aluminum rosinate precipitate is an excellent retention aid.
2. The sizing is compatible with other wet-end additives.
3. The problems in repulping waste are minimal.

With the above advantages, rosin size in its various forms still represents the most important size chemical for papermaking.

Since rosin itself is water insoluble, it is first necessary to convert the rosin to a form that is dispersible in the papermaking system. Two major methods are used to make it dispersible in practice. One is to saponify the rosin with alkali to a rosin salt -- the rosin soap. Another is to disperse or emulsify the rosin as a fine particle in solution -- the dispersed rosin. Neither rosin soap nor dispersed rosin is capable of inducing sizing by itself because of its negative charge in the papermaking system. The reaction of rosin with alum to form an aluminum rosinate is considered to be a critical step in the sizing process. The chemistry of sizing development is the same

for both types of rosin size, but the point at which the reaction between rosin and alum occurs is different for the two forms. With soap size the reaction takes place in the pulp slurry before the sheet is formed. While for dispersed rosin the reaction happens only when the sheet passes through the drier section. Several advantages of dispersed rosin have been reported over soap rosin (7), such as higher operating pH at the wet end, stronger paper strength and higher sizing efficacy. The inherent difference lies in their reactivates with alum in the process of sizing formation (8,43).

### 1.3.2 Alum chemistry

Papermakers' alum,  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ , dissociates in pure water into sulfate ions and hexahydrated, trivalent aluminum ions. The aluminum ions then tend to undergo several successive hydrolysis reactions to form aluminum cations. The chemistry of alum in the papermaking system is very complex. The interaction of alum with other materials is still not completely understood. Our understanding of the chemistry of aluminum in the papermaking system is largely attributed to the work by Arnson (9).

Arnson showed that the alum is hydrolyzed in the papermaking system into several species depending on the system pH and the ion concentration. It is also found that the pH range (4.0 to 5.0) where optimum size is achieved coincides with the pH range where maximum aluminum is

adsorbed onto wood fibers in the major form of  $Al_8(OH)_{20}^{4+}$  species. Therefore, the sizing process was explained as electrostatic interactions between alum and rosin and alum and fibers (10). This pure electrostatic mechanism dominated sizing theory for many years even though it often faced difficulties in the explanation of some other sizing phenomena. For example, why is it not possible to induce a good sizing by substituting alum with cationic starch in the rosin sizing system? It is true that the electrostatic interaction between cellulose fibers and rosin particles can lead to the adsorption of the size particles onto the fibers. However, it may not be correct to attribute it to the final bond connecting size and fibers in paper products. Size retention and size bonding or anchoring are two different steps and the latter has much more meaning for sizing performance in paper products. Unfortunately, this important issue has never been given appropriate attention in sizing research. The coordination chemistry of alum is closely linked to this issue.

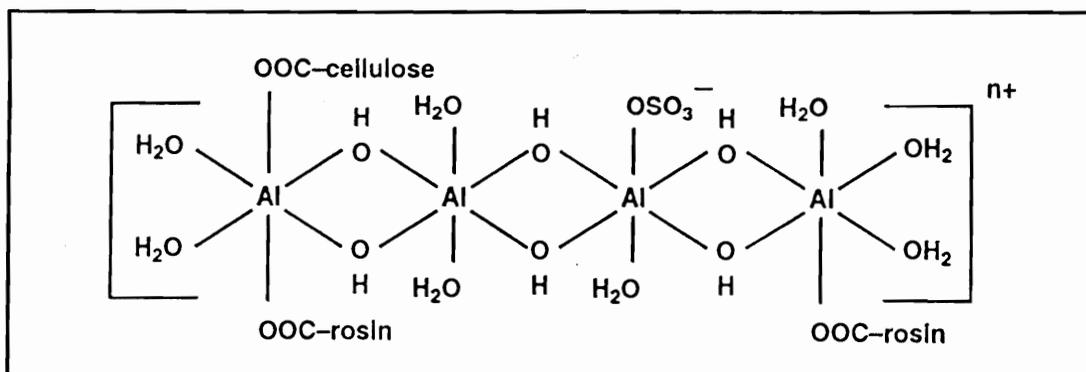
### 1.3.3 Coordination chemistry of aluminum

The coordination chemistry of aluminum was introduced into rosin sizing research as early as 1935 by Thomas (11). It was suggested that the multinuclear aluminum cations act as a Lewis acid -- an electron pair acceptor and could complex with neutral or anionic molecules which are referred to as ligands. These multinuclear aluminum cations have

strong tendency to coordinate with the carboxyl groups from rosin and hemicellulose and even with hydroxyl groups from cellulose to form the relative strong size bonds. This hypothesis was then verified by Wilson's work on aluminum bonds (12), by Price (13) and by Cameron on alum and the alum-rosin precipitate (14), and by Duston (15) and Porter and Lane's work on the use of aluminum chloride (16). However, this coordination theory has not predominated the views on sizing and the importance of this hypothesis has been undermined until the considerable work by Subrahmanyam and Biermann in 1992 (17).

Subrahmanyam and Biermann first introduced a mordant concept into rosin sizing and proposed the structure of aluminum rosin complex as in Figure 1.2 (17,18). A series

Figure 1.2 The hypothetical structure of aluminum rosin fiber complex



of coordinating metal ions were investigated as mordants for rosin soap sizing and proved efficacious in various pH

ranges. It was found that the effectiveness of any metal ion as a sizing mordant was dependent on its first acid ionization constant  $pK_1$ . The peak value of its effectiveness was at a pH in the vicinity of the  $pK_1$  value of the metal ion. This guideline allows us to predict the ideal pH to use with any suitable mordant in sizing. Based on this coordination theory, rosin soap sizing was found to be effective at pH above 10 if polyamine was used as the mordant in place of alum (19). Unbleached kraft pulp and mechanical pulp, which are generally very difficult to size, were reported to achieve a very good sizing if ferric or ferrous was used in the sizing system (20). Alkali-soluble styrene-maleic anhydride copolymer (SMA) was also found to be a very good sizing agent for unbleached kraft pulp and unbleached thermal mechanical pulp when ferrous or alum were used as mordant (21). These abnormal findings were successfully explained by the mordant theory. However, the theory will be further confirmed if the size efficacy of the paper can be inspected on the basis of coordination reaction. One objective of this research is to provide the evidence of this coordination bond in rosin alum size and describe its chemical characteristics. This information should help us to find a more effective way to use rosin as a sizing agent and broaden our understanding of rosin sizing and predict its size efficacy when it is in service.

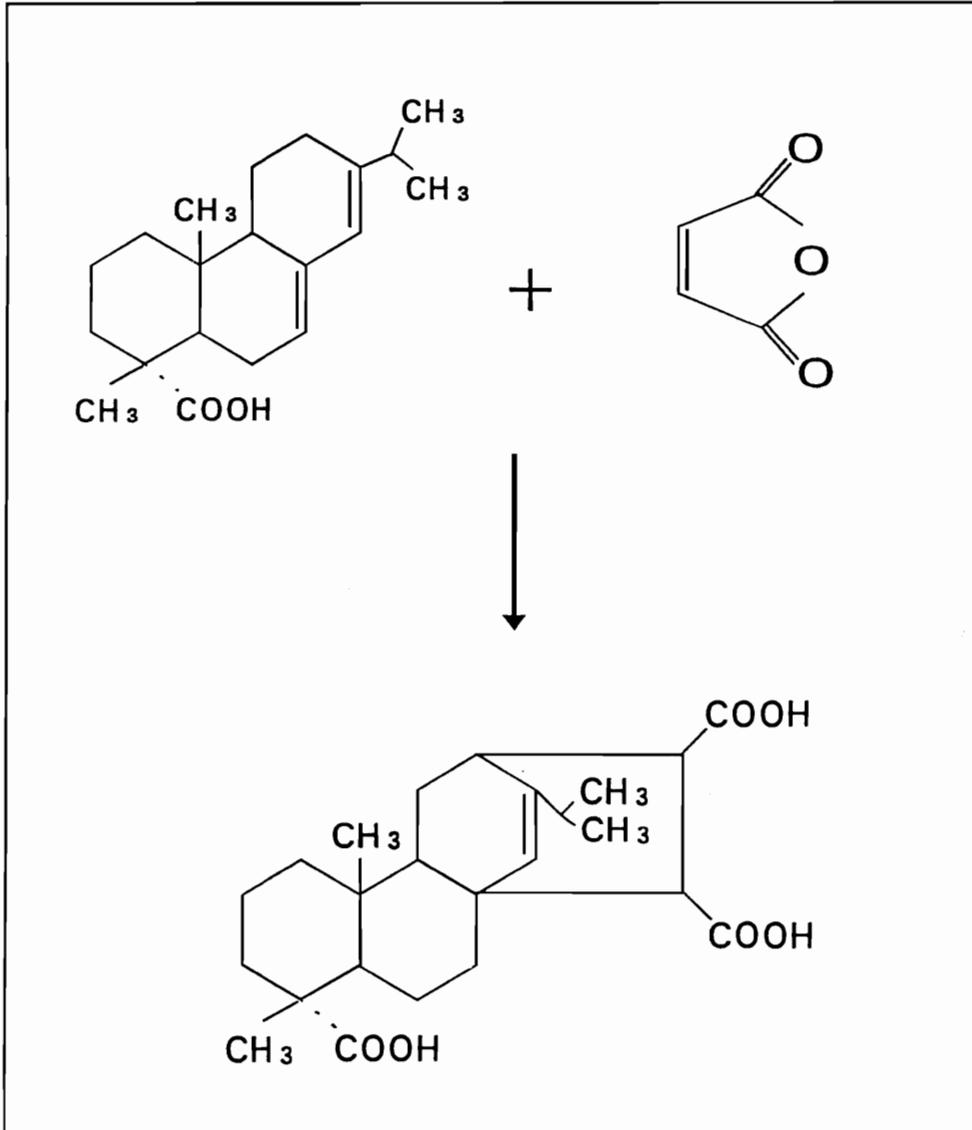
Based on this coordination theory we could have a new understanding about the higher sizing efficacy of fortified

rosin, which has been overlooked in the past. Fortified rosin is a modified rosin product with the treatment of maleic or fumaric anhydride which offers three carboxylic acid groups on each molecule (**Figure 1.3**). The introduction of additional carboxyl groups increases the electronegative character in each rosin molecule and results in a smaller particle size, more uniform distribution, and greater surface coverage. These all contribute to good sizing (7). However, the critical point related to the improvement is the increase of its coordinating ability as a ligand with aluminum cations, which could contribute to a stronger sizing bonding in the paper. That is why fortified rosin is the major part of rosin used in current paper industry.

Alum has been used by papermakers since the days of hand papermaking. In addition to rosin sizing, alum has been applied extensively as a retention aid, formation aid, drainage aid, pitch control agent, and the pH control agent. However, as a sizing additive, it basically requires the system be operated at acidic conditions, which poses several disadvantages and potential problems for rosin sizing:

1. Rosin size cannot develop enough sizing by certain tests, such as lactic acid and alkali, because the lactic acid complexes with alumina and redissolves the floc (22).
2. Alkali converts the hydrophobic rosin back to the water-soluble soap form.

Figure 1.3 The reaction of abietic acid with maleic anhydride to produce fortified rosin



3. Paper strength is significantly reduced if hard sizing was achieved.
4. Sizing of stocks filled with calcium carbonate presents considerable problems with a rosin-alum system. The alkaline carbonate is readily decomposed by the acidic alum resulting in the release of carbon dioxide, which can cause foam problems and render the alum useless.

Although some attempts have been made at using rosin and alum at alkaline conditions, such as using polyaluminum chloride (16), the systems are fundamentally incompatible. The paper industry experienced a very important transformation from acid paper making process to an alkaline process in the last 30 years. The availability of alkaline sizing agents promoted this transfer and made it profitable economically and operationally.

#### 1.4 Neutral and alkaline sizing

The incentives for using alkaline sizing agents usually arises from the benefits of the sizing itself and the benefits of the papermaking system. The significant differences of synthetic sizing from rosin sizing are (1) synthetic sizing works on neutral or alkaline papermaking conditions; (2) the synthetic sizing agent can react with cellulose to form direct strong covalent bond with cellulose. Many advantages of alkaline sizing over acidic sizing have been reported, which include (23-25):

- Improved sheet strength.
- Reduced cost (because the substitution of calcium carbonate for titanium dioxide).
- Enhanced paper permanence.
- Reduced energy consumption.
- Increased productivity.
- Reduced corrosion.
- Increased system closure.

Enhanced permanence and reduced cost have been widely proved by many reports in the past. In order to achieve most of the other benefits, it is necessary to understand the sizing mechanism, choose the right sizing agent, and control the wet end conditions.

ASA is an unsaturated fatty acid anhydride. The anhydride group is very reactive. **Figure 1.4** shows its reactions with cellulose and with water. It reacts with cellulose hydroxyl to form a chemical bond -- a cellulose ester. This orients the hydrophobic alkenyl group away from the fiber to impart sizing. This reaction is very rapid, normally being 80 to 100 percent complete on the paper machine (26,27). However, its high reactivity with water results in poor sizing, and often cause press picking problems. When using ASA as the sizing agent, it is important to minimize hydrolysis.

AKD is a ketene dimer with two alkyl chains produced from two fatty acid molecules by dimerization of their acid chlorides. **Figure 1.5** depicts the reactions of AKD with

Figure 1.4 Hydrolysis and cellulose reactions of alkenyl succinic anhydride (ASA)

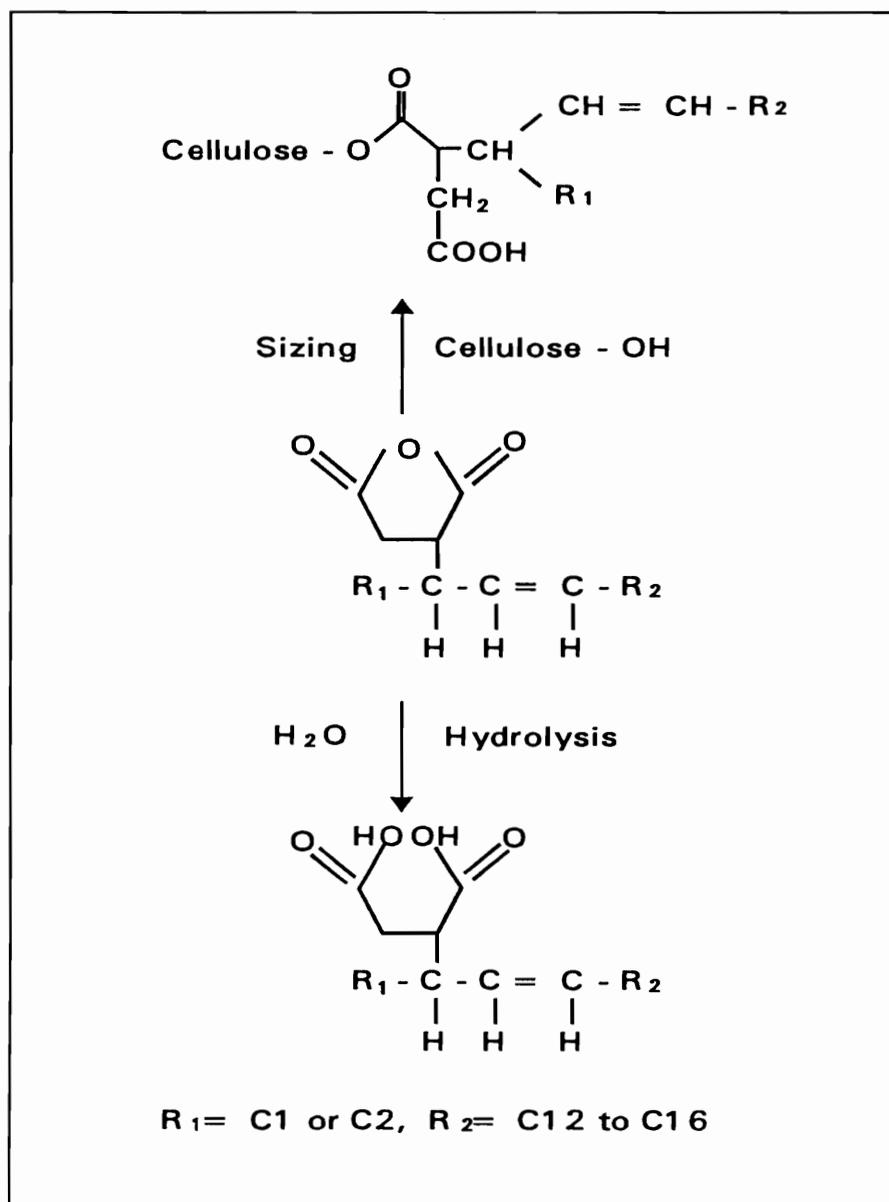
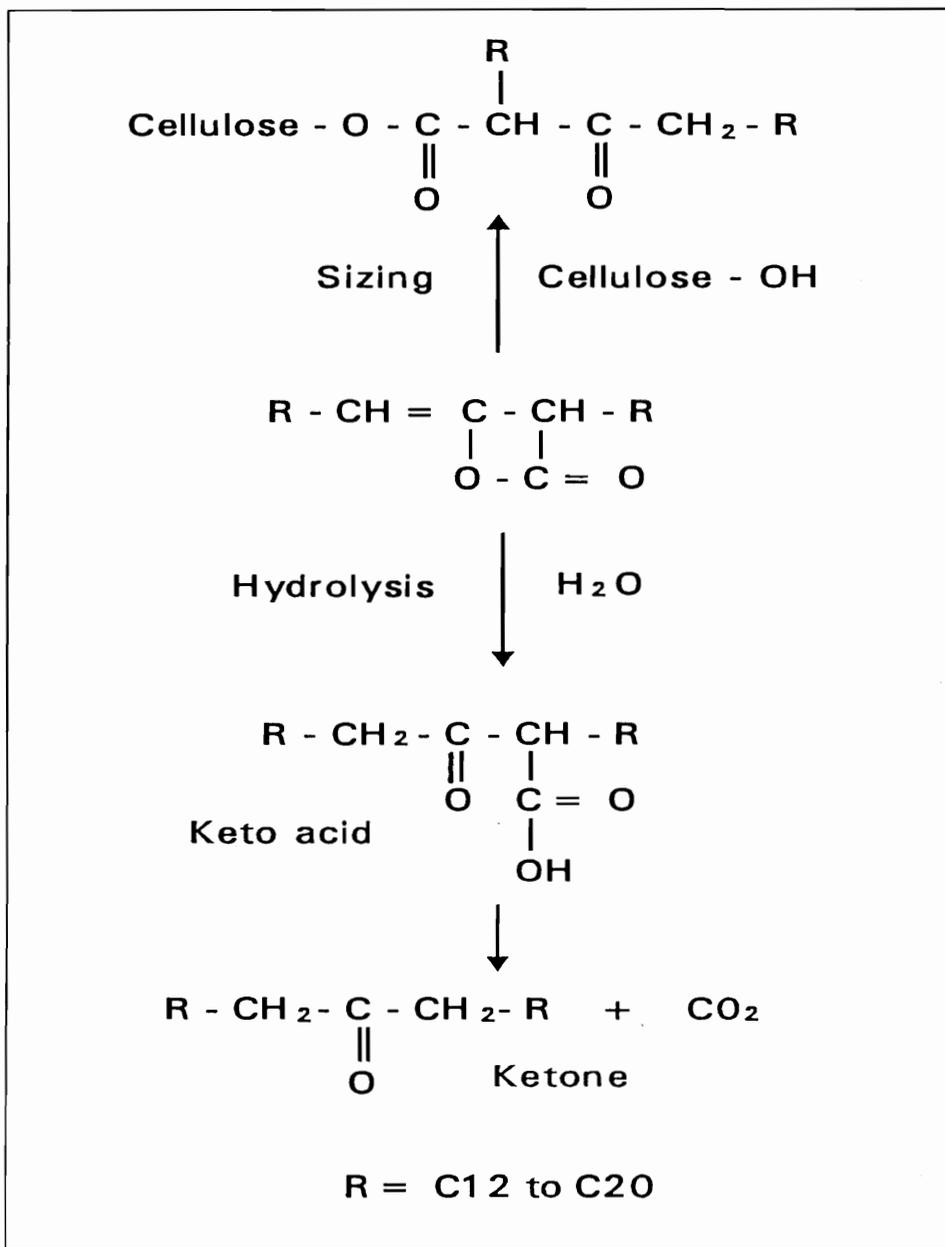


Figure 1.5 Hydrolysis and cellulose reactions of alkyl ketene dimer (AKD)



cellulose for sizing and with water for hydrolysis. AKD tends to be less reactive than ASA. AKD does not hydrolyze as rapidly, and the size reaction does not process as rapidly as ASA. The reaction of AKD with cellulose to form the  $\beta$ -keto ester is the primary mechanism by which AKD sizes paper. This covalent bond formation provides immobilization and orientation of the hydrophobic tails outward, away from the fiber surface.

This covalent bond mechanism for sizing has been traditionally supported by its sizing efficacy -- the good resistance to both acid and alkaline penetrants, and also by the fact that the sizing is unaffected when a solvent for AKD is used to extract an AKD sized sheet. However, this mechanism has been questioned recently because of the inability to analytically detect ester bonds in AKD-sized paper (28,29). This has led to alternative explanations of AKD sizing that do not require ester formation. The  $\beta$ -keto acid hydrolysis product and its salts were claimed to be the major source of the sizing (23). Some research even concluded that AKD was just physically adsorbed to fibers without any chemical connections (30). However, these alternative theories are disproved by several new observations (31,32). In this research, the characteristics of the size linkage between AKD and fibers will be extensively evaluated by different chemical desizing agents.

A very good comparison of acid and alkaline sizing system is provided by Crouse and Wimer (33). The key points are summarized in Table 1.1:

A substantial difference is found in their sizing performance -- the capabilities to resist various types of penetrants. Rosin-alum sized paper has very poor resistance to acidic or alkaline penetrants, while AKD sized paper demonstrates a very good resistance against both acidic and alkaline penetrants. We believe this capability is directly related to the bonding characteristics of the size. Based on this belief, we developed a desizing approach to study

Table 1.1 Comparison of acid and alkaline sizing systems

	Acid Rosin Sizing	Alkaline Sizing
Effective wet-end pH range	3.5-6.0	7.0-10.0
Resistance to penetrants of varying pH	neutral	2.0-10.0
Time to full sizing development	seconds minutes	hours days
Typical size doses, wt % based on fiber	0.25-1.50	0.1-0.4
Compatible with CaCO <sub>3</sub>	no	yes
Compatible with Alum	yes	depends

the sizing mechanism and successfully explain several confusing phenomena in rosin related sizing system.

## 1.5 Liquid penetration and sizing test

### 1.5.1 Liquid penetration theory

All sizes function by retarding the rate of flow of the penetrant through the capillaries formed between fibers. Washburn equation is often used to demonstrate the factors involved in influencing the rate of penetration in ideal cases.

$$\frac{dl}{dt} = \frac{1}{4} \frac{r}{l} \frac{\sigma}{\eta} \cos\theta$$

where

$dl/dt$  = rate of liquid penetration

$l$  = depth of liquid penetration

$t$  = penetration time (sec.)

$r$  = capillary radius (cm)

$\sigma$  = surface tension of liquid (dyn/cm)

$\eta$  = liquid viscosity coefficient (poise)

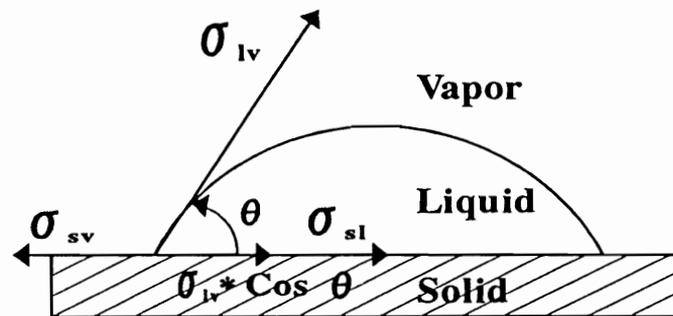
$\theta$  = contact angle

These factors can be classified into the properties of paper itself and of the liquid used. Internal sizing agents only affect the fiber hydrophobicity -- the contact angle of the liquid with the paper surface. This can be ideally expressed in Young's equation and depicted in **Figure 1.6**.

Where  $\theta$  is the contact angle, and the  $\sigma'_s$  refer to the interfacial tensions and the subscripts lv, sv and sl denote the liquid-vapor, solid-vapor and solid-liquid interface, respectively. Even though this equation is only true for ideal, smooth, flat, homogeneous and non-deformable surfaces, it is still very helpful for understanding the mechanism of sizing and sizing test. In the sizing process, after the low energy sizing agent replaced the high energy fiber surface, the interfacial tension  $\sigma_{sv}$  is reduced, so is the  $\cos\theta$ . A higher contact angle will discourage the penetrant from moving into the sheet. On the other hand, in the sizing test, when a bit of surfactant is added into the test ink,  $\sigma_{lv}$  and  $\sigma_{sl}$  will become smaller, so  $\cos\theta$  is increased, the paper become easily wetted, resulting in the increase of the rate of the liquid penetration and shortening the test time for a given paper and test condition.

This simple equation offers us a good explanation about some sizing phenomena. However, it is too simplified and has often been over emphasized. Some important factors involved in this extremely complex process are often ignored. That is why we are often confused by the fact that a paper product exhibiting a very good sizing in one use may fail completely in another application. The chemical stability of the size is a critical issue. The reactivity of the penetrant with the size in the paper may enforce a

Figure 1.6 Contact angle and Young's equation



$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv} * \cos \theta$$

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}}$$

dramatic effect on the liquid penetration. Unfortunately, this issue has never been given adequate attention in the research of paper sizing and has rarely been discussed in the past. This research will demonstrate the importance of chemical stability of the size to the sizing performance in practical applications. It will also clarify some important issues related to the choice of sizing agents and the sizing test and provide reliable prediction for the sizing performance in the end use and help us to achieve an optimum sizing result in the existing sizing conditions.

#### 1.5.2 Sizing test

The measurement of the degree of sizing is a topic that has long been discussed by papermakers. Because of the complexity of the process of liquid penetration into the paper, which involves surface effects, diffusion, fiber swelling, and chemical reactions, there is no one universal method for size testing. More than fifty test methods were reported in the past (34) and new test methods are continuously developed. Different sizing tests are often found to rank papers in quite different orders. Therefore, the degree of sizing is said to be defined by the test used to measure it (35). A valuable test for a specific product is the one that can tell whether the paper will meet the end user requirement.

A summary of all test methods currently available to papermakers for measuring the degree of sizing paper was

provided by Keavney and Kulick (44). A brief description of three commonly used methods are given below with the introductions of their application in this research:

#### 1.5.2.1. Hercules Size Test (HST)

Hercules size test measures the penetration rate of test liquids from the top to the bottom side of the paper (36). A fixed volume (10 ml) of test ink is applied to the top of the sheet. A photoelectric cell registers the drop in reflectance of the opposite side of the sheet as a function of time as the test ink penetrants. When the reflectance drops to a preset percentage of the original, the automatic timer stops, indicating that the end point has been reached. This method is widely used because it is simple, convenient, and easily reproduced. All types of liquids can be used according to the specific sizing requirement for that paper. This advantage has been used in this research to study the sizing mechanism through a desizing approach. Besides the regularly recommended test inks, a series of chemicals were chosen to formulate specific test inks to study their chemical reactivity with the size. From this research, we not only obtain a reliable information about sizing bonding mechanisms but also demonstrate some drawbacks when this test method is generally used for testing some types of paper.

#### 1.5.2.2. Cobb test

This test exposes a pre-weighed paper sample to water for a specific time period and reflects the paper's ability of absorption to the liquid (37). A fixed volume of water is poured inside a metal retaining ring which is clamped to the sheet. After a specific period of time, the water is poured off and the free water blotted from the surface. The sample is immediately reweighed. This test is simple to operate, and the test apparatus is inexpensive. However, it is relatively insensitive for hard sized paper. This method can not compare the degrees among the hard sized papers. This method was employed in Chapter 3 to study the paper sized by direct attachment of rosin soap, and produced quite different results from the HST method. The result from the Cobb test may give more reliable data in this case.

#### 1.5.2.3 Contact angle

As discussed in Section 1.5.1, liquid contact angle measurement is a sensitive and fundamental measure of the wettability of the paper surface by liquid. Sizing materials that raise the contact angle between a drop of water and paper are effective in retarding the penetration of aqueous liquids. Extensive work will be introduced in Chapter 4, in which contact angle measurement is used as a tool to study the surface energetic and acid/base characteristics of sized and unsized papers. Some important

information relating to sizing mechanism has been obtained from this study.

No matter what method is employed, the values obtained often depend on the test conditions, which may significantly affect the rate of liquid penetration into the paper. The important factors are as follows:

1. The properties of test fluids, such as the pH (38), surface tension (34), viscosity (39) and its reactivity with the size (40);
2. The test environment, such as the temperature (41) and the humidity (42).

The factors should be considered in selecting a specific test, and precisely controlling the test conditions is an essential part of obtaining meaningful indications about the sizability of the paper.

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## Chapter 2

### INVESTIGATING THE MECHANISM OF PAPER SIZING THROUGH A DESIZING APPROACH

#### 2.1 Introduction

The objective of internal sizing is to make the originally hydrophilic fiber surfaces relatively hydrophobic so that a certain degree of water repellency can be achieved in paper products. Normally, an amphipathic material is applied to achieve this goal. The hydrophilic part of the amphipathic material should bind to the fiber surfaces, and the hydrophobic part should extend outward to cover the fiber surfaces. When sufficient surface coverage is reached, the paper will have suitable water repellency.

It is apparent that to achieve effective sizing in any internal sizing system, the following basic requirements must be met (1, 2):

1. The size precipitate must have relatively high hydrophobicity.
2. The size must be well retained on fibers.
3. The retained size must be distributed throughout all fiber surfaces.
4. The size precipitate must be strongly bound to the fiber surfaces so that the bonding will not be broken down by fluids.

The importance of high hydrophobicity, good retention and uniform distribution of size molecules to explain the various sizing phenomena and to improve sizing techniques has been fruitful (1, 3). On the other hand, the importance of bonding between size precipitates and fibers has not been well addressed. Anchoring is an ambiguous word frequently used to describe this bonding process (7). However, the relationship between the bonding strength and sizing effectiveness has never been clearly specified. The bonding strength is a critical matter not only for sizing development, but also for the performance of the sized products in service. Completely understanding the bonding characteristics in different sizing systems will provide us fundamental information about sizing mechanisms and help us to understand some unsolved problems in sizing classification, size testing, and in the search for new size agents.

In the paper industry, traditional rosin soap sizing is often called acid sizing since it normally works at pH 4.5 in the paper machine wet end, while alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) sizing are called neutral or alkaline sizing because they are applied at pH above 7. However, the pH difference is not the fundamental difference for these two types of sizing systems. Actually, rosin could be used at neutral or even at alkaline conditions (4). The fundamental difference is in the bonding mechanisms that hold the sizing agents onto

the fibers. From this point of view, direct sizing or indirect sizing would be the suitable terminology for this classification. In the indirect rosin soap sizing system, alum usually is the necessary additive; alum forms polyaluminum ions in solution first, which then react with rosin to form rosin aluminate. This cationic substance is retained with the anionic fibers and bond to the fiber as the sheet is dried. Aluminum serves as a bridge linking both rosin molecules and fibers. In the direct AKD sizing system, AKD molecules are generally believed to react directly with the cellulose hydroxyl groups and form covalent ester bonds with fibers (5, 6).

The actual bonding mechanisms, the chemical properties, and the bond strengths of the size-fiber bond in the final paper still remain controversial. For example, electrostatic forces are often alleged as the main force in rosin-alum sized paper since the positive polyaluminum complex could attract the negative rosin and negative fibers (7, 8, 18). This may be a good explanation for size retention but not for sizing development. Sizing development is another interaction, which should provide the size with enough strength to resist possible attack by water or other liquids. We hypothesize that electrostatic forces, hydrogen bonding, or Van der Waals forces would be too weak to withstand the attack of water. We have proposed the hypothesis that coordination bonds are the most likely linkage in the rosin-alum-fiber bonds. Aluminum acts as a

mordant, while rosin and fiber act as ligands in the size complex (9). Even though the  $\beta$ -keto ester linkage is the widely accepted bond for AKD size, there are still reports claiming that the AKD molecules are physically trapped in the sheet (10) or anchored into fibers by hydrogen bonding (11). The critical point of these arguments actually is about the chemical properties of size bonding. If there are fundamental chemical differences in the size bonds, there should be remarkable differences in their behavior when they are exposed to water, and especially to the chemical additives in the sizing test ink designed for testing various types of bonds.

The Lucas-Washburn equation has been frequently used as the basis for the explanation of sizing development and sizing test results. In the sizing process, sizing agents cover the fiber surface with a lower energy film. The aqueous liquid will form a higher contact angle on the surface, which will obstruct water from wetting and penetration. During the sizing test, we normally assume that this contact angle is constant, so that the liquid viscosity and surface tension are ascribed as the major factors in controlling the rate of liquid wetting and penetration (12). The lower the surface tension of the testing ink, the smaller the contact angle that will be formed, and the greater the rate at which the testing ink will penetrate through the paper. To speed up the sizing test for some hard sized papers, some penetrants with lower

surface tension than water can be used (to decrease the contact angle). Formic acid in the Hercules Sizing Tester (HST) has been claimed for this purpose.

However, the liquids to which the paper is exposed during its use are various. The process of liquid penetration involves not only the surface interaction, but often the chemical interaction between components of the liquid and the size-fiber bond, which may break these bonds. Thus, the orientation of the size molecules on fibers will be altered, the surface properties of the fiber will be changed, and the contact angle will vary with time as the size molecules are released from the fibers. In the extreme situation, the sizing agent will be detached from the fibers. Under these conditions, the Lucas-Washburn equation is no longer applicable, and the chemical stability of the size bond will play an important role in determining the rate of ink penetration. This important issue, which has been overlooked in the past, is the basis of our desizing approach to investigate the mechanism of paper sizing.

In the desizing approach, a variety of ink solutions are formulated to test a variety of sized papers on the Hercules Size Tester. It is the purpose of this paper to try to infer the mechanism of different sizing methods from their responses to different test fluids. The specific interactions between these chemical inks with rosin-mordant-fiber bonds or size-fiber bonds will demonstrate the importance of the bonding strength to sizing performance and

clarify the principle difference between direct sizing and indirect sizing. This method will provide us more realistic and valuable information about the sizing mechanism than other complex and unrealistic analytical techniques. Based on this information, we may make a reliable prediction of the paper sizing performance in service. This will also benefit our search for new sizing agents.

## 2.2 Experiments

### 2.2.1 Handsheet formation

**Pulp:** Softwood bleached kraft pulp was beaten to 380 ml Canadian Standard freeness in a double-disk refiner. Handsheets ( $60 \text{ g/m}^2$ ) were prepared from this kraft pulp using tap water and rosin soap size solution or AKD emulsion in the British Sheet Mold (TAPPI Test Method 205 om-58). All handsheets were pressed in the standard press cycle and conditioned at Tappi standard conditions (72 °F and 50% RH) for one week before being tested.

**Rosin size:** Fortified rosin soap at 1% solids based on dry pulp as a 0.1% solution (Stafor®, Westvaco Chemicals) was added to thick stock (1%). The stock was stirred and adjusted to about pH 4.5 (unless indicated) with HCl (2%), then 2% alum (based on dry pulp) was added. The pH was adjusted again, and the stock was stirred for another 5 minutes and diluted to 0.2% with tap water. The pH of the pulp slurry was adjusted again before the formation of

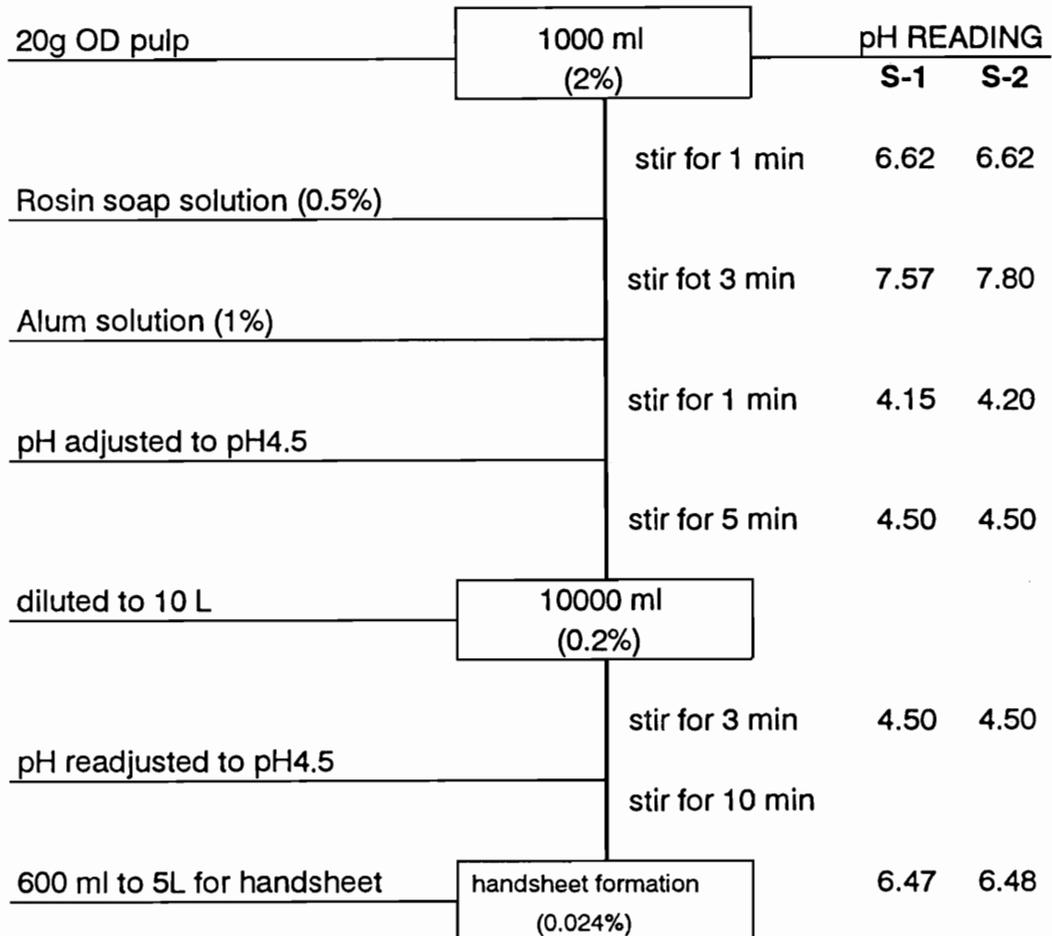
handsheets. The process of making handsheets with rosin alum sizing is illustrated in **Figure 2.1**.

AKD size: AKD (0.3%) based on dry pulp (Hercon®, Hercules Inc.), as a 12.5% emulsion, was added to thick stock (1%). The stock was stirred and adjusted to pH 8.5 with NaOH (2%). For AKD-alum, 0.5% alum was then added after 1 minute and the pulp pH was adjusted to 8.5 (or 4.5 as mentioned). The stock was diluted to 0.2% with tap water, and the pH was adjusted again to the set value before the formation of the handsheet. The details of handsheet making with AKD sizing at various conditions is shown in **Figure 2.2**

#### 2.2.2 HST testing

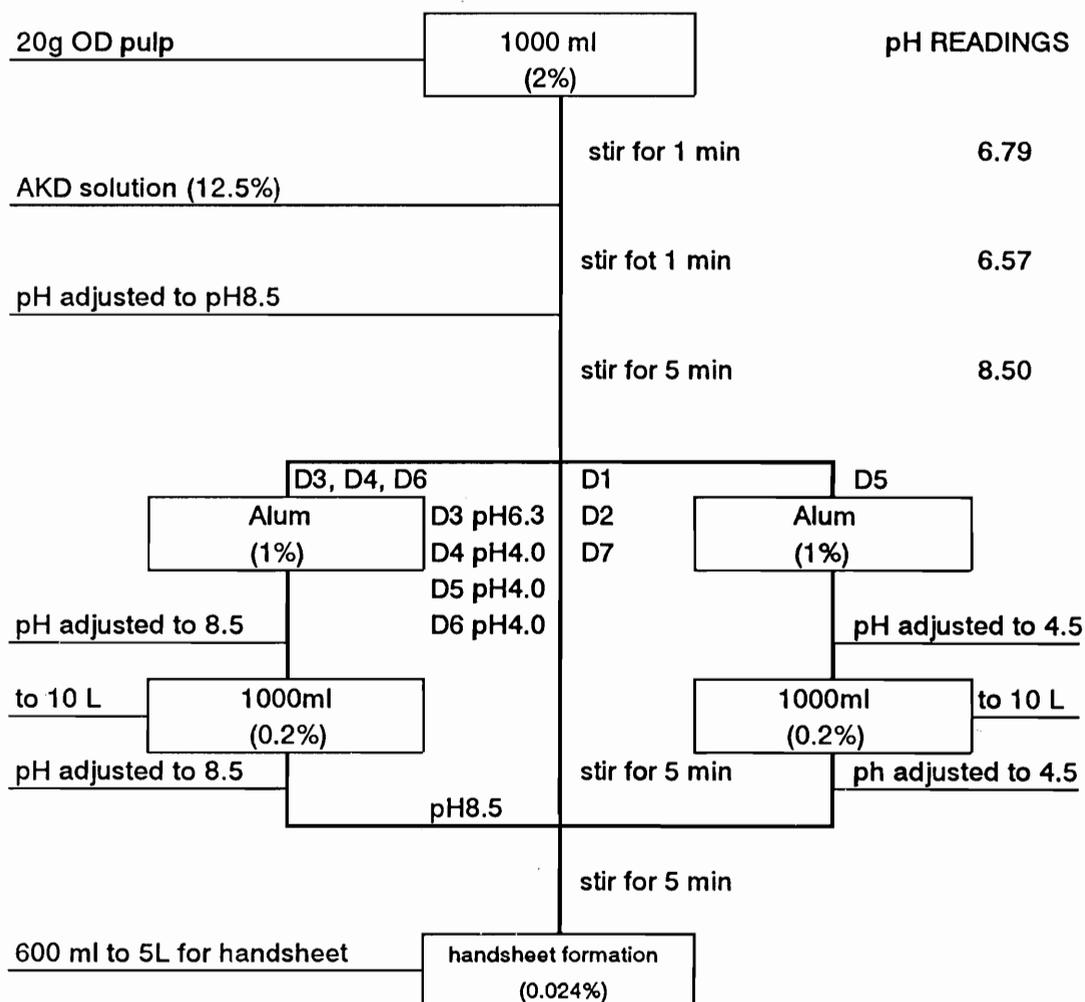
1. Neutral ink and 1% - 10% formic acid inks were prepared according to Tappi Test Method T530 pm-89.
2. The penetrant inks were prepared to equal molar concentration of 1 % formic acid (0.22 M) and adjusted to pH 7 for testing, except as specified.
3. Surfactant ink: Tween 20 from ICI Americas Inc. (HLB value is 16.7) was used to prepare concentrations of 0.1%, 0.25% and 0.5% in the ink.
4. Ink penetration Test: The HST was set for 80% reflectance for all normal penetration tests. The reflectance was changed with time in those cases where reflectance is shown as a function of time.

Figure 2.1 Schedule of handsheet making for rosin soap sizing



No	Rosin (0.5%)	Alum (1%)	Pieces
S-1	1% (40ml)	2% (40ml)	30
S-2	3% (120ml)	5% (100ml)	15

Figure 2.2 Schedule of handsheet making for AKD sizing



No	AKD (12.5%)	Alum (1%)	Pieces
D-1	0.15%(0.24g)		15
D-2	0.30%(0.48g)		30
D-3	0.30%(0.48g)	0.1% (2ml)	15
D-4	0.30%(0.48g)	0.5% (10ml)	30
D-5	0.30%(0.48g)	0.5% (10ml)	30
D-6	0.30%(0.48g)	1.0% (20ml)	15
D-7	0.60%(0.92g)		15

Surface Tension Measurement: The surface tensions of all inks were measured with a DuNouy Tensiometer (CSC Scientific, Fairfax, Virginia). Calibration was carried out with the known surface tension of pure water.

The results of HST test are summarized in **Table 2.1**. Three handsheets were used for HST tests and two measurements with each ink were made on each handsheet. Normally the first three test results were averaged if there is no physical defects affecting the result on the test.

## 2.3 Results and discussions

### 2.3.1 The effect of ink pH on the HST sizing value

The Hercules Sizing Tester is a widely used instrument which measures the rate of liquid penetration into paper. For a given sized paper and a controlled environmental condition, the penetration rate is primarily determined by what ink is used. Neutral ink and formic acid ink are the standard inks used for this method. For some experimental handsheets hard-sized with rosin, use of these two different types of inks can result in 5 to 50 times differences of HST values (9). The use of formic acid seems to be based on historical use without much knowledge of why it shortens the test time. The only explanation in the literature is that formic acid has a lower surface tension than water so it can accelerate the liquid penetration into the paper (13). It is not difficult for us to disprove this statement with a simple experiment.

Table 2.1 The summary of HST sizing test

Sizing	Ink Properties	Neutral Ink				Formic acid Ink			Formate Na	Citrate Na	NaF	Tiron	Tween20 neutral ink
		pH2.2	pH4	pH7	pH10	1%	5%	10%					
	Ink pH w/o adjusted	6.80	6.80	6.80	6.80	2.20	1.79	1.49	7.10	3.72	6.90	2.91	
	Ink pH adjusted to	2.20	3.97	7.00	10.00	2.20	1.79	1.49	7.03	7.00	7.00	7.00	7.00
	Desizind agent Conc.					(pH not adjusted)			0.22M	0.22M	0.22M	0.22M	0.5 %
	Ink Surface tension			73.1		62.7	60.8	59.3	66.4	64.8	59.8	58.5	
S-1	Rosin/Alum 1% / 2%	167.6	326.6	258.9	176.8	141.3	80.7	29.6	291.0	59.4	7.3	36.3	65.9
		175.1	362.9	248.0	154.6	144.9	73.4	35.4	264.0	76.8	7.6	42.2	57.9
		163.4	325.6	260.3	166.7	130.2	74.4	36.4	270.6	67.7	7.4	56.4	41.6
		165.7	338.4	255.7	166.0	136.6	76.2	33.6	275.2	68.0	7.4	45.0	55.1
S-2	Rosin/Alum 3% / 5%			483.9		262.9					11.5		
				481.5		214.7					11.8		
				475.2		234.2					11.4		
				480.2		237.3					11.6		
D-1	AKD/pH8.5 0.15%			48.6		59.4					63.6		
				46.3		54.6					80.4		
				60.2		60.4					60.0		
				51.7		55.1					66.0		
D-2	AKD/pH8.5 0.3%	198.1	199.6		150.3		179.2	167.8	191.7	274.4	186.8	208.1	6.5
		186.9	197.4		145.9		190.0	181.4	181.4	332.7	192.0	192.8	6.7
		184.2	172.6		167.4		174.4	159.2	184.9	322.2	174.2	187.4	5.8
		169.7	169.9	160.4	154.5	165.4	161.2	169.5	166.0	309.6	184.3	196.1	6.3
D-3	AKD/Alum/pH8.5 0.3% / 0.1%			216.4		219.0					209.5		
				201.1		223.9					250.2		
				234.3		239.4					180.3		
				217.6		227.4					213.5		
D-4	AkD/Alum/pH8.5 0.3% / 0.5%	164.1	172.6		157.0		154.5	179.7	161.5	184.8	157.8	148.9	13.4
		182.2	176.8		122.9		189.6	142.6	159.9	179.2	185.1	169.6	14.7
		187.1	168.9		138.7		170.3	163.4	168.7	203.4	152.7	171.2	12.9
		177.6	172.6	175.2	139.5	164.6	171.6	161.9	163.4	169.1	165.2	163.2	13.7
D-5	AKD/Alum/pH4.5 0.3% / 0.5%	176.4	246.9	226.6	195.3	168.6	158.5	155.5	217.7	281.7	154.8	210.2	3.1
		163.5	251.7	259.7	209.8	179.4	162.2	137.1	260.0	255.8	152.6	227.4	4.1
		177.5	232.8	242.9	207.1	180.4	144.2	153.1	228.0	264.4	142.1	194.4	5.4
		172.5	245.6	243.1	204.1	176.1	165.0	148.6	255.2	267.3	149.5	210.7	4.2
D-8	AKD/pH4.5  ( 07/18 tested )	129.5		174.4		146.0					163.3		4.1
		169.3		177.4		164.9					173.8		3.9
		130.9		162.0		167.4					140.5		4.7
		143.2		171.3		159.4					166.2		4.2

Note: the shade values are the means of three tests.

Different concentrations of formic acid inks were employed for this investigation. **Table 2.2** lists the actual values of ink surface tensions and their HST values on the same rosin-alum sized handsheets.

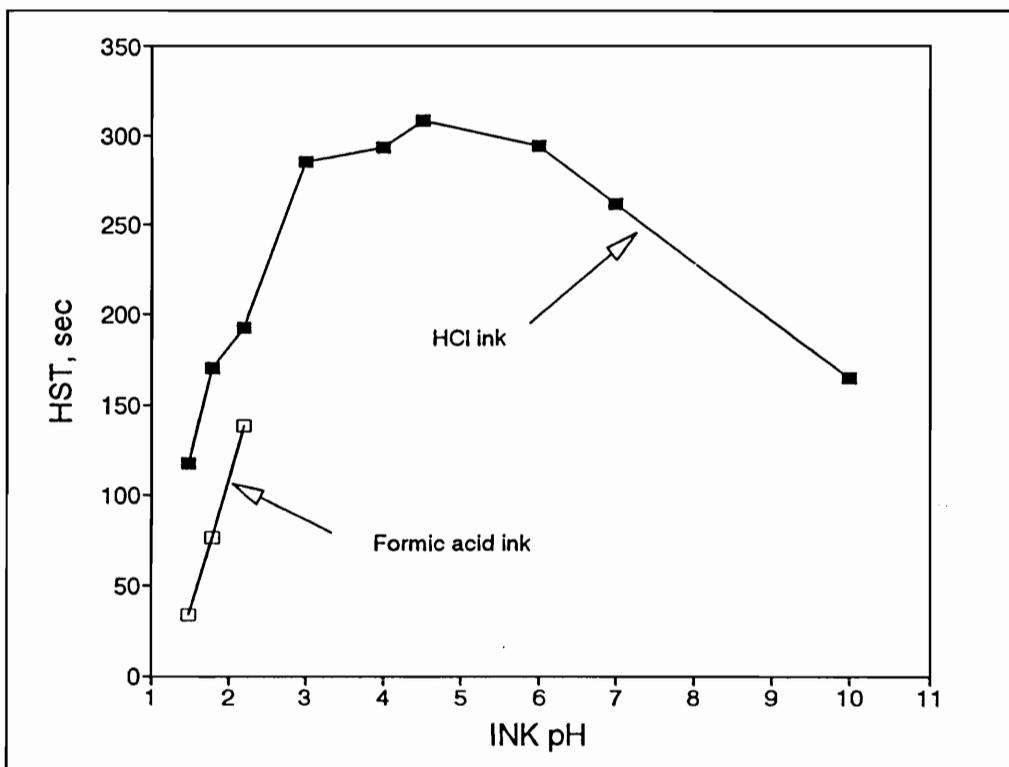
**Table 2.2** HST Values for rosin sized paper with different concentrations of formic acid inks

Formic Acid (%)	Surface tension (dyn/cm)	HST Values (sec.)	Ink pH
0	73.0	225.7	7.00
1	62.7	138.8	2.20
5	60.8	76.2	1.79
10	59.3	33.8	1.49

Table 2.2 shows that there is not much difference in the surface tensions of these inks, especially among those inks containing formic acid, while their HST values differ greatly. Therefore, formic acid must work by a mechanism other than lowering the surface tension. The relatively strong acidity of formic acid ink is worth considering; the  $pK_a$  of formic acid is 3.75 at 25°C.

In order to obtain data about the pH effect, hydrochloric acid was used for comparison with formic acid. Sodium hydroxide was used to give ink with higher pH values. **Figure 2.3** shows that ink pH does greatly affect its penetration rate, especially at the extreme acidic and alkaline conditions. The best HST value was reached when

Figure 2.3 The effect of ink pH on HST value of rosin alum sized paper

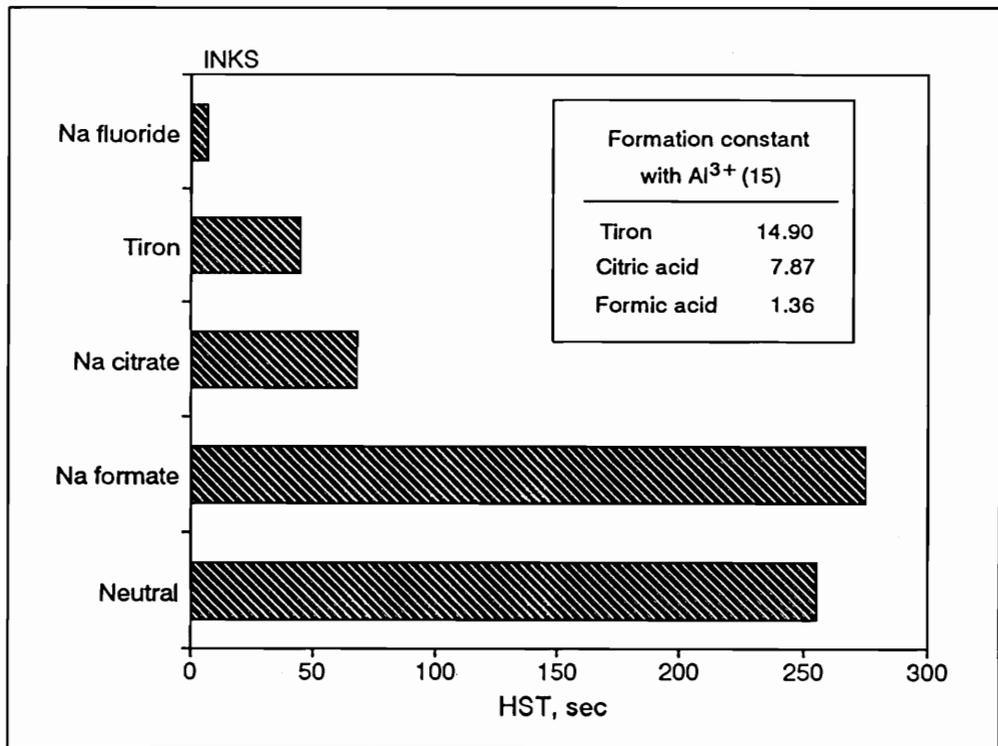


the ink pH is 4.5, which is also the optimum pH where rosin sizing can be effectively developed. Is it a coincidence, or is some important factor involved? We have pointed out that at pH 4.5 aluminum is in the form of a polynuclear complex, which is an effective mordant with the capability to bind with the ligands from rosin and fiber components (14). When the pH is below 3, most of the aluminum ions will exist in the form of trivalent  $Al^{3+}$ ; when the pH is near 7, aluminum will be in the major form of insoluble  $Al(OH)_3$ . They both are non-complexing forms without any capability for size anchoring. If the ink pH causes the aluminum complex to change to these non-complexing forms, the size precipitate would be broken. It is suggested here that the change of ink pH, initiating the change of the aluminum complex and resulting in the separation of the size bond, is the most important reason for the effect of formic acid on liquid penetration. This assumption can be proved by more direct evidence.

### 2.3.2 Ligand substitution reaction demonstrates the desizing process of rosin-alum sized paper

In order to clearly demonstrate the size bonding mechanism in the rosin-alum system, we selected a series of ligands having different affinities for aluminum, which act as chemical penetrants, to formulate various test inks for HST testing. **Figure 2.4** shows the HST results and the desizing ability of these penetrants on rosin-alum sized paper at the same molar concentration (0.22 M, the same

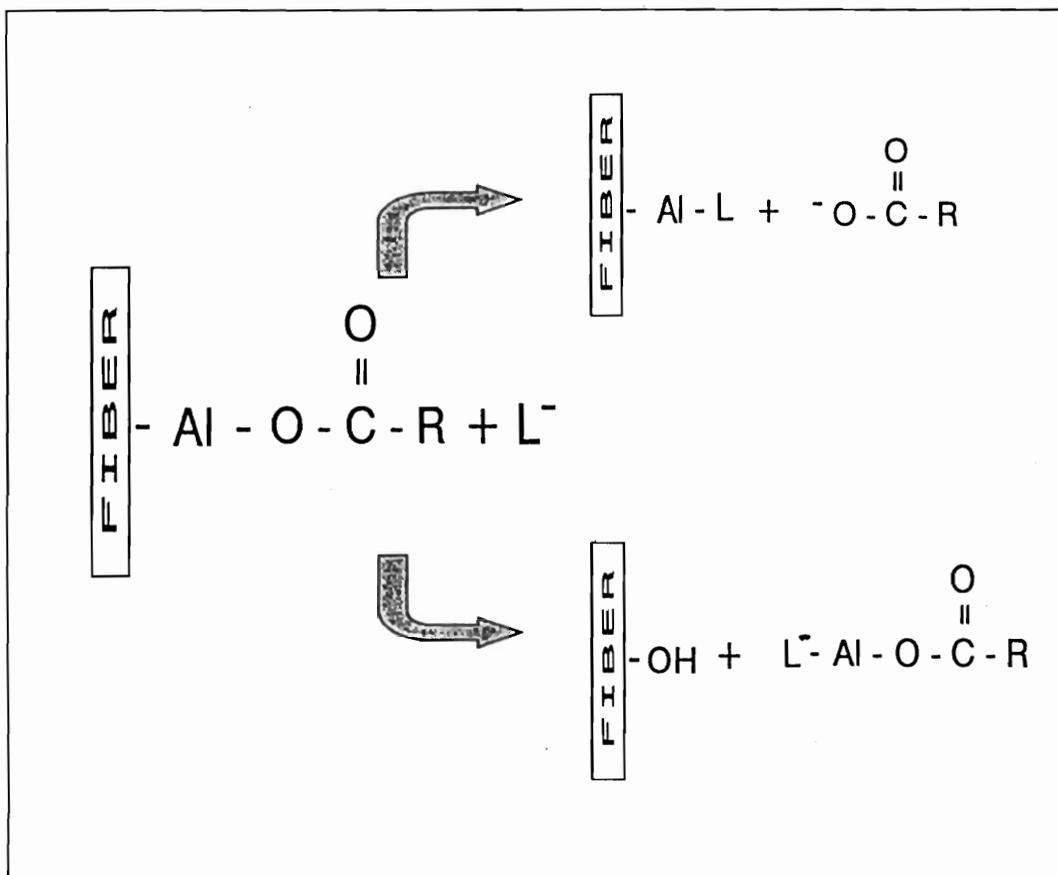
Figure 2.4 Results of different desizing agents on rosin alum sized paper



concentration as 1% formic acid) and the same pH (7.0). Their formation constants with aluminum (15) are also listed for reference. Even though these constants could not be used for quantitative comparison, they clearly demonstrate that the higher the formation constant with aluminum, the stronger the effect of the penetrant on the desizing process. From the view of coordination chemistry, they all follow the reaction of ligand substitution -- the stronger ligand replaces the weaker ligand of carboxylates from rosin or fibers, resulting in part or all of the size agent separating from the fibers or from rosin molecules. **Figure 2.5** depicts two of these possible reactions.

Since sodium formate contains the same ligand as formic acid, but does not demonstrate desizing ability under these conditions, there is no reason to expect that ligand substitution reactions take place in the process of HST testing with formic acid. As stated before, pH is the critical factor influencing the penetration rate of formic acid ink on rosin size. Citrate is a strong chelating agent to aluminum; it exhibits a greater effect than formate on ink penetration. The citrate chelating ability to aluminum ions was also demonstrated by the fact that a small amount of citrate in pulp resulted in a great loss of sizing because the high affinity of citrate ties up the aluminum ions (16). Since fluoride is a hard base with very high formation constants with aluminum (the successive pK values of the formation constants are 6.10, 11.15, 15.00, 17.75,

Figure 2.5 Two possible substitution reactions in the desizing process



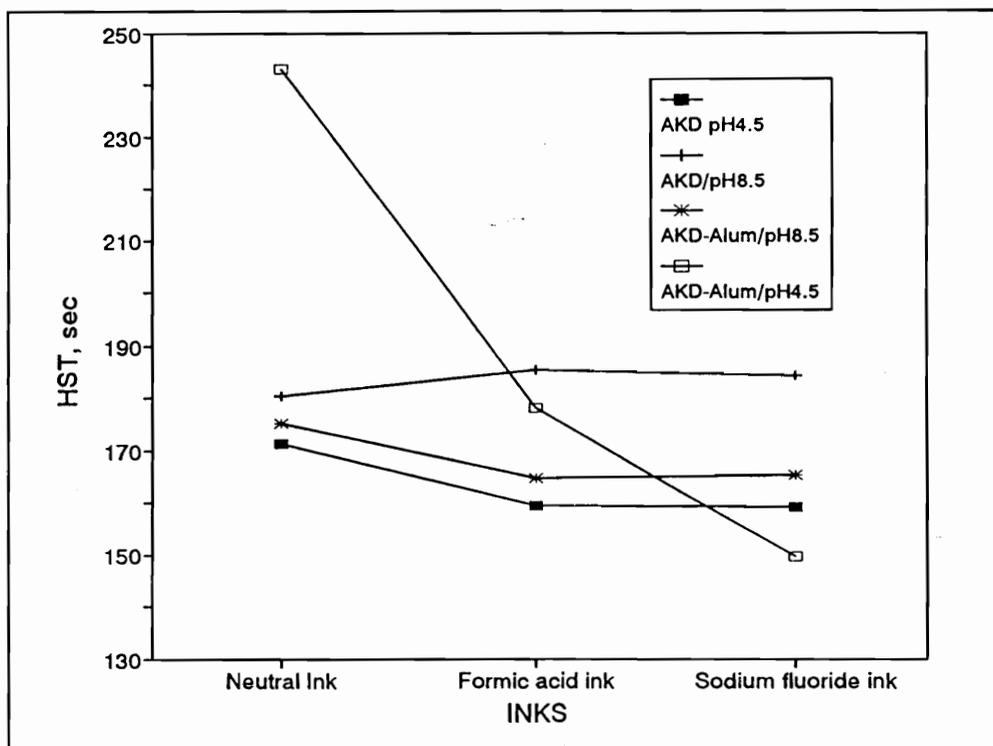
19.37, and 19.84), it gives sodium fluoride a special affinity for aluminum and demonstrates the strongest influence on the ink penetration into the rosin-alum sized paper (15).

### 2.3.3 AKD sizing bond is covalent bond and strong enough to resist the desizing agent attack

The existence of coordination bonds in the rosin-alum-fiber complex is the basis for these aluminum-complexing ligands carrying out ligand substitution. If the size bond does not contain coordination bonds, one would not expect these ligands to exhibit desizing effects with the HST test. Paper sized with AKD is a good material with which to test this hypothesis. In **Figure 2.6**, for paper sized with AKD only, these desizing agents have very little effects on the ink penetration. If AKD was anchored by hydrogen bonding, one would expect a low pH to have an effect on the size performance. The effect of formic acid on calcium carbonate filled papers is only a measure of the reaction of acid with carbonate, which destroys the structure by the formation of carbon dioxide gas.

However, when AKD sized handsheets were formed with 0.5% alum, a very different phenomena was observed. When paper is sized at pH 8.5, alum is somewhat detrimental to size. On the other hand, when paper is sized at pH 4.5, the highest HST value was obtained by neutral ink and the lowest value was observed with fluoride ink.

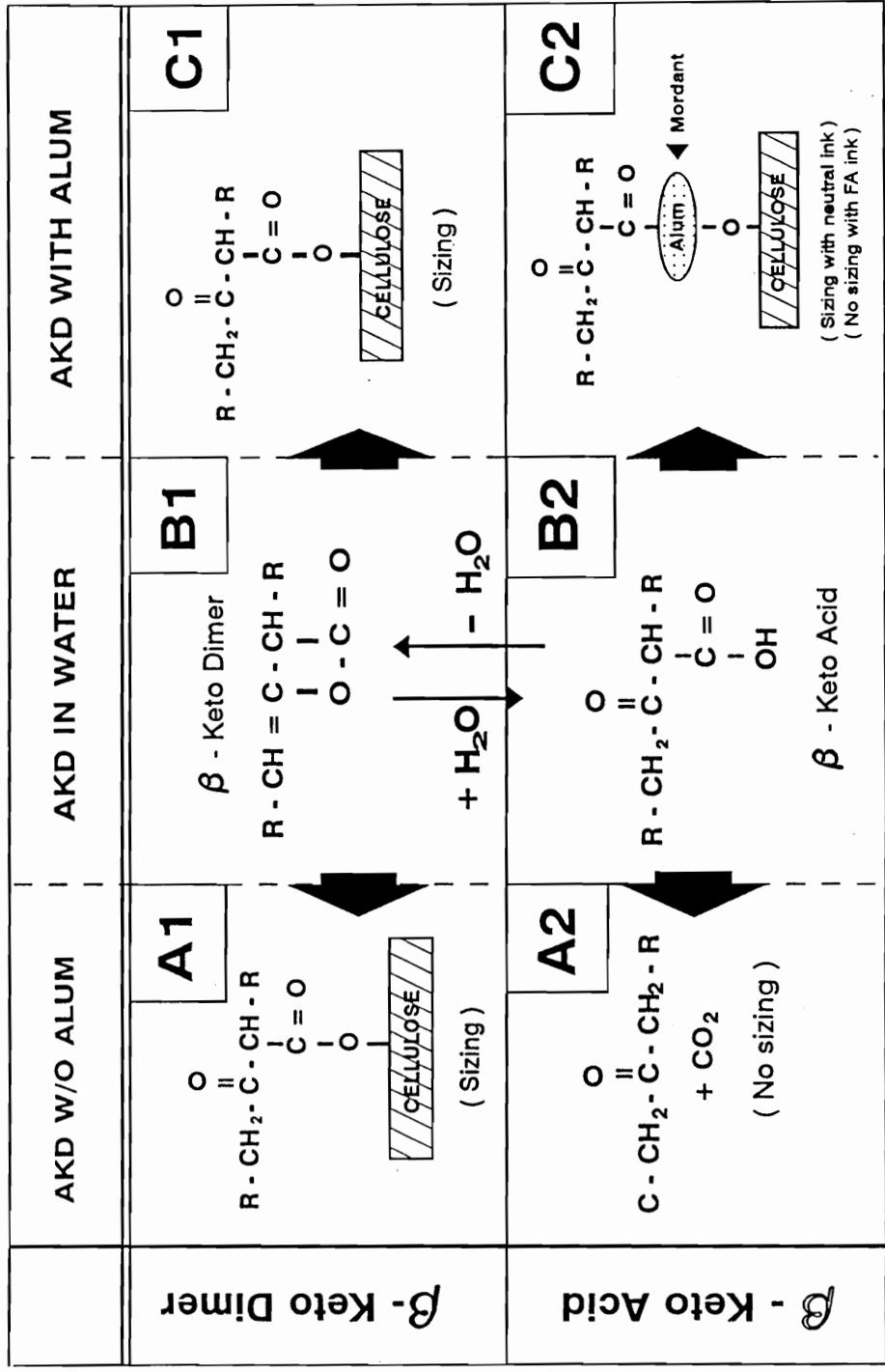
Figure 2.6 Effect of desizing agent on AKD sized paper



These "abnormal" phenomena can also be explained from the mechanism of size bonding and the theory of the coordination chemistry of aluminum. It is well known that AKD can react with water slowly at room temperature to form the unstable  $\beta$ -keto acid, which will decarboxylate to form a ketone (**Figure 2.7A2**). This hydrolyzed product has been traditionally viewed as a non-size. It will not adhere well to the cellulose and may cause picking problems. It is washed away from the system if there is no retention aid in the system.

Therefore there are two types of AKD in the pulp system, the major type is the  $\beta$ -keto dimer (**Figure 2.7B1**) and the minor hydrolysis product is  $\beta$ -keto acid (**Figure 2.7B2**). The former can react with fibers directly to form the strong  $\beta$ -keto ester bond (**Figure 2.7A1** and **2.7C1**), providing the paper with long time stability in exposure to water, acid or other chemical inks. The latter can be retained on the fibers if there is a suitable retention aid, such as polyaluminum from alum at pH 4.5. It can bind to fibers through a mordant similar to the rosin-alum-fiber bond in rosin size. AKD is likely bound by two different mechanisms at pH 4.5. One is the direct ester bond (**Figure 2.7 A1**); the other is the indirect coordinate bond (**Figure 2.7 C2**). The existence of this indirect bond is indicated by the fact that neutral ink gives a much higher HST value than formic acid or fluoride ink (**Figure 2.6**). With neutral ink, both types of size bonds will be effective in sizing

Figure 2.7 The proposed mechanism of reactions in the AKD sizing system



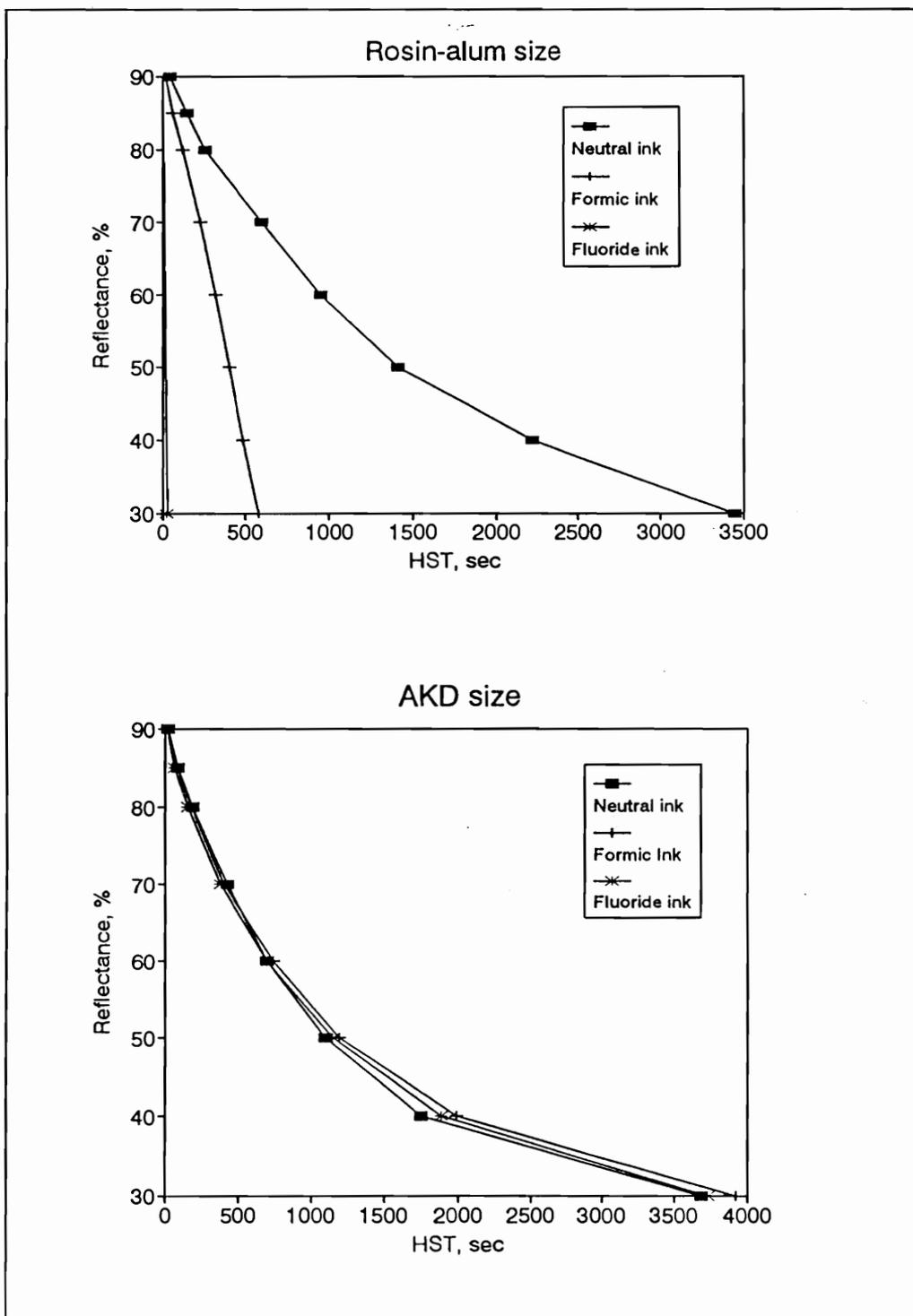
test, but only the ester-bond size provides the effective resistance to ink penetration with fluoride or formic acid. Since only the strong ester bond exists in the other sizing conditions, there is no appreciable difference in their HST values by neutral or fluoride inks.

On the basis of these results, it is believed that alum has a small negative effect on AKD sizing at normal alkaline conditions. It may have some benefit to water drainage. However, the addition of alum should be controlled to the lowest possible level, or it may induce more AKD to hydrolyze, reducing the effective resistance of the size to chemical attack (17). However, under some conditions, particularly low pH, alum may improve AKD sizing against neutral ink.

#### 2.3.4 The fundamental difference between rosin alum sizing and AKD sizing

One of the advantages of the HST size test is that one can observe the rate of ink penetration into paper. The bonding difference between rosin size and AKD size is also reflected in their reflectance-time curves shown in **Figure 2.8**. For AKD sized paper, the neutral ink and fluoride ink both penetrate at the same rate throughout the test. For rosin size, the rate of penetration of fluoride ink is much higher than that of neutral ink. The size bond itself appears to be an important factor controlling the penetration rate in rosin alum size. Fluoride ink almost

Figure 2.8 The rate of ink penetration with time



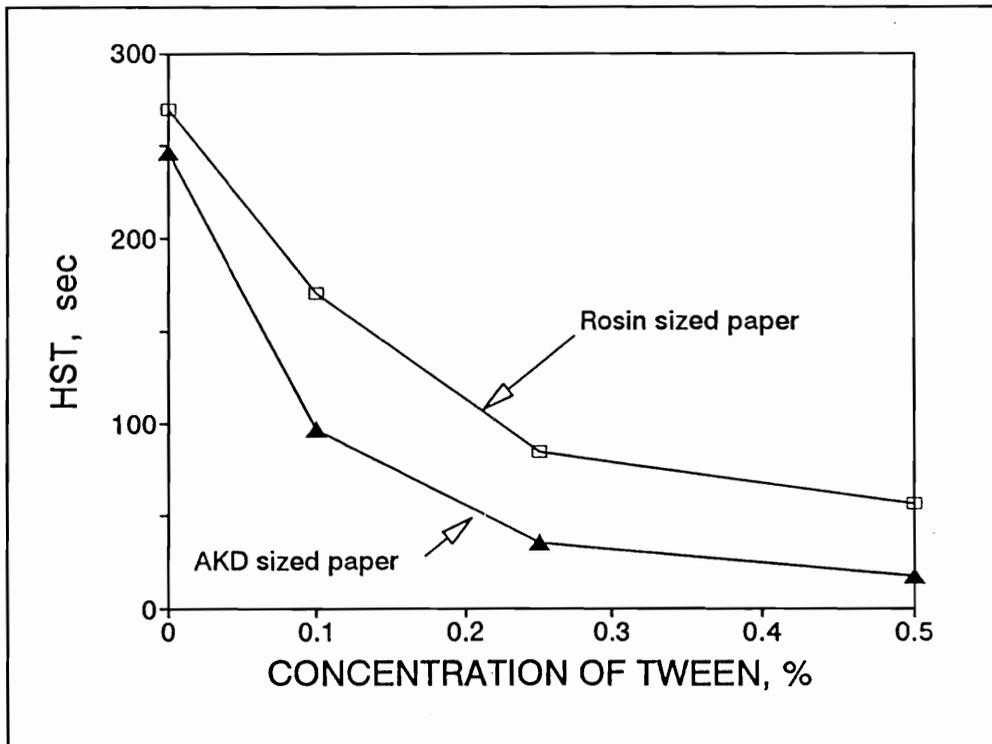
soaked the paper immediately while neutral ink seems to follow the Lucas-Washburn equation.

From the above discussion, one can see that rosin and AKD sizes have substantial differences in their size bonds. The  $\beta$ -keto ester bond is very strong and almost inert to acid and other chemicals. This strong bond provides one of the advantages of AKD size over rosin size. In rosin soap sizing, fortified rosin has been demonstrated to give better performance than conventional rosin size. However, this improved performance is achieved only from its multi-functional groups, which allow the size to be more easily retained and more evenly distributed on the fiber surfaces. The size bond is still a coordination bond, which has relatively weak chemical stability. Good sizing agents normally must have a high degree of chemical inertness toward the impinging liquid. Therefore, if research on rosin sizing could lead to a new bonding mechanism for the rosin-fiber bond, it would be a revolutionary change and greatly extend the usefulness of this inexpensive, stable sizing material. This possibility should not be ignored. Some experimental evidences on this issue will be presented and discussed in details in Chapter 3.

#### 2.3.5 Surfactant can be used as good penetrant to accelerate ink penetration in any sized paper

Actually, the surface tension of the ink does have an effect on the its rate of penetration, and it becomes

Figure 2.9 Effect of surfactant "Tween" on ink penetration



important if one can reduce the ink surface tension rastically. Several commercial surfactants were chosen for this study, the result of nonionic surfactant Tween 20 is reported here. The surface tension of 0.1% Tween 20 neutral ink was 30.0 dyn/cm. Inks with different concentrations of surfactant were employed for HST testing of rosin and AKD sized paper. **Figure 2.9** shows that the higher the level of addition of surfactant to the ink, the faster the liquid penetration. Notably, both the indirect coordinate rosin-alum bond size and the strong direct ester-bond AKD size are found to be affected by the surfactant in a similar fashion. This is mainly attributed to the lower surface tension of the ink, which reduces the contact angle of ink with paper. Ink containing a surfactant may be used to replace the formic acid ink for quick HST tests of AKD sized paper with calcium carbonate fillers since interference from the formation of CO<sub>2</sub> is avoided.

#### 2.4 Conclusions

1. Substantial differences between rosin alum size and AKD size bonding mechanisms were demonstrated by their much different responses to a series of chemical penetrants.
2. Indirect rosin-alum-fiber size is formed through coordination bonds, which are stable in water at neutral pH, but can be greatly affected by acid, alkaline, and other chemicals. Ligand substitution was the major cause of this desizing process.

3. AKD can react with cellulose and form direct  $\beta$ -keto ester bonds with fibers. This strong covalent bond is almost inert to acidic and alkaline solutions. Even the strongest aluminum-complexing ion, fluoride, has no effect on the ink penetration.
4. If alum is used along with AKD sizing at low pH, there can be two types of bonds formed between the size and the fiber, the major direct ester bond and the minor indirect coordinate bond. Therefore, neutral ink will result in much higher HST values than formic acid or other penetrant inks. The use of alum in AKD sizing systems for its other positive effects on drainage and retention should be carefully considered since alum's preferential attraction to AKD molecules could reduce the effective strong covalent bond in the final size.
5. The surfactant Tween-20 can be used to as a penetrant to accelerate the testing of hard sized papers, which will reflect the real rate of ink penetration without interference with the size bond itself.

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## Chapter 3

### A NEW APPROACH ON ROSIN SIZING WITHOUT MORDANTS

#### 3.1 Introduction

One of the most remarkable features of cellulosic fibers is that they contain many hydroxyl groups. The existence of these hydroxyl groups provides fibers with unique physical and chemical characteristics. Without these hydroxyl groups, fibers could not be used as a good material for papermaking. Fibers would not be dispersible in water and paper would have little strength since it is the hydrogen bonding between these hydroxyl groups that provide the foundation of paper strength. However, the inherent hydrophilicity of the hydroxyl groups also renders the paper products very vulnerable to water. Sizing is therefore a necessity for many paper applications.

The most common purpose of the sizing process is to make the originally hydrophilic fiber surfaces relatively hydrophobic so that a certain degree of water repellency can be achieved. One way to achieve this goal is to apply an amphipathic (polar/nonpolar) material such as rosin size onto fiber surfaces. Ideally, the hydrophilic part of the amphipathic material should bind to the fiber surfaces and its hydrophobic part should extend outwardly (1) to cover the fiber surfaces. When sufficient surface coverage is reached, the paper can have good water repellency.

Previous work (2-5, 9) showed that the bonding strength between rosin size and fiber components is critical to the effectiveness of sizing. Rosin molecules must be bound to fiber surfaces through primary chemical forces such as dative bonds or other type of covalent bonds to effect sizing. Secondary chemical forces such as Van der Waals forces and hydrogen bonds are not strong enough to resist the attack of incoming polar fluids like water.

Traditionally, rosin size is regarded as a non-reactive sizing agent (17) because it is believed that rosin size cannot directly react to fiber components so as to strongly bind on fiber surfaces. This is the reason why mordants (2-5) are usually required in rosin sizing. Mordants such as alum and iron ions are chemicals which function to retain and chemically bind rosin size on fibers. Of course, if under certain conditions rosin size can retain and chemically bind on fibers without the presence of mordants, rosin sizing without mordants should be possible. Sizing with synthetic sizing agent such as AKD (alkyl ketene dimer) and ASA (alkenyl succinic anhydride) does not require mordants because direct reactions between size molecules and fiber components can occur (13-15).

Other work (6) showed that esterification reactions between multifunctional carboxylic acids such as citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA) and cellulose can occur under certain conditions. Caulfield (7) reported similar results. Since fortified rosin acid is also a

multifunctional carboxylic acid, there is reason to believe that direct esterification reactions between rosin acid and cellulose could occur under certain conditions. This leads to our work on rosin soap sizing without mordants. The retention of rosin was ensured by dipping handsheets in rosin solution and drying at a controlled temperature. Additional heating treatment after drying was applied to promote the possible reactions between rosin molecules and fiber components.

## 3.2 Results and discussions

### 3.2.1 Direct sizing in various pulps

Handsheets made from different pulps were simply immersed (dipped) in rosin soap solution for 45 seconds and then dried on a sheet dryer at 121°C for 3 min or in air after surplus liquid has been removed. No mordant was applied. Sizing was then tested on the rosin-treated handsheets and the results are summarized in **Table 3.1**. The concentration of the rosin soap solution was 1.0 %.

**Table 3.1** shows that the handsheet drying conditions, either from which the pre-dipping handsheets were obtained or under which the after-dipping handsheets were dried, have critical effects on the sizing results. When both pre-dipping drying and after-dipping drying were carried out on a dryer (121°C for 3 min), handsheets made from unbleached

Table 3.1 Sizing results by direct size application<sup>a</sup>

Pulp type	Rosin adsorbed (%)	HST (s) (neutral)	HST (s) (1% FA <sup>b</sup> )	Cobb size (g/m <sup>2</sup> /2min)	Handsheets drying	Drying after dipping
Unbld. SW KP	1.76	4479	7623	28.4	Dryer	Dryer
TMP	2.00	6307	>10,000 <sup>c</sup>	33.5	Dryer	Dryer
Bld. SW KP	1.20	244	415	32.2	Dryer	Dryer
Bld. HW KP	1.35	199	1597	51.6	Dryer	Dryer
Unbld. SW KP	1.85	2008	4606	34.6	Air	Dryer
TMP	2.18	230	475	Soaked	Air	Dryer
Bld. SW KP	1.36	4.8	36.2	Soaked	Air	Dryer
Bld. HW KP	1.47	0.4	5.1	Soaked	Air	Dryer
Unbld. SW KP	1.85	2746	4561	35.2	Dryer	Air
TMP	1.89	9.0	8.3	Soaked	Dryer	Air
Bld. SW KP	1.14	4.6	4.3	Soaked	Dryer	Air
TMP	1.89	>10,000 <sup>c</sup>	>10,000 <sup>c</sup>	---	Dryer	Air+Heat <sup>d</sup>
Bld. SW KP	1.14	7.6	7.4	Soaked	Dryer	Air+Heat <sup>d</sup>

a. Concentration of rosin soap dipping solution: 1.0%.

b. Formic acid ink.

c. Test terminated at this point.

d. Handsheets were heated at 160 °C for 1 minute after dipping rosin and air-drying.

softwood kraft pulp (Unbld. SW KP) and thermomechanical pulp (TMP) possess high level of sizing (Exp. No.1-2). The HST value with 1% formic acid ink in the TMP pulp exceeds 10,000 seconds, which is a very high level of sizing. Handsheets made from bleached softwood kraft pulp (Bld. SW KP) and bleached hardwood kraft pulp (Bld. HW KP) also possess moderate sizing. If either pre-dipping or after-dipping drying is by air-drying, handsheets from all pulps except unbleached SW KP possess practically no sizing (soaked in Cobb size tests, Exp. No.6-8 and 10-11). Even though unbleached chemical pulp has always been known to be a most easily-sized pulp, the experimental fact that even air-drying after dipping rosin soap solution can give fairly good sizing (Exp. No. 9) is beyond what the existing theories can explain.

The most possible bonding mechanism which binds rosin soap size on fibers so as to effect the sizing in the above process is the ester linkage. The esterification reaction between rosin acid and cellulose can be simplified and depicted as:



This mechanism can explain why dryer-drying after dipping rosin can give much better sizing than air-drying since the heat can remove water molecules quickly, shift the

chemical equilibrium (Equation 3.1) toward the right and promote the esterification reaction.

The fact that pre-dipping drying conditions are also critical in this sizing process (sizing is always much better when the original handsheets are obtained from dryer-drying than when they are from air-drying) may also be explained along this line. since the dryer-dried handsheets will have a lower moisture content than the air-dried handsheets due to the hysteresis phenomenon (8). It is also possible that a surface activation reaction is occurring.

As in other sizing processes, different pulps demonstrated very different sizability. Unbleached pulp has much higher sizing value than bleached pulps under the same conditions, which is a well known sizing phenomenon. As in rosin soap sizing with iron ions as the mordants (3), TMP was sized much more effectively than bleached pulps; and bleached softwood pulp was sized better than bleached hard wood pulp. These trend are not observed in the conventional rosin-alum sizing process.

Heat treatment on dipped and air-dried handsheets which originally show no sizing has great effect on the sizing development in TMP pulp (Exp. No.12 vs No.10). Heating at 160°C for just one minute can promote the handsheets from no sizing (Exp. No.10) to a very high level of sizing (HST values >10,000 sec., Exp. No.12). However, the same heat treatment seems to have no effect at all on the sizing development in bleached softwood KP (Exp. No.11 vs Exp.

No.13). Further investigation is needed to explain this unusual phenomenon. More work on the effect of heat treatment on sizing development will be reported below.

Another extraordinary phenomenon, also indicated in **Table 3.1**, is that the HST values with 1% formic acid ink are always higher than that with than that with neutral ink in this sizing process. It is well known (9) that formic acid has an accelerating effect on the HST measurements in rosin-alum sized paper and little accelerating effect on the HST tests in AKD-sized paper, but it has never been reported that formic acid has a slowing effect on the HST tests. Under some conditions excess sizing agent can act as a surfactant and therefore lower the level of sizing (18); it is possible that unreacted rosin is less effective as a surfactant at lower pH, and this contributes to higher sizing level with formic acid ink.

Also unusual about this sizing process is the phenomenon that even though the HST values show that the handsheets have high to very high level of sizing, in many cases the Cobb size test shows that the sizing is only moderate (Cobb values seldom go below 25 g/m<sup>2</sup>), indicating that the ink penetration resistance of paper does not always coincide with the water pickup resistance. For example, for the bleached hardwood KP (Exp.4), even though it has as high as 1600 HST value with 1% formic acid ink, its Cobb size test shown that the handsheets can almost be soaked by water.

### 3.2.2 Effect of the concentration of dipping solutions

The effect of the concentration of rosin and rosin pickup on sizing is reported in **Table 3.2**. Commercial use of rosin size is about 10 lb/ton. The sizing results were obtained with dryer-dried handsheets and the handsheets were dryer-dried again after dipping in rosin solution. **Table 3.2A** shows that the concentration of the rosin soap solution has a critical effect of the sizing in bleached softwood KP. Only when the concentration of dipping rosin solution is 1.0% can effective sizing be achieved. Lower or higher concentration can not give good sizing.

However, the situation is very different in the case of unbleached SW KP, as shown in **Table 3.2B**. The concentration of dipping solution has little effect on sizing when it varied from 0.5% to 2.0%. Again, this phenomenon is yet to be explained.

Efforts were made to calculate the amount of rosin adsorbed in the handsheets and the results are also reported in **Table 3.1** and **3.2**. However, no relationship between the sizing and the amount of rosin adsorbed can be drawn from the data, which is quite surprising.

Table 3.2 Sizing results with dipping solutions of varied rosin concentrations<sup>a</sup>

A. In bleached softwood KP handsheets

Rosin concn. (%)	Rosin adsorbed (%)	HST (s) (neutral)	HST (s) (1% FA <sup>b</sup> )	Cobb size (g/m <sup>2</sup> /2min)
0.5	0.60	3.0	2.4	Soaked
1.0	1.20	244	415	32.2
1.5	1.84	1.0	1.0	Soaked
2.0	2.41	0.2	0.4	Soaked

Note: All values are the means of at least three time tests. It demonstrates the substantial differences caused by the concentration of the dipping solution.

B. In unbleached softwood KP handsheets

Rosin concn. (%)	Rosin adsorbed (%)	HST (s) (neutral)	HST (s) (1% FA <sup>b</sup> )	Cobb size (g/m <sup>2</sup> /2min)
0.5	0.91	3227	5393	30.1
1.0	1.76	4479	7623	28.4
1.5	2.78	4706	7926	28.2
2.0	3.61	5173	8815	28.1

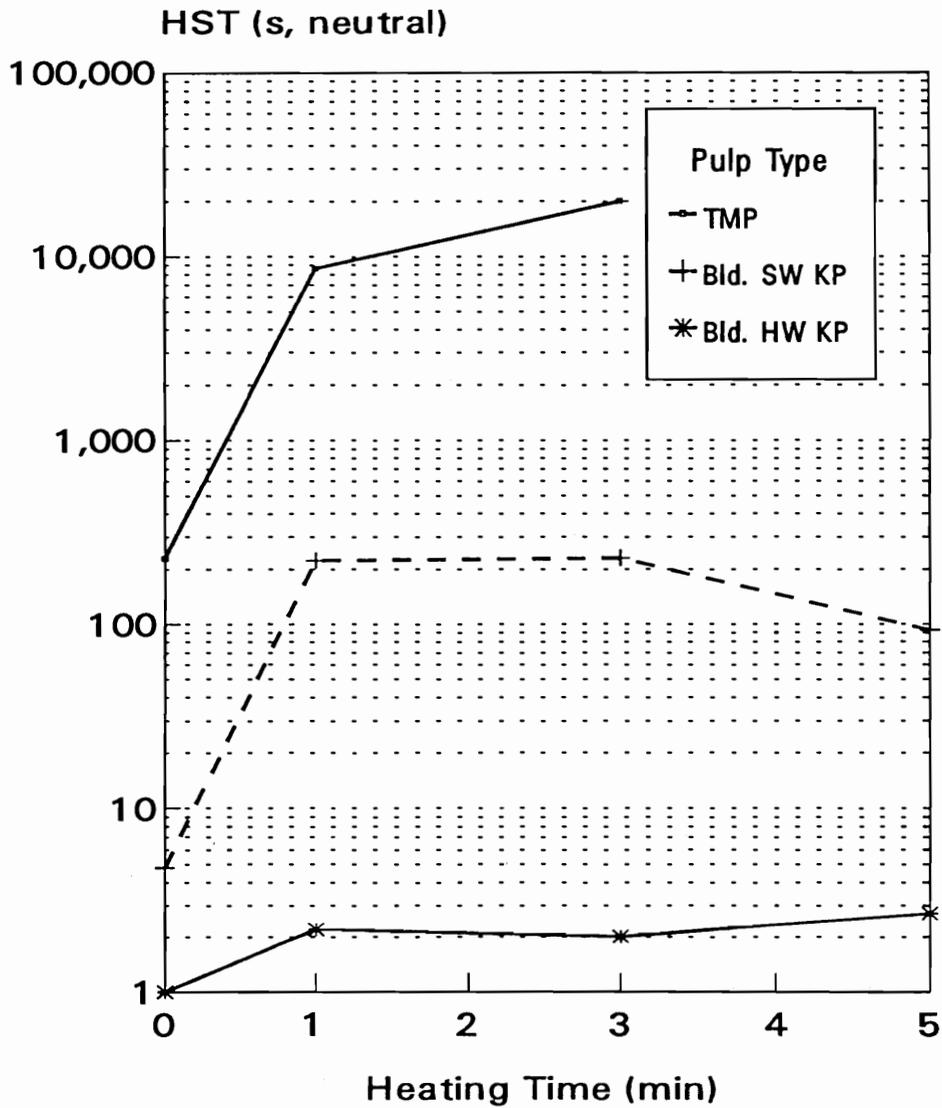
- a. With dryer-dried handsheets; dryer-drying after dipping rosin.
- b. Formic acid ink.

### 3.2.3 Effect of heating treatment on sizing

As shown in **Table 3.1** (Exp.6 to 8), no sizing can be observed in air-dried handsheets made from TMP and bleached pulps after the handsheets were dipped in a 1.0% rosin soap solution and dried on a dryer at 121°C for 3 min. However, when the dipped handsheets were further treated with heat at 160°C for just 1 min., as shown in **Figure 3.1**, very high level of sizing can be observed in the handsheets made from TMP and good sizing can be observed in the handsheets made from bleached softwood pulp, while there is still no substantial sizing observed in the handsheets made from bleached hardwood pulp even after a longer period of heating. **Figure 3.1** gives the effect of heating time (at 160°C) on the development of sizing in rosin-dipped and then air-dried handsheets. When the dipped handsheets were further treated with heat at 160°C for just a min., as shown in the figure, a very high level of sizing can be observed in the handsheets made from TMP and good sizing can be observed in the handsheet made from bleached softwood pulp, while there is still no substantial sizing observed in the handsheets made from bleached hardwood pulp even after a longer period of heating.

It is believed that heat treatment at 160°C can promote the esterification reaction between rosin size and cellulose and hemicellulose so as to develop the sizing in the handsheets since it has been reported (6,7,10,11) that

Figure 3.1 Effect of heating treatment on sizing

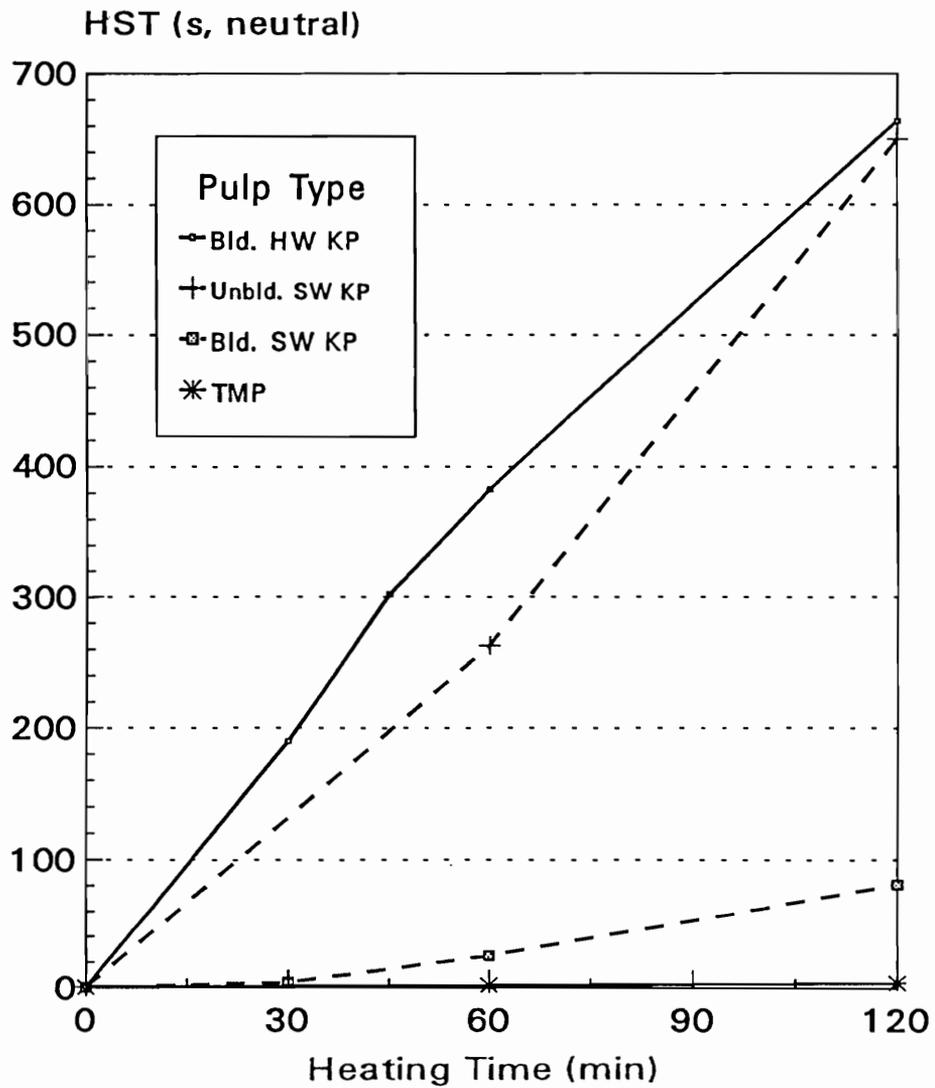


NOTE: Heating temperature 160 °C, air-dried handsheets, dryer-dried after dipping, 1% dipping concentration of rosin soap.

similar heating treatment can promote the esterification reactions between multicarboxylic acids and cellulose. However, the experimental results that high level of sizing can be developed very quickly with the heat treatment in the less cellulose-rich TMP handsheets but no sizing can be developed with the same heat treatment in the more cellulose-rich bleached hardwood KP handsheets can not be explained along this line.

Even more interesting is the fact that good sizing can be developed in control handsheets (no sizing agent or any other chemicals was added) made from bleached or unbleached chemical pulps under prolonged heating at 160°C, as shown in **Figure 3.2**. Sizing can be developed even more quickly in the control handsheets when heating at a higher temperature such as 180°C, but the results are not reported here. Even though the ink penetration resistances (HST values) of the handsheets are not very high in the control handsheets after prolonged heating, the water pickup resistances (Cobb size, tested but not reported) are actually quite high, which is in opposite to the situations when sizing is developed by dipping in rosin solution. We have difficulty to explain this phenomenon. A hypothetical explanation is that at high temperatures some type of crosslinkage is formed between cellulose molecules which manifests itself by affecting the capillary action during the process of ink penetration in the HST test.

Figure 3.2 Sizing in control handsheets after heating



NOTE: No rosin, heating temperature 160 °C, dryer-derived handsheet

### 3.2.4 Effectiveness with other rosin samples

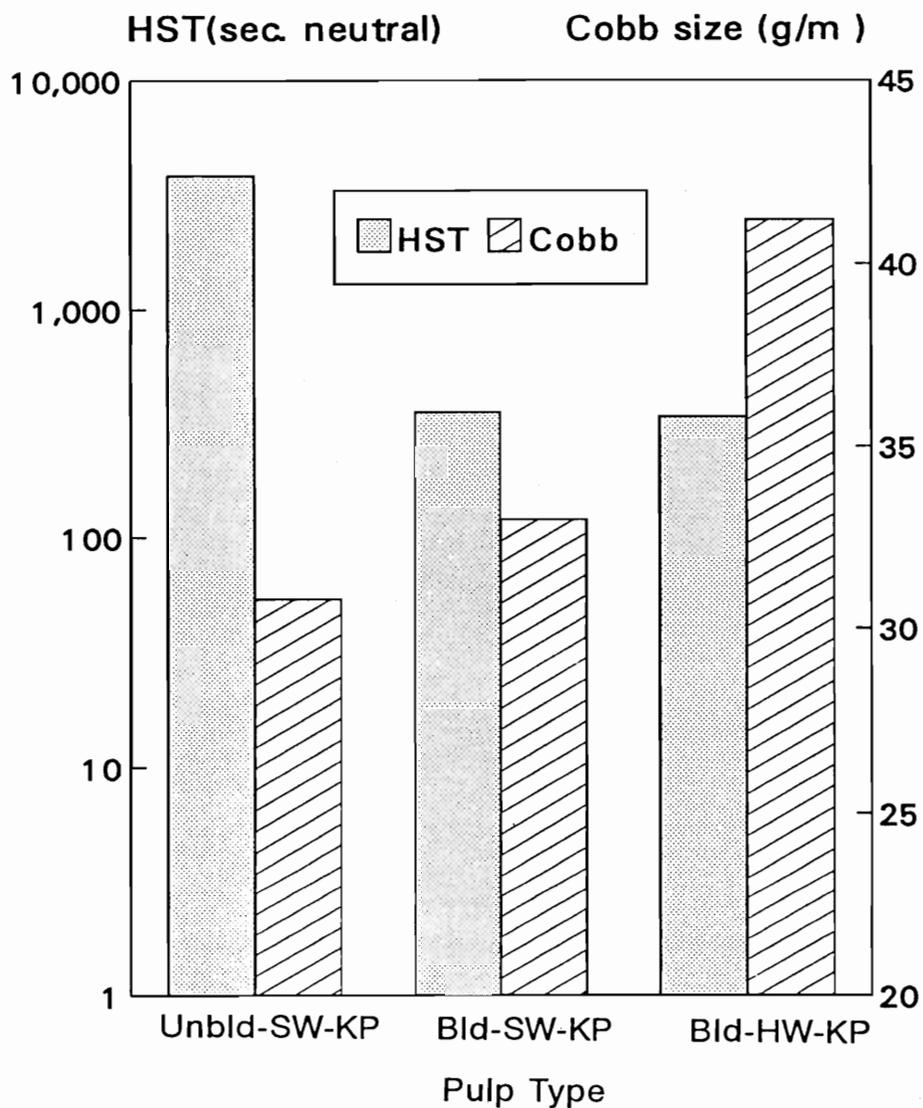
Rosin soap size has been used in the paper industry for nearly 200 years, but it has always been used as an internal sizing agent, rather than a surface sizing agent. The dip treatment is designed to simulate internal sizing while avoiding the issue of retention. Dipping is different from surface sizing in that dipping involves a low viscosity fluid in an unsized sheet that completely penetrates the sheet. Surface size is designed to use high molecular weight material that remains on the surface of the sheet.

Is the sizing achieved by immersing paper in the size solution an unique phenomenon for the particular rosin size used (Stafor, Westvaco chemicals), or a common property for any rosin size? The following experiments were designed to answer this question.

**Figure 3.3** shows the effectiveness of another fortified rosin soap size, Plasmine PLH-55. Dryer-dried (121°C for 3 min) handsheets were dipped in a 1% Plasmine PLH-55 solution for 45 seconds and then dryer-dried again after removing the excess solution. Comparing to the results in **Table 3.1** (Exp. 1, 3 and 4), it can be seen that Plasmine PLH-55 (ammonium salt of fortified rosin) size is as effective as Stafor size (potassium salt of fortified rosin) size.

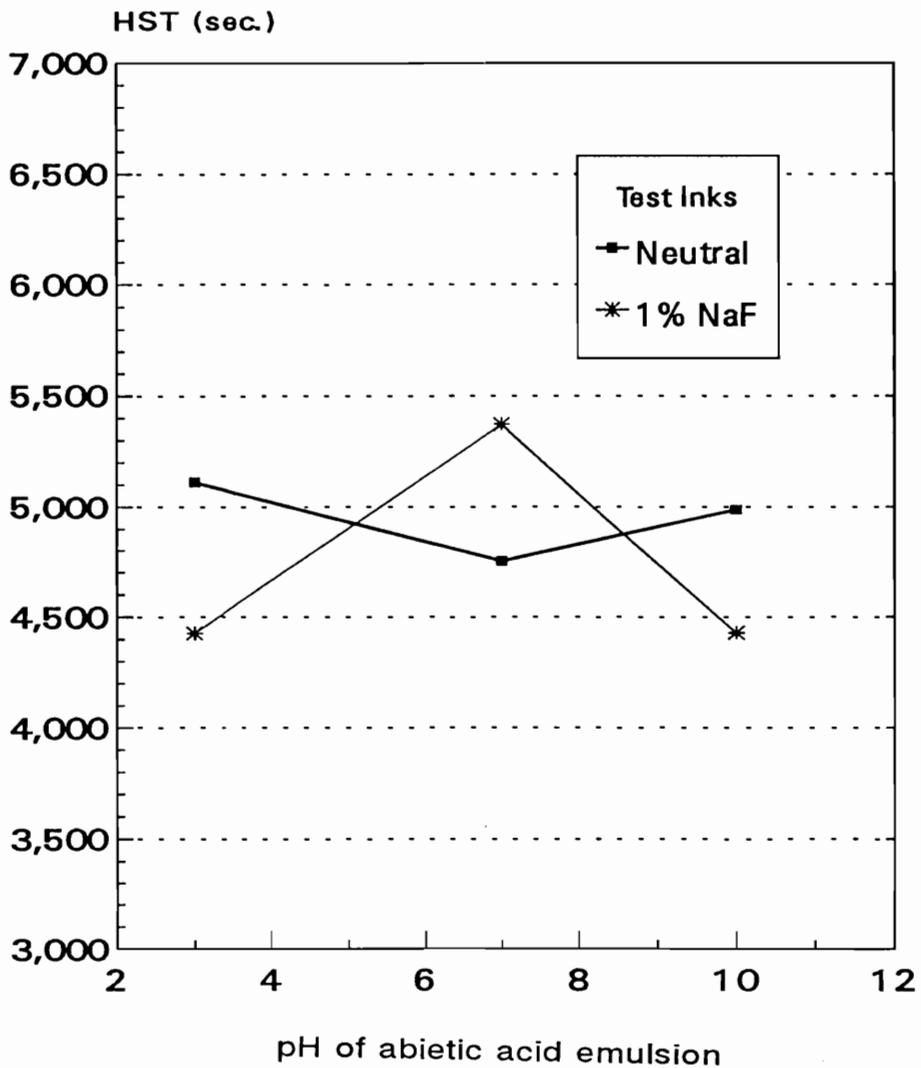
It can be seen from **Figure 3.4** that abietic acid can also be used to achieve sizing in the same way. Abietic

Figure 3.3 Effectiveness with other rosin  
(Plasmine PLH-55)



NOTE: Dryer-dried handsheets, dryer-dried after dipping, 1% dipping concentration of rosin soap.

Figure 3.4 Effectiveness with abietic acid



NOTE: Unbleached-SW-KP, dryer-dried handsheets, dryer-dried after dipping, 1% dipping concentration of rosin soap.

acid shows similar effectiveness. Since abietic acid is not water soluble, it was dissolved in a small amount of ethanol first and then diluted with water to make an emulsion. The change of the emulsion pH from 3 to 11 did not seem to have significant effect on the sizing results.

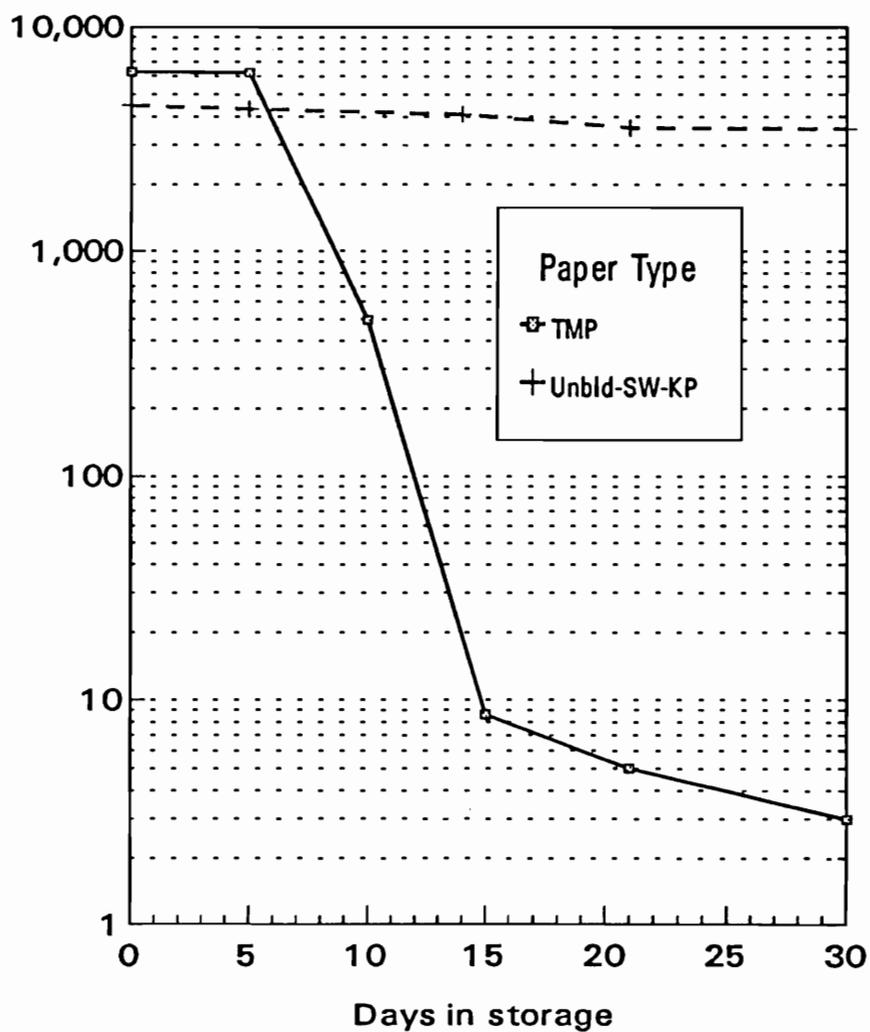
### 3.2.5 The fugitiveness of sizing

The fugitiveness of sizing with synthetic sizing agents is a well known phenomenon (12, 16). The same phenomenon occurs in the dip treatment of handsheets with rosin soap size in some pulps. As shown in **Figure 3.5**, after dipping in 1% rosin soap solution and drying at 121°C, handsheet made from TMP possessed very high level of sizing in the first week, but the sizing dropped dramatically after that and the sizing almost completely disappeared after 10 to 15 days. However, in the handsheets made from unbleached softwood KP and treated with rosin solution in the same way, the sizing can last for a much longer period of time, as can be seen from **Figure 3.5**. Sizing is still very high even after 100 days. Again, the different behaviors among pulps are yet to be explained.

### 3.2.6 HST measurement with different inks

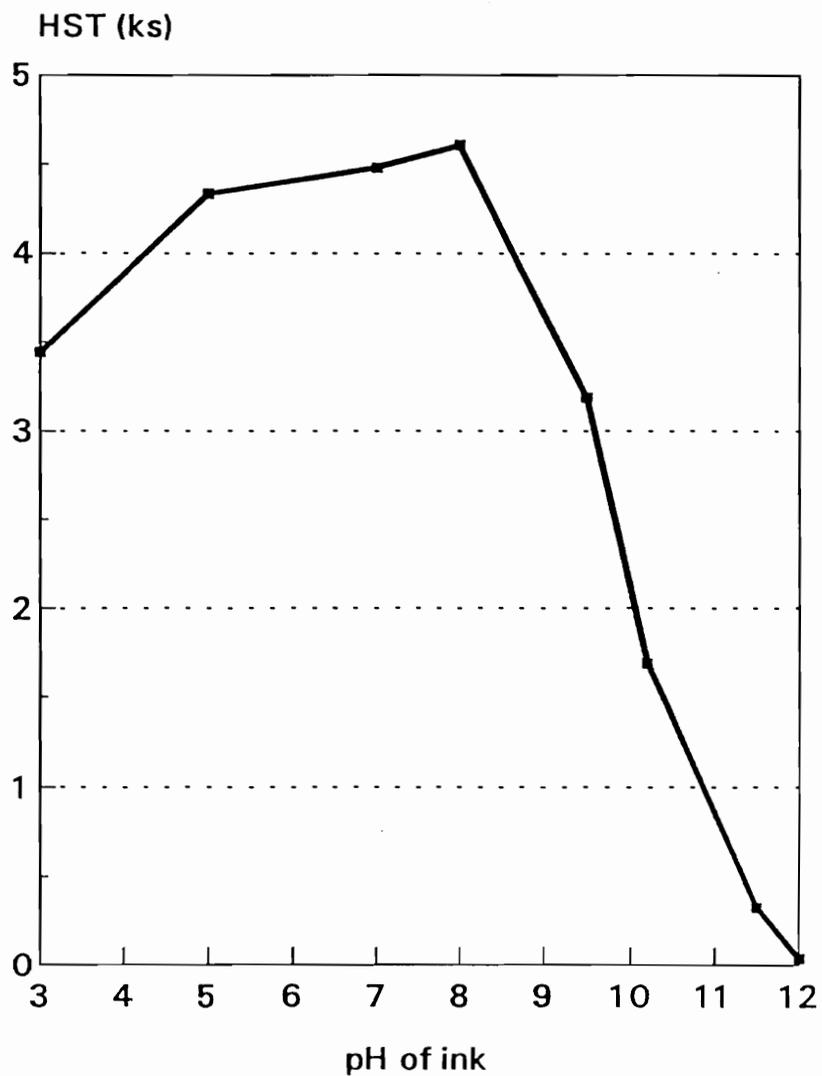
It is known (9) that the ink pH and compositions have great effects on HST values in rosin-alum sized paper, but much less in AKD sized paper. The reason is because the size bonding in the former is much less resistant to the

Figure 3.5 The fugitiveness of sizing



NOTE: Dryer-dried handsheets, dryer-dried after dipping, 1% dipping concentration of rosin soap.

Figure 3.6 Effect of ink on HST measurement



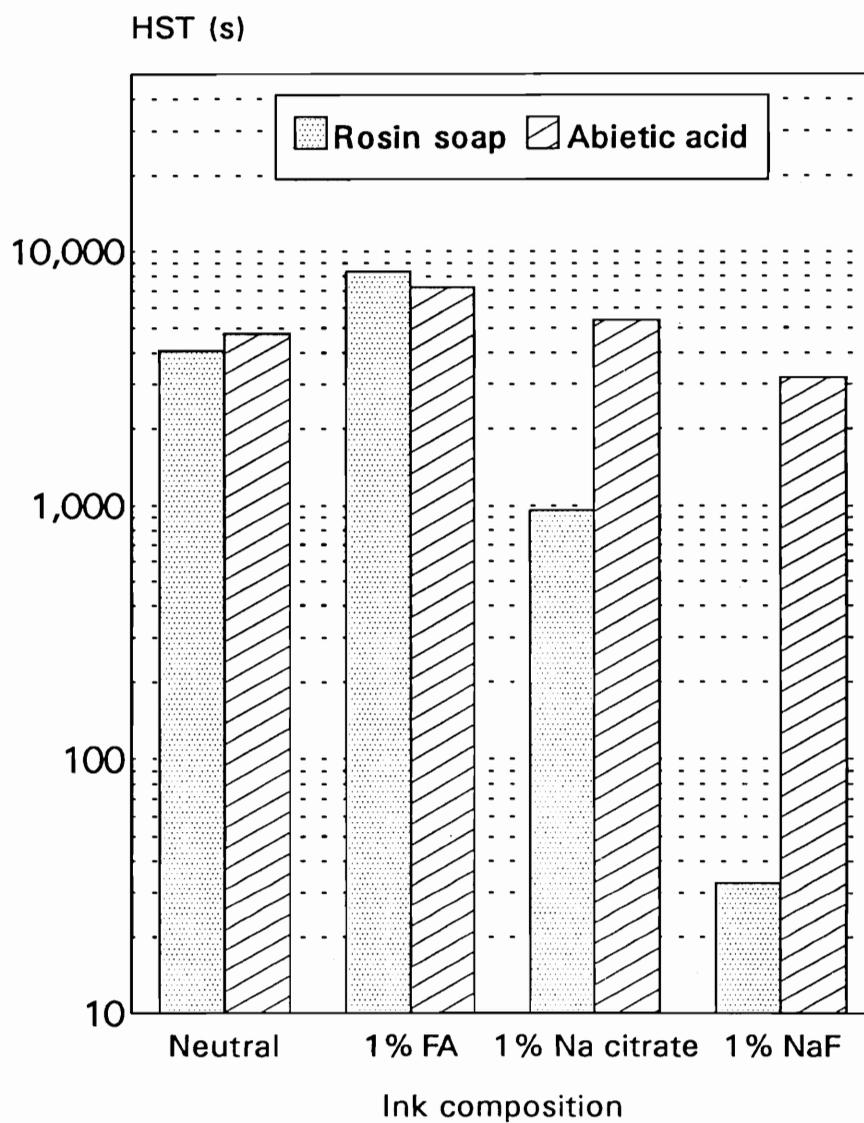
NOTE: Unbleached-SW-KP, dryer-dried after dipping, 1% dipping concentration of rosin soap.

acidic pH and the ligand species in the testing ink. Measuring HST values with inks of different pH and compositions can help us understand the bonding mechanism between size molecules and fiber components.

**Figure 3.6** shows the effect of ink pH on HST values of handsheets sized by dipping in rosin solutions. The ink solutions with different pH were obtained by adjusting the pH of the neutral ink with 1% HCl and 1% NaOH aqueous solutions. The sizing is quite resistant to the acidity in the ink solution, which is not true in the wet end sizing with rosin-alum system, showing the differences in the bonding mechanism between the two rosin sizing processes, but the sizing is not resistant to the alkalinity in the ink solution, which is expected if the rosin forms an ester linkage.

It was reported (9) that 1% sodium citrate has a great desizing effect on rosin-alum sized paper and 1% sodium fluoride ink can soak the rosin-alum sized paper instantly, but both chemicals have little desizing effect on AKD sized paper. The reason is because citrate anions, and especially, fluoride anions, have very high formation constant (coordination potential) with  $Al^{3+}$  so they can easily break the dative bonds which bind rosin molecules on fibers by a ligand substitution reaction, but they are unable to break the ester linkage which bind AKD molecules on fibers.

Figure 3.7 Effect of ink composition on HST measurement



NOTE: Unbleached-SW-KP, dryer-dried after dipping, 1% dipping concentration of rosin soap.

**Figure 3.7** shows that 1% formic acid, sodium citrate, and sodium fluoride have little desizing effect on handsheets sized by dipping in 1% abietic acid emulsion. This result is a strong indication that when sized by dipping in abietic acid solution, the bonding between abietic acid and fiber components is a covalent linkage which is resistant to coordination anions, probably by an ester linkage. However, **Figure 3.7** shows that 1% sodium fluoride has profound desizing effects on handsheets sized by dipping in rosin soap solution. This phenomenon is unable to be explained based on our present understanding about sizing mechanism. The 1% sodium citrate ink and 1% sodium fluoride ink were made in exactly the same way as the 1% formic acid ink except that 2% sodium citrate solution and 2% sodium fluoride solution were used instead of the 2% formic acid solution.

### 3.3 Summary

Dipping handsheets in rosin soap solution and then drying them with heat can result in effective sizing. No mordant is needed in this process. Sizing with this method can be easily achieved in unbleached softwood KP and TMP handsheets, but less so in handsheets made from bleached pulps, especially bleached hardwood pulp. Sizing achieved with this method is quite fugitive in the TMP handsheets, but is stable in unbleached softwood KP handsheets.

Effective sizing can also be achieved by dipping handsheets in abietic acid emulsion.

There are many factors which can affect the sizing with this method. The handsheet drying conditions in both pre-dipping and after-dipping stages seems to be critical. Dryer-drying (at 121°C for 3 min) in the two drying stages were shown to be indispensable to achieve effective sizing. Air-drying in either stage will result in no sizing in the handsheets from all the pulps except for the unbleached softwood KP.

The concentration of rosin in the dipping solution is also an important factor. While it is critical in the sizing of handsheets made from bleached softwood KP, it is much less so in the sizing of handsheets made from unbleached softwood KP. No relationship between the sizing results and the amount of rosin adsorbed has been found.

Heating the dipped handsheets, which originally have no sizing because of air-drying in one of the two drying stages, at 160°C for just one minute can promote a high level of sizing in handsheets from TMP and good sizing in handsheets from bleached softwood KP. But the same or even longer heating treatment seems to have no effect on the sizing development in the handsheets made from bleached hardwood KP. Heating the control handsheets (with no added size agent) made from bleached or unbleached chemical pulps at 160°C or higher temperature for more than one hour can

also develop good sizing in them, but the same heating treatment has no effect on TMP control handsheets.

HST tests with inks of different pH and different compositions indicated that the bonding interaction between abietic acid and fiber components which effect the sizing is more likely an ester linkage, but the effecting bonding interaction between rosin soap molecules and fiber components is much less clear.

### 3.4 Experiments

#### 3.4.1 Materials

The unbleached Douglas-fir kraft pulp had a Canadian Standard freeness (CSF) of 650 ml and a 40 ml permanganate (K) number of 62. The bleached Douglas-fir kraft pulp and the bleached hardwood chemical pulp had a CSF of 330 ml and 360 ml, respectively. The mechanical pulp was TMP of western U.S. true firs and hemlock.

The rosin soap size used in this study was Stafor (Westvaco Chemicals) except when specified (Plasmine PLH-55). The abietic acid was a 85% purity grade chemical from Aldrich (Milwaukee, WI).

#### 3.4.2 Procedures

Handsheets of 60 g/m<sup>2</sup> basis weight were made according to TAPPI Test Method 205 om-88 in the British Sheet Mold, but the total water volume in the mold was 5.0 liters instead of 7.0 liters as is the standard. The standard

press cycle was used, and then the handsheets were dried in a sheet dryer at 121°C for 3 min or in a standard TAPPI room (22.2 °C and 50% relative humidity).

After conditioning in the standard TAPPI room for at least 2 hours, the handsheet was weighed to the nearest 0.001 g and then dipped in a rosin soap solution or abietic acid emulsion for 45 seconds. The handsheet was removed from the solution (or emulsion) and put in the middle of four blotting paper sheets. With slightly pressing on the blotting paper sheets to remove the surplus liquid, the handsheet was immediately reweighed to the nearest 0.001 g. Then drying the handsheet either in a sheet dryer at 121°C for 3 min (dryer-drying) or in a standard TAPPI room (air-drying) as required.

The amount of rosin adsorbed in the handsheet was calculated by subtracting the conditioned weight of the handsheet from its final weight, multiplying by the concentration of rosin in the dipping solution, and dividing by the conditioned weight of the handsheets.

After conditioning in TAPPI room for at least another 2 hours, Cobb Size values of the handsheets were determined by TAPPI T441 om-90. Ink resistance was determined on a Hercules Sizing Tester according to T530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution.

## 3.5 References

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## Chapter 4

### SURFACE ENERGY AND ACID/BASE CHARACTER OF SIZED AND UNSIZED PAPER HANDSHEETS

#### 4.1 Introduction

Sizing is the process of using chemical agents to change the hydrophilic surface of the cellulosic fibers of paper to a surface with more hydrophobic character; this provides the paper with the ability to resist liquid wetting and penetration. The interactions between the liquid and solid (paper) are of the primary interest for paper chemists. The fundamentals related to these interactions such as surface tension, surface energy, and surface chemical characteristics have been successfully used to explain some phenomena regarding sizing and provide valuable guidelines for the choice of sizing agents.

Unsize paper is easily wetted by water because both water and paper are very compatible in their surface energies. The favorable adhesion promotes this wetting process. It is important to understand and control the surface energetic characteristics of paper and make it incompatible with the liquid contacted, the primary objective of paper sizing.

The surface energy and the surface acid/base (hydrogen bonding) character of paper are often considered to be the critical properties in predicting the paper's wetting

contact angle analysis. Many researches have been conducted. An early paper by Herczeg (2) measured the critical surface tension of Douglas-fir. Lee and Luner (3) investigated the wetting behavior of cellulose, hemicellulose, and lignin. Klunness (4) and Hodgson and Berg (5) and Krueger (13) used the Wilhelmy technique to measure surface characteristics of various types of pulp fibers. However, this method has not been recognized as a useful method in the study of paper sizing. This research will demonstrate its usefulness in understanding sizing mechanism and the fundamental differences existing in sizing systems.

Surface energy is often separated into polar and non-polar components. Two methods, geometric mean and harmonic mean, are extensively used in calculating the surface energy and its components. Borch (1) has tabulated some surface energy data for cellulosic substances obtained from different publications. The values of surface energy and its components often depend not only on the exact nature of the substrate analyzed, but also on the liquids chosen for contact angle analysis and on the calculation approaches. It is very difficult to determine a value of the absolute surface energy. For cellulosic materials, two particular difficulties exist in the study of the surface energy based on the contact angle analysis. First, the porosity and surface roughness make it especially difficult to obtain a thermodynamically equilibrated contact angle. Second, the

great contribution of hydrogen bonding to the interfacial forces may cause the theoretical basis of the geometric / harmonic mean approaches to be far from reality (6). Nevertheless, the notion of the surface energy is still extensively used and is often considered as an indicator of the surface treatments.

The surfaces of cellulosic materials have a great number of acid/base sites, which are the hydrogen bonding moieties. The acid/base interaction is a dominating contribution to the interfacial forces when a liquid with the potential to form hydrogen bond is present. The work of acid/base interaction is a good indicator of the surface wettability. This work can be readily calculated by using contact angle analysis.

The focus of this research is to investigate the role of the surface energy in affecting the paper's wettability or its sizing ability. The method of dynamic contact angle analysis is used to investigate the work of acid/base interaction of the paper handsheets (sized and unsized) with various probe liquids.

#### 4.2 Theory

Surface energy is defined as the change in Helmholtz free energy of the surface associated with unit increase of surface area. The surface free energy of a liquid has the same value as the surface tension which can be easily measured. But for a solid, the surface tension is difficult

to be measured directly and it is not necessarily equal to the surface energy. Nevertheless, the solid surface energy is often estimated by using contact angle analysis.

The earliest notions of surface energy and contact angle for a drop on a solid surface are expressed by the familiar Young's equation (Equation 4.1), which is the theoretical foundation to estimate the surface energy of a solid:

$$\gamma_s - \gamma_{sl} = \gamma_l \cos\theta \quad (4.1)$$

where  $\gamma_s$  and  $\gamma_l$  are each the surface tension of the solid and the liquid,  $\gamma_{sl}$  and  $\theta$  are each the interfacial tension and the contact angle between solid and liquid. For a solid of which the surface tension can be assumed to be equal to the surface free energy, Young's equation is a relation between the surface thermodynamic functions and the interaction at a liquid/solid interface. The contact angle between a liquid with known surface tension and the solid substrate can be, therefore, used to study the solid surface energy property.

In general terms, the thermodynamic energy of interaction,  $W_a$  (equivalent to the work of adhesion) is given by the reversible energy difference on separating a liquid from a solid:

$$W_a = \gamma_s + \gamma_l - \gamma_{sl} \quad (4.2)$$

combining Equation (4.1) and (4.2) yields

$$W_a = \gamma_{lv} (1 + \cos \theta) \quad (4.3)$$

Hence, the thermodynamic energy of interaction at an interface is readily determined from the contact angle measured with a liquid of known surface tension.

Another critical theory about surface energy and interfacial tension theory was proposed by Fowkes(8), which suggests that the surface energy of a material could be broken into parts, corresponding to various contributions from different interactions:

$$\gamma = \gamma^d + \gamma^p \quad (4.4)$$

or, more generally, in terms of work adhesion (thermodynamic energy of interaction)

$$W_a = W_a^d + W_a^p + W_a^h + W_a^i \quad (4.5)$$

where the superscript d refers to London dispersion forces, p to dipole-dipole interaction; h to hydrogen bonding, and i to induced dipole interactions. Since the dipole (p) and

induced dipole (i) are usually quite small, Equation (4.5) is more generally expressed as

$$W_a = W_a^v + W_a^{ab} \quad (4.6)$$

where v refers to Van der Waals force of which the predominant contribution is dispersion forces. All other forces, denoted as (ab), are described as acid/base (donor acceptor) interactions, which cover any interaction that involves the sharing of an electron pair, including hydrogen bonding.

Fowkes (5) also suggested that the work of adhesion (the dispersion force interactions between two liquids or between a liquid and a solid), when only the dispersion force is present at the liquid/solid interface, can be predicted by the geometric mean of their internal forces:

$$W_a^d = 2 (\gamma_l^d \gamma_s^d)^{1/2} \quad (4.7)$$

or, in terms of interfacial tension,

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 (\gamma_l^d \gamma_s^d)^{1/2} \quad (4.8)$$

Fowkes' equation has been extended to account for 'polar' interactions by Owens and Went and used extensively by Kaelble (8). This extension leads to

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 (\gamma_l^d \gamma_s^d)^{1/2} - 2 (\gamma_l^p \gamma_s^p)^{1/2}$$

(4.9)

Combining the equation 4.9 with Young's equation gives

$$\gamma_l (1 + \cos \theta) = 2 (\gamma_l^d \gamma_s^d)^{1/2} + 2 (\gamma_l^p \gamma_s^p)^{1/2} \quad (4.10)$$

The equation 4.10 is the theoretical basis of the well known geometric mean method used in calculating solid surface energy and its components.

However, the above extension has been criticized repeatedly, even by Dr. Fowkes himself (9). Since the predominant contribution of the so called "polar" part of the surface energy is actually acid/base interaction which is completely independent of the dipole moment of the materials. No relation exists between the work of adhesion resulting from acid/base interaction and the bonding within either material, expressed in the term of the polar part of the surface free energy  $\gamma^p$  or  $\gamma^{ab}$ .

According to Fowkes' theory, the polar or acid/base part of the solid surface energy can not be calculated by using contact angle analysis. Instead the adhesion work of acid/base interaction with a particular liquid (surface

tension is  $\gamma_1$ ) is used to characterize the acid/base property of a solid surface. The method is based on the following equation:

$$W_a^{ab} = W_a - W_a^d = \gamma_1 (1 + \cos\theta) - 2 (\gamma_s^d \gamma_1^d)^{1/2} \quad (4.11)$$

The dispersion contribution of the liquid surface energy  $\gamma_1^d$  can be obtained by measuring the contact angle of the liquid against a solid with only dispersive surface energy (usually Teflon). The dispersion contribution of the solid surface energy  $\gamma_s^d$  is obtained by measuring the contact angle of a neutral, non-self-associating probe liquid (i.e., one with no acid/base character) against the solid. Since  $\gamma_1 = \gamma_1^d$  and  $W_a^{ab} = 0$ , Equation 4.11 becomes:

$$\gamma_s^d = \frac{\gamma_1 (1 + \cos\theta)^2}{4} \quad (4.12)$$

It must be noted that the surface of paper and other cellulosic materials are dominated by hydroxyl groups. The acid/base interactions can be described as predominantly hydrogen bonding, which is the donor-acceptor interaction and its work  $W_a^h$  can not be considered by  $2(\gamma_1^h \gamma_s^h)^{1/2}$ . Therefore, the acid/base approach can be considered as theoretically more reliable than the surface energy approach in the characterizing the surfaces of cellulosic materials.

Another different approach to calculate the surface energy is the so called harmonic mean equation proposed by Wu (10),

$$\gamma_{sl} = \gamma_s + \gamma_l - 2 \frac{\gamma_l^d \gamma_s^d}{\gamma_l^d + \gamma_s^d} - 2 \frac{\gamma_l^p \gamma_s^p}{\gamma_l^p + \gamma_s^p}$$

(4.13)

This is actually an empirical approach and was considered to be more suitable than the geometric mean in calculating the polar component of a series of polymers. However, they both are extensively used.

### 4.3 Materials and methods

#### 4.3.1 Materials

**Pulp:** Softwood bleached kraft pulp was beaten to 500 ml Canadian Standard freeness in a double-disk refiner. handsheets (60 g/m<sup>2</sup>) were prepared from this kraft pulp, tap water and rosin soap size solution or AKD emulsion in the British Sheet Mold (TAPPI Test Method 205 om-58). All handsheets were pressed in the standard press cycle and conditioned at TAPPI standard conditions (72 °F and 50% RH) for one week before being tested.

**Rosin size:** Fortified rosin soap at 1% solids based on dry pulp as a 0.1% solution (Stafor®, Westvaco Chemicals)

was added to thick stock (1%). The stock was stirred and adjusted to about Ph 4.5 (unless indicated) with Hcl (2%), then 2% alum (based on dry pulp) was added. The Ph was adjusted again, and the stock was stirred for another 5 minutes and diluted to 0.2% with tap water. The Ph of the pulp slurry was adjusted again before the formation of handsheets.

AKD size: AKD (0.3%) based on dry pulp (Hercon®, Hercules Inc.), as a 12.5% emulsion, was added into thick stock (1%). The stock was stirred and adjusted to pH8.5 with NaOH (2%). For AKD-alum, 0.5% alum was then added after 1 minute, pulp Ph was adjusted to 8.5 (or 4.5 as mentioned). The stock was diluted to 0.2% with tap water, and the Ph was adjusted again to the set value before the formation of handsheets.

#### 4.3.2 Handsheet preparation

The preparation of the handsheet samples is specified in **Table 4.1**. One control group (unsized) and three other groups with different sizing treatments:

#### 4.3.3 Contact angle measurements

The contact angle was measured by the Wilhelmy method using a CAHN DCA System. The paper handsheets were cut into 10x25 mm specimens. The advancing contact angles were obtained by scanning the specimen with various liquids. The

Table 4.1 Specification of the handsheet samples

Samples	Sizing Condition
G - 0	Control
G - 1	0.3% AKD, pH8.5
G - 3	1.0% AKD, 0.5% Alum, pH8.5
F - 1	1.0% Rosin, 2% Alum, pH4.5

Table 4.2 Surface energy (surface tension) and its components of the probe liquids<sup>a</sup>

Probe Liquids	Geometric			Harmonic		
	$\gamma_1$	$\gamma_1^d$	$\gamma_1^p$	$\gamma_1$	$\gamma_1^d$	$\gamma_1^p$
Water	72.80	22.50	50.30	72.80	22.10	50.7
Methylene iodide	50.80	48.50	2.30	50.80	44.10	6.70
Formamide	58.20	39.50	18.70	58.20	36.00	22.2
Ethylen Glycol	48.30	29.30	19.00	48.30	29.30	19.0

<sup>a</sup> Units are mJ/m<sup>2</sup>

liquids used were methylene iodide (neutral), formamide (a Lewis base), ethylene glycol (a Lewis acid), and water (bifunctional). The surface energy values of these liquids are listed in **Table 4.2**.

#### 4.4 Results and discussion

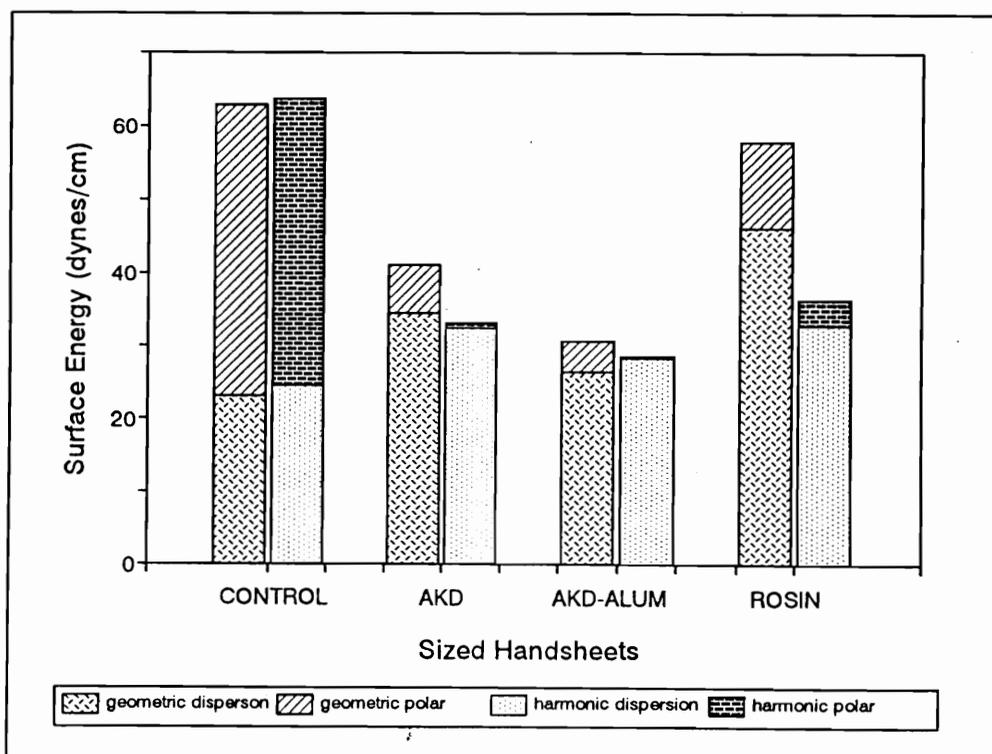
Table 4.3 and Figure 4.1 show the data of surface energy and its components of paper handsheets. Both geometric and harmonic methods were used. The two liquids were water, with a large polar component of surface energy ( $\rho$ ), and methylene iodide, with a large dispersion component of surface energy ( $d$ ).

For the unsized handsheet, it has much higher surface energy than the sized handsheets. The primary difference in the surface energy is in the polar components. All of the three size treated handsheets appeared to significantly reduce the polar contribution of the surface energy. This explains why the sized paper surface is hydrophobic. Since water has a large polar surface energy component and it is difficult to spread onto a surface (such as the sized handsheets) which does not provide a compatible polar part (Hydrogen bonding) at the interface. The sizing treatment also appeared to increase the dispersion part of surface energy, especially for the sample of rosin sized paper. This may be due to the existence of its large tricyclic organic structure of the abietic acid. For AKD-sized

4.3 Surface energy of handsheet calculated by geometric/harmonic two-liquid methods

HANDSHEETS	Geometric			Harmonic		
	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$	$\gamma_s$	$\gamma_s^d$	$\gamma_s^p$
Control	62.84	22.95	39.89	63.76	24.43	39.33
AKD	41.13	34.63	6.50	33.37	32.40	0.97
AKD-Alum	30.77	26.35	4.42	28.61	28.31	0.30
Rosin	57.95	46.19	11.76	36.58	32.89	3.69

Figure 4.1 Surface energetics of paper handsheets of various natures calculated by using both geometric and harmonic methods



samples, the two methods, geometric /harmonic mean, give very similar results. But for the rosin-sized sample, geometric mean results in the much higher surface energy values than harmonic mean does.

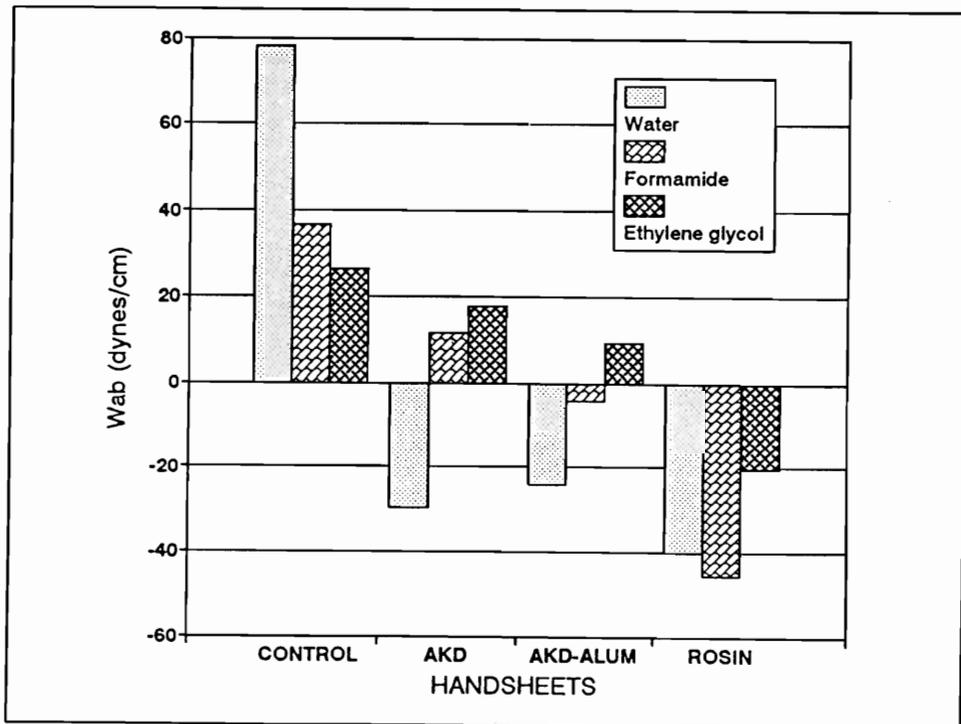
**Table 4.4** and **Figure 4.2** show the results of the acid/base work of adhesion with three different probe liquids including water, formamide and ethylene glycol. These probe liquids were chosen according to their acid-base properties. Ethylene glycol is slightly acidic; water is neutral with a strong self-association force (hydrogen bond); formamide is slightly basic. The values  $\gamma_s^v$  in **Table 4.4** are calculated from wetting data in methylene iodide and **Equation 4.13**, as well as values of  $W_a [= \gamma_1 (1 + \cos \theta)]$ . These data were used in **Equation 4.11** to calculate the other values in **Figure 4.2**.

The unsized handsheet shows strong interactions with all of the three liquids. This suggests a great number of both acidic and basic sites existing on the unsized surface which can be characterized as bi-functional. Also, the higher  $W^{ab}$  value of formamide compared to that of ethylene glycol indicates that the unsized paper surface is acidic (i.e. having more acid sites). The handsheet treated with 0.3% AKD covers some acid/base sites, which is indicated by the significant decreases of  $W^{ab}$  for each liquid. This treated surface is still bi-functional with more basicity indicated by a higher  $W^{ab}$  value of ethylene glycol. Sizing with AKD-Alum covers more acid/base moieties and causes the

Table 4.4 Van der Waals surface energy component and acid/base work of adhesion of the handsheets

Handsheets	$\gamma_s^d$	$W_{form}^{ab}$	$W_{water}^{ab}$	$W_{EG}^{ab}$
Control	36.20	36.74	78.06	26.47
AKD Sized	27.23	11.66	-29.41	17.79
AKD-Alum Sized	20.93	-4.14	-24.09	9.34
Rosin Sized	34.98	-45.84	-40.19	-20.43

Figure 4.2 Acid/base work of adhesion for paper handsheet of various natures



surface to be slightly basic. The reason was explained on chapter 2.

Sizing with rosin and alum covers all of the acid/base sites which is indicated by the negative values for all of the three liquids. There may be two possible reasons for the negative values in this test. The first is a base-base (or acid-acid) interaction that is actually repulsive in nature. Hence, these surfaces should show a positive interaction with a liquid of the opposite type. The second cause may be just the result of a relatively high surface tension liquid trying to move over the surface of a lower energy solid. This may also reflect the some limitations in using the acid/base method to judge the sizing ability.

The studies of surface energetics of regenerated cellulose film or cellulosic fiber have been well documented (1). A comparison is made in **Table 4.5**. The surface energy data of paper handsheets obtained in this study is very similar to that of cellulose film. Some other matches can also be found. The difference among the various AKD-treated materials may be due to the different treatment methods.

#### 4.5 Conclusions

Sizing is the process to modify the energetic characters of paper surface with sizing agents. The changes of its surface energy and its acid/base character directly

relate to its ability to resist liquid wetting. These changes can be characterized indirectly through thermodynamic analysis with the measurements of contact

Table 4.5 Surface energy and acid/base work of adhesion data for various cellulosic materials<sup>a</sup>

		Handsheet		Cellulose film		Fiber <sup>b</sup>	
		UNSIZ ED	AKD-sized	UNSIZ ED	AKD-sized	UNSIZ ED	AKD-sized
$\gamma_s^v$ dynes/cm	Total	62.8	41.1	59.5	34.0-49.1	--	--
	Dispersion	23.0	34.6	19.9	29.7-32.6	--	--
	Polar	39.9	6.5	39.6	1.4-19.4	--	--
$W_a^{ab}$ mJ/m <sup>2</sup>	Formamide	36.7	11.7	41.9	11.6	34.6	24.6
	Water	78.1	-29.4	77.5	28.1	73.0	--
	Ethylene glycol	26.5	17.8	--	5.4	21.9	20

<sup>a</sup> Data for the cellulose film and fiber is from reference (1) and (11)

<sup>b</sup> Bleached kraft  $\alpha$ -cellulose fiber

angle. Even through there are many arguments on the theories used to determine the surface properties of a solid and the existing difficulties in assigning absolute values of paper substrate, this method was found to be useful in the study of paper handsheets treated with various sizing agents.

The wetting measurements prove that treated cellulosic paper with AKD or rosin results in a hydrophobic surface and much low values of its acid/base interaction with various liquids. The effects of sizing treatments can be discerned with the changes of these properties. For various sizing treatments, the data obtained indicate a similar trend, i.e. a decrease in the surface energy level and its polar contribution, and a decrease in the acid/base work of adhesion. This technique provides us an alternative to evaluate and predict the suitability of the paper which is treated with some specific chemicals and used for some specific conditions. The results from this research indicates that the effects of sizing or other surface modifications on paper surface properties may be studied directly by using handsheet.

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## Chapter 5

## CONCLUSIONS

1. Substantial differences between rosin alum size and AKD size bonding mechanisms were demonstrated by their much different responses to a series of chemical penetrants.
2. Indirect rosin-alum-fiber size is formed through coordination bonds, which are stable in water at neutral pH, but can be greatly affected by acid, alkaline, and other chemicals. Ligand substitution was the major cause of this desizing process.
3. AKD can react with cellulose and form direct  $\beta$ -keto ester bonds with fibers. This strong covalent bond is almost inert to acidic and alkaline solutions. Even the strongest aluminum-complexing ion, fluoride, has no effect on the ink penetration.
4. If alum is used along with AKD sizing at low pH, there can be two types of bonds formed between the size and the fiber, the major direct ester bond and the minor indirect coordinate bond. Therefore, neutral ink will result in much higher HST values than formic acid or other penetrant inks. The use of alum in AKD sizing systems for its other positive effects on drainage and retention should be carefully considered since alum's preferential attraction to AKD molecules could reduce the effective strong covalent bond in the final size.

5. The surfactant Tween-20 can be used to as a penetrant to accelerate the testing of hard sized papers, which will reflect the real rate of ink penetration without interference with the size bond itself.
6. Dipping handsheets in rosin soap solution and then drying them with heat can result in effective sizing. No mordant is needed in this process. Sizing with this method can be easily achieved in unbleached softwood KP and TMP handsheets, but less so in handsheets made from bleached pulps, especially bleached hardwood pulp. Sizing achieved with this method is quite fugitive in the TMP handsheets, but is stable in unbleached softwood KP handsheets. Effective sizing can also be achieved by dipping handsheets in abietic acid emulsion.
7. There are many factors which can affect the sizing with this method. The handsheet drying conditions in both pre-dipping and after-dipping stages seems to be critical. Dryer-drying (at 121°C for 3 min) in the two drying stages were shown to be indispensable to achieve effective sizing. Air-drying in either stage will result in no sizing in the handsheets from all the pulps except for the unbleached softwood KP.
8. The concentration of rosin in the dipping solution is also an important factor. While it is critical in the sizing of handsheets made from bleached softwood KP, it is much less so in the sizing of handsheets made from

unbleached softwood KP. No relationship between the sizing results and the amount of rosin adsorbed has been found.

9. Heating the dipped handsheets which originally have no sizing because of air-drying in one of the two drying stages at 160°C for just one minute can promote a high level of sizing in handsheets from TMP and good sizing in handsheets from bleached softwood KP. But the same or even longer heating treatment seems to have no effect on the sizing development in the handsheets made from bleached hardwood KP. Heating the blank handsheets (with nothing added or adsorbed) made from bleached or unbleached chemical pulps at 160°C or higher temperature for more than one hour can also develop good sizing in them, but the same heating treatment has no effect on the sizing development of blank TMP handsheets.
10. HST tests with inks of different pH and different compositions indicated that the bonding interaction between abietic acid and fiber components which effect the sizing is more likely an ester linkage, but the effecting bonding interaction between rosin soap molecules and fiber components is much less clear.
11. Sizing is the process to modify the energetic characters of paper surface with sizing agents. The changes of its surface energy and its acid/base

character directly relate to its ability to resist liquid wetting. These changes can be characterized indirectly through thermodynamic analysis with the measurements of contact angle. Even though there are many arguments on the theories used to determine the surface properties of a solid and the existing difficulties in assigning absolute values of paper substrate, this method was found to be useful in the study of paper handsheets treated with various sizing agents.

12. The wetting measurements prove that treated cellulosic paper with AKD or rosin results in a hydrophobic surface and much low values of its acid/base interaction with various liquids. The effects of sizing treatments can be discerned with the changes of these properties. For various sizing treatments, the data obtained indicate a similar trend, i.e. a decrease in the surface energy level and its polar contribution, and a decrease in the acid/base work of adhesion. This technique provides us an alternative to evaluate and predict the suitability of the paper which is treated with some special chemicals and used for some special conditions. The results from this research indicates that the effects of sizing or other surface modifications on paper surface properties may be studied directly by using handsheet.

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