

AN ABSTRACT OF THE THESIS OF

Jinfeng Zhuang for the degree of Doctor of Philosophy  
in Forest Products Presented on May 2, 1995

Title : UNDERSTANDING THE CHEMISTRY OF ROSIN SIZING AND  
DEVELOPING NEW SIZING TECHNOLOGIES

Abstract approved: ( Signature redacted for privacy.  
Christopher James Biermann

First, a thermodynamic analysis was carried out upon a sizing-desizing process. The energetic analysis shows that rosin soap size should be bound to fibers through primary chemical forces such as covalent bonds to effect sizing. Secondary chemical forces are all thermodynamically unstable to the attack of water molecules. It is also shown that the stronger the bonding between size and fibers is, the higher the degree of sizing of paper can be.

Then ferric and ferrous ions were investigated as mordants for rosin soap size. While ferric ion at pH 3.0 to 4.0 and ferrous ion at pH around 5.5 are able to induce a very high level of sizing to unbleached Douglas-fir kraft pulp, they have virtually no effect on bleached Douglas-fir kraft pulp and bleached hardwood chemical pulp. The reason is believed to be due to the difference in lignin content of the unbleached and bleached pulps. Two possible structures of the complex formed between these transition metal ions and

lignin are postulated. The excellent sizing results induced by iron ions in mechanical pulp strongly support this hypothesis.

Finally, metal ions  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  are used with polyamines as mordants of rosin soap size. While  $Mg^{2+}/PEI$  and  $Mn^{2+}/PEI$  shows no effect and  $Fe^{3+}/PEI$  is very effective in an acidic pH range,  $Zn^{2+}/PEI$  can induce moderate sizing and  $Fe^{2+}/PEI$  and  $Cu^{2+}/PEI$  can induce very high levels of sizing under neutral to alkaline conditions (up to pH 10 with  $Cu^{2+}/PEI$ ) in various pulps. The incorporation of polyamines can also greatly improve the sizing efficiency when alum is the mordant. The tensile and bursting strength of the handsheets can also be improved by 20-30% with these mordants. It is observed that the pH of maximum sizing efficacy of these metal ions is in the vicinity of their  $pK_1$  values. In addition, their performances as mordants of rosin soap sizing coincide with the Irving-Williams Effect which describes the general trends in the stability of metal complexes.

UNDERSTANDING THE CHEMISTRY OF ROSIN SIZING AND  
DEVELOPING NEW SIZING TECHNOLOGIES

by

Jinfeng Zhuang

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirement for the  
degree of

Doctor of Philosophy

Completed May 2, 1995

Commencement June 11, 1995

Doctor of Philosophy thesis of Jinfeng Zhuang presented on  
May 2, 1995

APPROVED:

Signature redacted for privacy.

---

Major Professor, representing Forest Products

Signature redacted for privacy.

---

Head of /Department of Forest Products

Signature redacted for privacy.

---

Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

/

Signature redacted for privacy.

---

Jinfeng Zhuang, Author

## ACKNOWLEDGEMENT

This thesis is dedicated to my wife, Yizhen, my son, William, and my parents, for their love, inspiration, and sacrifices.

I wish to express my most sincere thanks to my major professor, Dr. Christopher J. Biermann, for his valuable guidance, numerous enlightening advises, and constant assistance throughout my Ph.D study.

I am very grateful to all the other members in my graduate committee for their time and their constructive critiques on my thesis work.

I am also indebted to Mr. Jerry Hull. He is always ready to help me in the lab whenever I need a help.

My special appreciation is extended to my dear friend, Sriram Subrahmanyam, for his great helps at the beginning of this research.

## TABLE OF CONTENTS

	<u>Page</u>
1. LITERATURE REVIEW . . . . .	1
1.1 GENERAL INTRODUCTION ABOUT SIZING. . . . .	1
1.2 ROSIN SOAP SIZING . . . . .	5
1.3 MORDANT OF SIZE AND CHEMISTRY OF ALUM . . . . .	12
1.4 NEUTRAL TO ALKALINE SIZING . . . . .	21
1.5 THE MEASUREMENT OF SIZING . . . . .	26
2. OBJECTIVE STATEMENT . . . . .	31
3. A THERMODYNAMIC ANALYSIS OF ROSIN SIZING PROCESS . . . . .	32
3.1 INTRODUCTION . . . . .	32
3.2 A THERMODYNAMIC ANALYSIS . . . . .	34
3.3 DISCUSSIONS . . . . .	42
3.4 CONCLUSIONS . . . . .	44
4. ROSIN SOAP SIZING WITH FERRIC AND FERROUS IONS AS MORDANTS . . . . .	46
4.1 INTRODUCTION . . . . .	46
4.2 RESULTS AND DISCUSSION . . . . .	49
4.2.1 Sizing in Unbleached Pulp. . . . .	49
4.2.2 Sizing in Bleached Pulp. . . . .	60
4.2.3 Sizing in Thermomechanical Pulp. . . . .	68
4.2.4 Effect of Heating Treatment on Sizing. . . . .	71
4.2.5 The Mechanism of HST Test with Formic Acid Ink . . . . .	73
4.3 CONCLUSIONS . . . . .	78
4.4 EXPERIMENTS . . . . .	79

## TABLE OF CONTENTS (Continued)

	<u>Page</u>
5. NEUTRAL TO ALKALINE ROSIN SOAP SIZING WITH METAL IONS AND POLYAMINES AS MORDANTS. . . . .	82
5.1 INTRODUCTION . . . . .	82
5.2 PRINCIPLES AND HYPOTHESIS . . . . .	84
5.3 RESULTS AND DISCUSSIONS. . . . .	91
5.3.1 Sizing in Bleached Hardwood Pulp . . . . .	91
5.3.2 Coordination Chemistry of Metal Ion Mordants . . . . .	100
5.3.3 Sizing in Other Types of Pulp. . . . .	103
5.3.4 Factors Affecting Sizing . . . . .	108
5.3.5 Strength Improvement in Handsheets . . . . .	122
5.3.6 HST Tests with Different Inks. . . . .	125
5.4 CONCLUSIONS . . . . .	129
5.5 EXPERIMENTS . . . . .	130
REFERENCES . . . . .	133

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1 Some commonly used sizing agents . . . . .	3
4.4 Formation of the hydroxo bridge with aluminum and ferric ions . . . . .	48
4.2 Effect of pH on rosin-Fe <sup>3+</sup> sizing . . . . .	53
4.3 Effect of Fe <sup>3+</sup> dosage on rosin-Fe <sup>3+</sup> sizing . . . . .	54
4.4 Effect of pH on rosin-Fe <sup>2+</sup> sizing . . . . .	55
4.5 Effect of Fe <sup>2+</sup> dosage on rosin-Fe <sup>2+</sup> sizing . . . . .	56
4.6 Effectiveness of ferrous sulfate as the mordant .	57
4.7 Sizing with ferrous sulfate as the mordant . . .	58
4.8 Postulated $\pi$ -complex and chelating ring formed between lignin and coordinating metal ions . . .	64
4.9 Representative $\pi$ -complexes between arenes and transition metals . . . . .	66
4.10 Effect of heating treatment on sizing . . . . .	72
4.11 Sizing in blank bleached hardwood handsheet after severe heating treatment . . . . .	74
4.12 Effect of ink surface tension on HST measurement	76
5.1 The $pK_1$ of metal ions . . . . .	87
5.2 Bonding between rosin and fibers . . . . .	90
5.3 Sizing results in bleached hardwood chemical pulp	94
5.4 The effect of the oxidation of ferrous ions on sizing . . . . .	98
5.5 Sizing in unbleached softwood kraft pulp . . . .	106
5.6 Sizing in softwood thermomechanical pulp . . . .	107
5.7 Effect of pH on rosin-Cu <sup>2+</sup> /PEI sizing . . . . .	109
5.8 Effect of Cu <sup>2+</sup> dosage on rosin-Cu <sup>2+</sup> /PEI sizing . .	110

## LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
5.9 Effect of pH on rosin-Fe <sup>2+</sup> /PEI sizing . . . . .	112
5.10 Effect of Fe <sup>2+</sup> dosage on rosin-Fe <sup>2+</sup> /PEI sizing . .	113
5.11 Effect of PEI dosage on rosin-Fe <sup>2+</sup> /PEI sizing . .	114
5.12 Effect of pH on rosin-alum/PEI sizing . . . . .	116
5.13 Effect of PEI dosage on rosin-alum/PEI sizing . .	117
5.14 Effectiveness of polyamine N634 . . . . .	118
5.15 Sizing with ferrous sulfate/PEI as the mordant .	120
5.16 Effect of drying condition on sizing . . . . .	121
5.17 Tensile strength of handsheets . . . . .	124
5.18 Effect of ink compositions on HST measurement . .	127
5.19 Effect of ink pH on HST measurement . . . . .	128

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
4.1	Sizing results of unbleached Douglas-fir kraft pulp . . . . .	51
4.2	Sizing results of bleached chemical pulps . . . .	61
4.3	Sizing results of thermomechanical pulp . . . . .	69
4.4	Surface tension of various aqueous ink solutions	75
5.1	Sizing results of bleached hardwood chemical pulp	92
5.2	Relationship between the $pK_1$ and pH of maximal sizing efficiency of metal ions . . . . .	100
5.3	The crystal field stabilization energy (CFSE) in a weak field . . . . .	103
5.4	Sizing results of unbleached kraft pulp and TMP .	105
5.5	Strength properties of the handsheets . . . . .	123

# **UNDERSTANDING THE CHEMISTRY OF ROSIN SIZING AND DEVELOPING NEW SIZING TECHNOLOGIES**

## **Chapter 1**

### **LITERATURE REVIEW**

#### **1.1 GENERAL INTRODUCTION ABOUT SIZING**

We know that most paper is made of cellulosic fibers. Because cellulose and hemicellulose contain many hydroxyl groups and hydrogen bonding interaction between water molecules and the hydroxyl groups on cellulosic fibers is very energetically favorable, water can readily wet and penetrate through paper, that is, paper does not have water repellency in nature. However, many end uses require that paper has certain degree of liquid repellency, so that the penetration, spreading and absorption of liquid such as water, aqueous inks, milk, coffee, blood, fruit juice, or other fluids can be retarded. Sizing is a process in papermaking which is designed to achieve this goal. Most grades of paper products used in printing, writing, packaging, wrapping, and construction applications need to be sized, while some other grades such as tissue, toweling and sanitary paper and blotters require good liquid absorptivity so sizing is inappropriate to them (1).

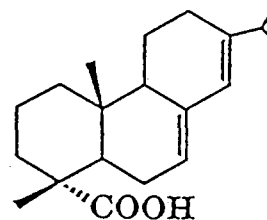
In general, sizing process can be divided into two categories: surface sizing and internal sizing. In surface

sizing, sizing agents are usually film-forming materials. They are applied to the surface of paper to form a more or less continuous film on it. Surface sizing agents can be applied on paper in a size press or a size tub by coating, spraying, or impregnating and a variety of different properties can be imparted to paper depending on the property of the materials applied. When rosin, wax or hydrophobic synthetic polymers are used, water repellency can be improved. However, the principal objective of surface sizing is to improve smoothness, surface strength and printability or to change the porosity and abrasiveness of the paper. At present starches, gums, glues, alginates, and synthetic polymers are commonly used for these purposes.

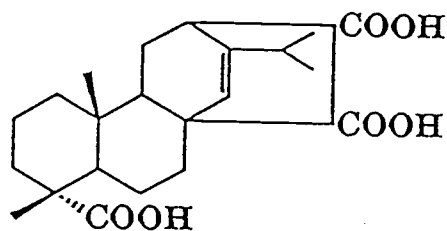
In internal sizing, sizing agents are usually some amphipathic (polar/nonpolar) compounds such as rosin, fortified rosin, alkyl ketene dimer or alkenyl succinic anhydride (**Figure 1.1**). They are added in the wet end of the papermaking process so retention aids are needed to retain them on fibers. Liquid repellency is usually the only property that internal sizing is aimed to impart to paper. Internal sizing is the subject of this study.

Although different end uses may require paper to have repellency to different fluids, water repellency is by far the most common property demanded by paper applications. By adding amphipathic molecules into pulp stock and arranging them on fiber surfaces in the way that their polar ends are anchored on fibers and their nonpolar ends are extended

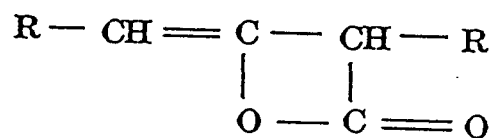
Rosin (abietic) acid:



Fortified rosin  
(abietic) acid:



Alkyl ketene dimer:



Alkenyl succinic anhydride:

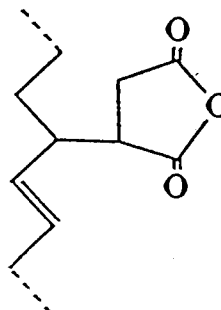


Figure 1.1 Some commonly used sizing agents

outward to form a hydrophobic layer, the hydrophilic fiber surfaces can be converted into hydrophobic ones and water repellency can be impart to paper.

Traditionally, capillary action is adopted to explain the wetting and penetration of liquid through paper because paper is a porous material. The rate of flow of a liquid through a capillary is described by Washburn equation (2):

$$dh/dt = (\gamma R) \cos \theta / 4 \eta h \quad (1.1)$$

where  $\gamma$  and  $\eta$  are surface tension and viscosity of the liquid,  $h$  and  $R$  are length already filled and radius of the capillary, and  $\theta$  is the contact angle between the liquid and the fiber surfaces. The objective of sizing is to provide the fiber surfaces with a relatively low surface energy layer, so that high energy aqueous liquids will form a high contact angle on the fiber surface and thus their penetration rates can be slowed down (3).

Since sizing is a fiber surface phenomenon, it is reasonable to believe that the amount of sizing agent required to achieve effective sizing will depend on the specific surface areas of paper furnish components and the molecular cross section of the sizing agent. Effective sizing should be obtained when a monomolecular layer coverage of the fiber surfaces is achieved. Theoretically, it has been calculated that 0.1-0.3% (based on dry pulp weight) of rosin size is needed to form a monomolecular

layer on beaten pulp fibers (3), even though other work (4) showed that to increase the contact angle of water on fibers from  $0^{\circ}$  to  $100^{\circ}$ , one quarter to one half of the fiber surface coverage with aluminum rosinate is sufficient. Mechanical pulps are well known to be more difficult to size than chemical pulps. Their higher specific surface areas were considered to be one of the main reasons.

In practice, about 5 times as much rosin size as the theoretical amount is needed in papermaking, while 0.1-0.3% (based on dry pulp weight) is usually an adequate amount for the so-called chemically reactive sizing agents such as AKD and ASA. This difference can tell much about the mechanism of these different sizing processes. While a higher percentage of the sizing agent added is effectively functioning in AKD and ASA sizing, the same number in the case of rosin sizing may be much lower. There are still much room for the improvement of sizing efficiency in the rosin sizing process.

## 1.2 ROSIN SOAP SIZING

Rosin soap sizing refers to the sizing process in which rosin soap size is used as the sizing agent. Modern sizing technology began in 1807 when Morris Illig developed an engine sizing process by precipitating rosin soap on pulp fibers with "papermaker's alum", aluminum sulfate while the

stock was being prepared. Before that time water repellency was obtained by dipping paper into a thin glue (5).

Rosin soap size is the oldest form of the sizing agent. It is inexpensive, water soluble and stable. Besides, the sizing process has following advantages (6):

- (a) the degree of sizing is easy to control,
- (b) the sizing operation is easy to handle,
- (c) the sizing chemicals are compatible with other wet-end additives, and
- (e) the problems in waste repulping are minor.

With the above advantages, rosin soap size in its various forms still represents the largest volume of rosin-based size used by the paper industry today. The disadvantages (6) of this sizing process are that the paper strength will be slightly affected and enough sizing against certain fluids such as lactic acid, milk and alkali cannot be developed. We will show in this study that the above statement about the disadvantages of rosin sizing systems is true when alum is used as the mordant, but is not always true when other mordant systems are used.

Despite the fact that rosin soap sizing has been with the paper industry for a long time and enormous amounts of research work has been done on it, there are still many aspects about this sizing process which are under debate. However, the following general consensus (3,5) about the necessary surface chemical conditions for effective sizing has been reached:

- (1) The formation of size precipitates that have a low free-surface energy and thus high hydrophobicity;
- (2) The sufficient retention of the size precipitates on fibers;
- (3) The uniform distribution and proper orientation of size precipitates on the fiber surfaces; and
- (4) The size molecules must eventually be well anchored to the fiber surfaces to form a stable, low-energy film, which stay fixed even when fluids are put in contact with it.

These proposed basic requirements have served as the guidelines in the investigation of sizing mechanism and the understanding of sizing phenomena. Great progress has been made ever since. However, people do not have equally good understanding upon all the four important factors and misinterpretations among the four factors occurred from time to time.

Cobb and Lope (7) measured the contact angles of water on dry lumps of different sizing materials and found that the contact angle of water on aluminum resinate is  $100^{\circ}$ , while that on calcium resinate and sodium resinate are only  $70^{\circ}$  and  $60^{\circ}$ , respectively. This discovery was believed to be the reasons why  $\text{Al}^{3+}$  can induce sizing but  $\text{Ca}^{2+}$  can not (would actually hurt sizing) and why rosin soap sizing is only effective at acidic pH, since at alkaline pH rosin size exists as sodium resinate which is not hydrophobic. However, Davison (3) pointed out that while the contact

angles measured may be true, the interpretations of the contact angle data could be misleading, because an oriented monolayer of calcium resinate and sodium resinate should exhibit the same high hydrophobicity as would an oriented monolayer of aluminum resinate since they all have the same hydrophobic molecular portions. The difference may be due to their mobility when contacting with water. While the oriented calcium resinate and sodium resinate molecules may be easily displaced or overturned when contacting with water, this is not true in the case of aluminum resinate.

There is no doubt that effective sizing can not be achieved without the sufficient retention of rosin size. For example, Marton (8) reported that if the retention of fines is poor, sizing efficiency suffers, because fines in the paper furnish can capture a substantial portion of the applied size and alum due to their larger specific surface areas. However, good retention of the sizing agent alone can not guarantee effective sizing. Strazdins (9) reported that when alum is used as the mordant at pH of 3.6, no sizing is obtained even though the rosin retention is high. The reason was believed to be due to the absence of an adequate amount of alumina (poor retention of aluminum) in the sheet at the low pH, which is not convincing enough. If the retention of aluminum ion is the issue, sizing at pH below 3.6 should be achievable by simply increasing the alum dosage, which is not true. In other work, Strazdins (10) reported that even without the addition of alum or any other

retention aid, gum rosin can have fairly high retention on fibers under pH 4. Of course, no sizing can be achieved under this condition.

As for the mechanism of rosin size retention, there has been general agreement (11-13) that colloidal forces, especially electrostatic attraction, play a major role in the process. Rosin soap size consists almost entirely of anionic soap ions. These anionic soap ions react with aluminum cations when alum is added to the pulp stock to form cationic size precipitates, aluminum rosinate, which then adsorb on anionic fiber surfaces by opposite charge attraction.

The importance of uniform distribution and proper orientation of rosin size on fiber surfaces is also obvious. Without an uniform distribution, the coverage of hydrophilic fiber surfaces by size molecules is not efficient and effective sizing can not be achieved. If size molecules are not oriented on fiber surfaces in the way that all polar ends anchor to fibers and nonpolar ends extends outward, sufficient surface hydrophobicity can not be obtained.

The recognition of the importance of uniform distribution has also been widely applied to explain many sizing phenomena, and because the importance is so obvious, it is often overemphasized. Dispersion size or emulsion size is known to have higher sizing efficiency than soap size, and it was believed (14) that the reason is because the former can be distributed on fibers more evenly. The free

rosin (dispersion size) precipitates sinter at  $75-90^{\circ}\text{C}$ , which is lower than normal paper drying temperature so even size distribution can be achieved in the drying section, while the soap rosin precipitates sinter at a much higher temperature ( $100-120^{\circ}\text{C}$ ) so size distribution cannot be improved as much in the same process. Fortified rosins are claimed to owe their improved sizing efficiency to their smaller particle sizes. It is more likely that the better performance is related to the greater number of carboxyl groups in each rosin molecule which would allow stronger bonding onto fibers (9). It was shown (15) that sizing improves upon adding certain colloids to the pulp stock, and improvement in size distribution was again suggested as the major mechanism, while the possibility that the added colloids may affect the coordination reactions among rosin size, alum and fibers and hence the bonding strength among them was not recognized. Calcium and magnesium ions are well known to give detrimental effect on sizing (6, 9, 16). The low hydrophobicity and higher sintering points (and hence less even distribution) of calcium and magnesium resinate are claimed to be the reason. The fact that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  do not have high coordinating potential and hence can not bind rosin size on fiber surfaces strongly enough has again never been considered in the literature. It is well known that the purest pulps, such as rag or high alpha-cellulose pulps, are difficult to size, while unbleached pulps are much more easy to size (17). The predominant

interpretation about this phenomenon is that unbleached pulps contains certain natural colloids that are beneficial to sizing (18), even though it is also possible that the higher carboxylic group and lignin content in unbleached pulps may enhance sizing by facilitating the chemical bonding between size and fibers.

While the importance of high hydrophobicity, sufficient retention, even distribution and proper orientation of size molecules on fibers has been well recognized and these basic principles have been widely used to explain various sizing phenomena, the view on the anchoring mechanism is much less clear. What kind of bonding can be strong enough to resist the attack of fluids so that the size molecules can stay fixed on fiber surfaces even when contacting with fluids has never been spelled out in the literature. The possibility that sizing may be improved by enhancing the bonding strength between size molecules and fiber components, just as sizing can be improved by improving the hydrophobicity, retention, distribution and orientation, as will be demonstrated in this study, has not been realized. Frequently in the literature, sizing improvement due to the enhancement of this bonding was attributed to other factors as stated in the previous paragraphs. The misleading effect of the traditional classification that rosin size is a non-reactive sizing agent should at least share some of the responsibility for this unfortunate reality.

### 1.3 MORDANT OF SIZE AND CHEMISTRY OF ALUM

After being added into pulp stock, size must be retained and then anchored strongly on fibers so as to give sizing. But rosin itself can not have high retention on fibers since both rosin soap size and fibers are negatively charged. Rosin is also unable to strongly bind on fiber surfaces directly under conventional conditions. Therefore, mordant is needed to fulfill the functions. "Mordant" is a term which has been widely used in the textile industry to describe the chemical that fixed dyes to a fiber material, but the term has not yet been widely used in the paper industry.

Traditionally, alum has always been the mordant of choice for rosin sizing in the paper industry, because it is inexpensive, colorless and effective. Some other metal ions such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cu}^{2+}$  were reported (19,20) to be effective mordants in certain types of pulp, but they all have color problem. Recently, Lanthanide series elements were tested (21) as mordants of rosin soap sizing. Many of them showed some efficacy, but the sizing levels are generally not as high as when alum is used.

The chemistry of aluminum ion in regard to rosin sizing has been a topic of study for many decades. The major concerns in the area are the distribution of aluminum species and the charge characters and chemical reactivity of various aluminum species in an aqueous solution under

different conditions, especially those under which commercial rosin sizing processes are carried out.

The complexity of the aqueous chemistry of aluminum ion originates from its high charge density (high charge number and small ionic radius). While extensive research work (22-29) has been done to investigate the distribution of aluminum species in an aqueous solution, rarely, if any, different researchers could come to the same conclusion. However, the predominant view at present (29) is now that in the conventional sizing pH range from 4.0 to 5.0, three distinct regions exist. One region is at the lower values of the pH range where  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  are the only species. Another region is at the middle of the pH range where the polynuclear species such as  $\text{Al}_8(\text{OH})_{20}^{+4}$  or  $\text{Al}_8(\text{OH})_{10}(\text{SO}_4)_5^{+4}$  predominates. The third region is at the high values of the pH range where formation of colloidal aluminum hydroxide precipitate  $\text{Al}(\text{OH})_3$  dominates.

Arnson (30) studied the adsorption of aluminum by oxidized cellulosic fibers from dilute solutions of aluminum chloride and aluminum sulfate. He found that in the trivalent cation region, the adsorption is low. He and other researchers (31-34) also found a sharp increase in the adsorption of aluminum between pH 4 and 5, and noticed that this sharp increase coincides well with the formation of the polynuclear species  $\text{Al}_8(\text{OH})_{20}^{+4}$  or  $\text{Al}_8(\text{OH})_{10}(\text{SO}_4)_5^{+4}$ . However, he did not relate the formation of polynuclear species to the optimal sizing efficiency.

Strazdins (35,36) and others (37-39) noticed the coincidence between the predominance of polynuclear species and the optimal sizing efficiency and pointed out that the working species in the sizing process are the polymeric form of aluminum ions that forms when the trivalent aluminum ion is partially neutralized with a base. Strazdins (35) believed "the colloidal efficiency of alumina", the product of the formal charge and the alumina retention, may be a key parameter. He found that the colloidal efficiency reaches a peak in the pH range 4.3-4.7, which corresponds to the dominating region of polynuclear species and also to the maximal sizing with rosin. He (36) also tried to assess the cationic charge character of aluminum salts by titration with an anionic polyelectrolyte and found that the maximal cationic charge of alum occurs at approximately the same pH range. Obviously, he believed that the charge characteristics of the aluminum species is the most important factor, and sizing can be optimized by maximizing the cationic charges on the aluminum species. He noticed that the polynuclear species are the active species in the sizing process but concluded that the reason is because the polynuclear species are more highly cationic.

One of the major goals in studying the chemistry of aluminum ion in rosin sizing is to explain why aluminum ion is an effective mordant at pH 4.0 to 5.5 and why it is not effective in the lower or higher pH range. Understanding these is the key to the discovery of new mordant systems

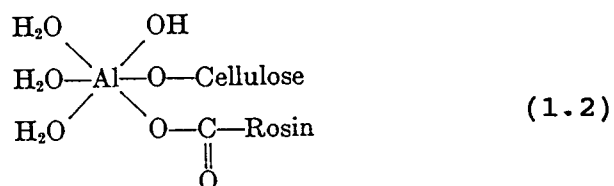
which could improve rosin sizing and/or allow rosin soap size to be applicable in a higher pH range. Sizing at a higher pH value is the trend of modern papermaking technology.

Strazdins (35) believed that the ineffectiveness of rosin-alum sizing at pH below 4.0 is because the predominant aluminum ion species at the pH range,  $\text{Al}^{3+}$ , does not form strong monomolecular films with rosin soap size and is also not retained on fibers in satisfactory amounts. He did not explain why strong monomolecular films can not be formed with  $\text{Al}^{3+}$ . He also believed that the ineffectiveness at pH > 5.5 is because the predominant aluminum ion species at the pH region,  $\text{Al}(\text{OH})_3$  (which is also positively charged within the pH range), does not have enough cationic charge to bind all the water soluble, anionic soap rosin so that some of the unbounded, polar soap acts as a contaminant of the hydrophobic film, converting the low-energy surface into a high-energy one. He was able to improve the sizing at pH above 5.5 by incorporating some polyamines with alum (40), but again he thought (35) the reason of the sizing improvement is because the polyamines he used are strongly cationic which can complement the insufficiency of the cationic charges on alum in the higher pH range.

Obviously, the role that coordination chemistry may play in the rosin-alum sizing process has not been fully recognized and the two distinct functions of the mordant: retaining and anchoring, have not been well differentiated

in the literature. There has been general agreement (3,9) that electrostatic interactions between the oppositely charged species play a major role in the retention of rosin soap size on fibers, even though the hydrophobic effect (the desire of hydrophobic molecules to escape from the aqueous medium) (2) could be another possible mechanism. However, no consensus has been reached on what interactions are acting to anchor rosin size on fibers so that rosin size can stay fixed and properly oriented even when water are brought in contact with it and paper can exhibit water repellency (sizing). Many (3,41,42) believed the same electrostatic forces act, others (43,44) believed hydrogen bonding and van der Waals forces may also be involved, even more researchers never bothered to differentiate the two processes, retention and anchoring, even though both are distinct processes.

Thomas (45) of Columbia University is the first one who postulated that aluminum might be effective in rosin sizing because the cation could coordinately bind both cellulose and anionic sizing agent, as shown below:



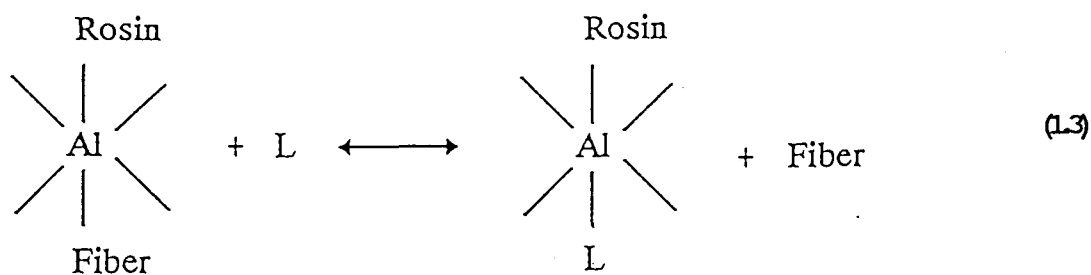
His hypothesis was then verified by Wilson's work on aluminum bonds (46,47), by Price and Cameron's work (48-50) on alum and the alum-rosin precipitate, and by Duston (51) and Porter and Lane's work (52) on the use of aluminum chloride.

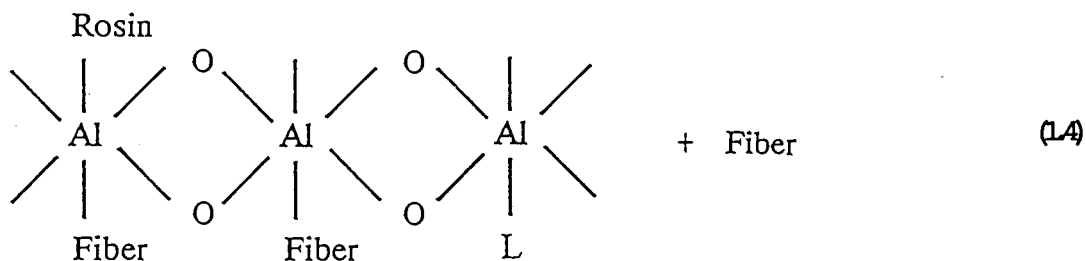
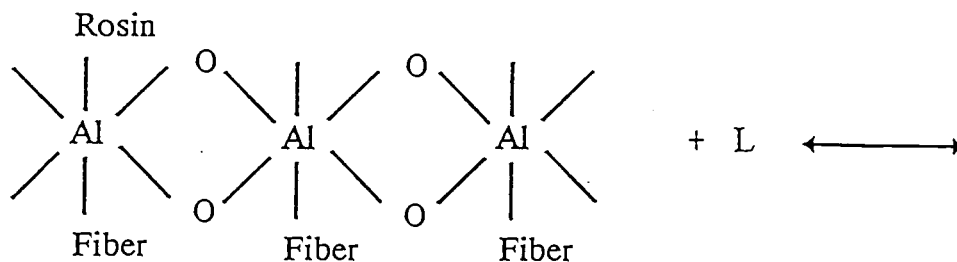
Thomas's coordination view has often been mentioned but has not been dominant in the literature, probably because the theory can not explain the fact that aluminum ion has always been the most effective mordant of rosin sizing even though many metal ions, such as transition metal ions have even higher coordinating capability. Aluminum ion's other unique property (it is unique in the sense that few other metal ions can do so) is its ability to form polynuclear species through the formation of hydroxo or oxo bridging (29,30,45), but the possible implication, or the importance of this unique property of aluminum ions, has never been considered, except for Strazdins' (35,36) recognition that the polynuclear species have higher cationic charges.

As mentioned in the previous paragraphs where research work on the distribution of aluminum species is reviewed, Strazdins (35, 36) and others (37-39) have noticed that the pH region where polynuclear species such as  $\text{Al}_8(\text{OH})_{20}^{+4}$  or  $\text{Al}_8(\text{OH})_{10}(\text{SO})_5^{+4}$  predominates coincides well with the pH region in which the optimal sizing efficiency occurs. They pointed out that the trivalent aluminum ion  $\text{Al}^{3+}$  can do nothing worth while in the sizing process. But they attributed the effectiveness of the polynuclear species to

their higher cationic charges and neglected the possibility that the polynuclear species could bind rosin size on fibers more strongly than  $\text{Al}^{3+}$  can if coordination reaction is the bonding mechanism.

It is well known (53) that chelating agents (polydentate compounds) such as citric acid and EDTA (ethylene diamine tetraacetic acid) can form much more stable complexes with various metal ions because they can form multiple dative bonds with the metal ions instead of the single dative bonds in the case of monodentate compounds. Similar bonding phenomenon could occur when polynuclear aluminum species replace  $\text{Al}^{3+}$  to bind rosin size on fibers through dative bonds, as shown below:





Fiber is used here in the formula instead of cellulose, as other researchers did, because the same bonding to other fiber components such as lignin and hemicellulose is also possible. When  $\text{Al}^{3+}$  is the dominant species, bonding between Al and fiber is only a single dative bond, as depicted in the left side of the equation (1.3). Fiber ligand could be easily displaced by an incoming ligand L such as  $\text{H}_2\text{O}$  or  $\text{OH}^-$ , resulting in the dissociation of aluminum rosinate from the fiber surfaces so no sizing can be observed. This could explain why sizing can not be achieved at  $\text{pH} < 4$  since in the pH region  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  are the dominant species. When polynuclear Al species are the dominant species, bonding between the Al species and fibers can be many dative bonds,

as depicted in the left side of the equation (1.4). The dissociation of aluminum rosinate from the fiber surfaces needs simultaneous substitution of fiber ligands by many incoming ligands, which is much less likely. So sizing can be observed. This could explain why sizing occurs at pH 4-4.5 and why few metal ions can be as effective as Al even though they may have even stronger coordinating potential, because Al is unique in forming polynuclear species.

One may argue that the dissociation of rosin molecules from fiber surfaces can also happen by the breakage of rosin-Al bond, which is the same when either  $\text{Al}^{3+}$  or polynuclear Al species are the dominant ones. But it is reasonable to believe that the bonding in rosin-Al is much stronger than that in Al-fiber since almost all rosin sizes currently used in the paper industry are fortified types, which contain multiple carboxylic groups in each rosin molecules. In other words, the bonding between rosin and Al will always be multiple bonds rather than a single bond.

Examining rosin-alum sizing process from the standpoint of coordination chemistry, as described above, builds the foundation for this thesis research work, as will be seen in the next chapters.

#### 1.4 NEUTRAL TO ALKALINE SIZING

Neutral to alkaline sizing refers to sizing over the pH range of 6.5-8.5, where calcium carbonate fillers can be used. As we know, the traditional rosin soap-alum sizing is only effective in an acidic pH range from 4 to 5.5. Papers from this acid system are less durable and tend to lose their strength rapidly when exposed to heat and light. This impermanence has been recognized as an alarming problem in archival papers.

Modern neutral to alkaline sizing (papermaking) began in the 1950s with the development of the AKD-based (alkyl ketene dimers) sizing agents by Weisgerber and others at Hercules (54). A few year later, a second sizing agent ASA (alkenyl succinic anhydrides) was developed by Wurzburg and Mazzarella (55) at National Starch and Chemical. Technology is now also available to extend the use of dispersion rosin to pH 6.5-7.5 by using polyaluminum chloride (PAC) as the mordant (56,57).

The mechanism of sizing development in AKD and ASA systems is quite different from that in rosin-alum system. Even though there are some doubts in the literature (58,59) about the formation of  $\beta$ -keto ester linkage in AKD, the predominant views are that covalent ester linkages are the bonding mechanism in AKD and ASA sizing. More recent research work and experimental evidences (60-63) also support the occurrence of  $\beta$ -keto ester linkage in AKD

sizing. The stronger bonding nature of the covalent bonds is probably the reason why AKD and ASA are more efficient than rosin on the same weight basis and why AKD and ASA sized papers are more resistant to certain fluids.

European manufacturers of wood-free printing and writing papers began shifting from the traditional rosin-alum acid sizing systems to alkaline sizing systems in the 1960s (64) and nowadays this shift is becoming a worldwide trend in the paper industry. The driving force behind this shift is the many advantages that neutral to alkaline papermaking systems have over the acid systems (65-67), as listed below:

1. Lower paper cost due to the substitution of less expensive calcium carbonate fillers for titanium dioxide and the substitution of fillers for fibers (higher filler content).
2. Improved paper strength due to papermaking at higher pH and the exclusion of multivalent metal ions (alum).
3. Improved paper stability on aging since cellulose degrades more slowly at higher pH.
4. Reduction in energy consumption since less refining is needed to achieve the same strength and GCC (ground calcium carbonate) drains faster than clay on paper machines so less amount of steam is needed for drying.

5. Increased productivity of paper machines because of the faster drainage.
6. Reduced corrosion to papermaking equipment since the corrosive oxidation reactions proceed much slower at higher pH than at lower pH.
7. Increased system closure.

In Europe, the calcium carbonates are both cheaper and less abrasive than the China clay (68). With less abrasion, a copper wire can last longer. All these economic benefits made the neutral to alkaline papermaking rapidly become the system of choice in Europe. For example, in 1991, 50-60% (69) of all the paper and paperboard made in Europe was from the neutral to alkaline processes.

But the incentives for the shifting were not as strong in North American. There were abundant supplies of cheap chemical pulps and paper-grade kaolin fillers were cheaper and less abrasive than the precipitated calcium carbonate (PCC) (70), so neutral to alkaline sizing systems did not become as popular as they did in Europe during the first twenty years. In late 1970s, when on-site manufactured precipitated calcium carbonate, which has high brightness and is cost-competitive with the high-brightness kaolins became available and another neutral to alkaline sizing agent ASA was developed, paper manufacturers in North America began to switch from the traditional acid condition to neutral to alkaline condition and the switching pace is now very rapid. In 1991, about 20% of all the paper and

paperboard made in North America was from neutral to alkaline processes, while this number is expected to grow fast throughout the 1990s.

The benefits of neutral to alkaline sizing do not come without costs, only that the problems are minor compared to the overwhelming advantages. The following is a list of the disadvantages (69,70) which have been reported in the literature:

1. Instability of the size emulsion

Acid rosin, AKD and ASA are not water soluble. They need to be emulsified with the addition of cationic polymers (e.g. cationic starch). The size emulsions all have limited shelf life (days in ASA, weeks to months in AKD, and up to 1 year in dispersion rosin) and usually prefer to be used shortly after make-up.

2. Size retention

Size retention is usually more difficult and critical in the neutral to alkaline sizing systems than it is in the rosin soap-alum sizing system. High retention requires careful implementation of retention aid technology.

3. Size hydrolysis

Hydrolysis of ASA and AKD sizes is also a problem, even though AKD does not hydrolyze as rapidly as ASA. Hydrolysis lowers the sizing efficiency since the hydrolysis products are not effective sizing components. Besides, it can cause wet press picking problems because of their tackiness. It has been reported that the effects of the size hydrolysis

can be minimized by applying suitable amount of aluminum ion (71). The underlying principles may be exactly like that in the rosin-alum sizing process because the hydrolysis products of ASA and AKD sizes are fatty acids like rosin acid.

#### 4. Low coefficient of friction

Alkaline sizing agents ASA and AKD are known to produce papers with a lower apparent coefficient of friction than rosin-based sizes. This slipperiness can cause problems in roll building and sheet tracking (66).

#### 5. Microbiological concerns

The traditional rosin-alum systems are generally free of microbiological contamination due to the operation in acidic pH range. Alkaline environments, on the other hand, tend to promote the growth of fungi and bacteria and result in the formation of biological slime. Proper use of fungicides or microbiocides is often essential to the alkaline systems.

It is obvious that all the disadvantages associated with the alkaline sizing systems except the microbiological concerns are due to the use of AKD and ASA sizes. If, however, neutral to alkaline sizing can be realized using the traditional rosin soap size, all the advantages that alkaline systems have could be achieved without facing the problems that are currently associated with the alkaline sizing systems. This is one of the major objectives of this thesis study.

### 1.5 THE MEASUREMENT OF SIZING

Sizing is a general term which refers to paper's resistance or repellency to various fluids in the end uses. Due to the wide varieties of the contacting fluids and the wide ranges of the sizing levels required in different paper grades, there is no universal "best" sizing test method. All we can do is to select a most suitable method that could most closely indicate the sizing property of paper in a specific situation.

In addition to the hydrophobicity and structural properties of paper, there are many experimental factors which can affect the sizing tests (18). The most important one must be the properties of the testing liquid. The surface tension, pH and chemical reactivity of the testing liquid will all have significant effects on the sizing testing results since all these properties will affect the physical and chemical interactions between the testing liquid and the sized paper. The second important factor is the temperature of the testing liquid, paper sample and the environment in which sizing test is conducted. Raising the temperature will decrease the surface tension and viscosity of the testing liquid which all have effects on the rate of liquid penetration according to Washburn equation. Raising the temperature could also facilitate the chemical reactions between the testing liquid and the sized paper. The moisture content in paper will also affect the absorption

and penetration of liquids. That is why careful conditioning of the test samples under standard conditions prior to testing is important. Another factor is the hydraulic head of the testing liquid. The higher the hydraulic head, the faster the rate of penetration will be.

There are several dozen sizing tests which are now available and this number is still increasing (73,74). Considering the wide varieties of fluids, sizing levels, sizing systems, and paper grades involved, it is no surprise that two different tests can often give contradictory results. Due to the large number of the testing methods and varied principles involved in the tests, there is also no classification system which can completely cover all the testing methods that have been devised to measure water repellency of paper.

One classification (74) is to divide the tests into fixed time period tests, such as Cobb Test, and variable time period tests, such as Ink Flotation Test and Hercules Size Test. Another common classification is to call the tests as either direct or indirect measurement (18). Direct methods involve the actual monitoring of the absorption of water on or the penetration of water into or through the paper. Indirect methods involve the monitoring of changes in paper properties (e.g., electrical conductivity) due to the entry of water into the paper structure. A third and the most common classification (1) is to divide the test methods into absorption tests, in which the amount of the

contacting liquid absorbed by the paper in a certain period of time is measured, penetration tests, in which the time it takes to achieve a given degree of penetration is measured, and surface tests, in which some surface properties of paper are measured. Cobb Test, Immersion Test and Wet-Break Test are examples of absorption tests. Hercules Size Test, Ink Flotation, Carson Curl Test and Dry Indicator Test are a few examples of penetration tests. Contact Angle Measurement, Drop Test and Ink Feathering (Pen and Ink) Test are among the category of surface tests.

Cobb Test (or Cobb Size Test) is still one of the most widely used tests in sizing measurement (1,73). In this test, a fixed volume of water is placed on paper for a certain period of time (45 s to 10 min.). The water is then decanted and free water on paper surface is blotted. After that, the amount of water absorbed by the paper is measured gravimetrically. The lower the Cobb size value, the better the sizing of paper. This method is very simple in concept and in equipment and offers great flexibility for varying the nature, temperature and exposure time of the testing liquid to suit different application requirements for papers. The tested area is fairly large, which can minimize the effect of the non-uniformity of paper samples, the results are readily duplicable, and the data obtained are valuable to papermakers. The disadvantages of this method is that it is not sensitive enough for hard-sized sheets. When hydrophobicity of the paper continues to rise at a high

level, further reduction in water pickup does not occur. This can lead to excessive use of sizing agent without realizing it in a paper mill.

Penetration tests can use either conductivity or reflectance to measure liquid penetration. The test procedures using the changes in electrical conductivity as the liquid penetrate through paper to determine the end point of the penetration includes Penetration Analyzer Tests, Valley Size, Currier and K.B.B. (1,73,74), etc. The disadvantage of these methods is their sensitivity to the pinholes and non-uniformity of paper samples. The test procedures using the changes in reflectance as the liquid penetrate through the sheets to determine the end point of the penetration include the Hercules Size Test (HST), the Photosize Liquid Penetration Tester, the Penetrace Liquid Penetration Tester, and the Pen-A-Size Tester (18). Among them, Hercules Size Test (HST) is probably the most commonly used one.

HST measures the time it takes for testing liquids (must be colored ink) to penetrate from the top to the bottom side of the paper or paperboard. A fixed volume of ink is applied to the top of the paper. The dye used in the ink must be non-substantive to paper. The change in reflectance during ink penetration is measured photoelectrically from the bottom of the paper. When the reflectance drops to a preset percentage (usually 80%) of the original value, the timer will stop automatically. The

higher the HST value, the better the sizing of paper. This method is quantitative, reproducible, and sensitive to changes in the level of sizing even for hard-sized papers. As in Cobb Size, the testing liquid can be changed (as long as it is colored) to suit different application requirements, so can the reflectance of the end point. Besides, reflectance versus time curves can be obtained to give more information about the sizing effect. However, comparison between different grades of paper and different sizing systems should be avoided, since dyes, colors, and interactions between testing liquids and sizing chemicals can affect the readings.

Among the surface tests, Contact Angle Measurement is very time-consuming and requires trained skills. Drop Test is not applicable to well-sized papers since the water drop may stay on paper surface for many hours. Ink Feathering (Pen and Ink) Test is subjective and is dependent on individual operation. It was important in old days when people used pens containing water-based inks, but is somewhat out of date in the time of ball point pens. These methods are not commonly used.

Cobb Size Test and Hercules Size Test were chosen in this study to measure sizing because of their advantages discussed above and their wide acceptance in the paper industry. Both methods are applied together in the sizing measurement for each sample so that more accurate judgement upon the degrees of sizing can be made.

## Chapter 2

### OBJECTIVE STATEMENT

The objectives of this study, as described by the title, are to understand the mechanism of rosin sizing process and to develop some new sizing technologies.

It is believed that mordants plays key roles in the sizing process. The goals of this study are to understand the chemistry and functions of the mordants, especially the traditional rosin sizing mordant, alum, and to develop some other mordants which can improve the efficiency of rosin soap sizing process or extend the effectiveness of the sizing process to neutral/alkaline pH range.

Even though rosin soap sizing has been applied in the paper industry for more than 180 years, there are still many mechanistic aspects which are unclear. For example, there is no general agreement on what forces anchor rosin on fibers to give the sizing, what are the roles of alum, why the effectiveness of rosin sizing is always pH dependent, why alum is very effective at pH 4 to 5.5, and why it is not effective at the lower or higher pH range, etc. This study was also aimed to clarify these important issues.

## Chapter 3

### A THERMODYNAMIC ANALYSIS OF ROSIN SIZING PROCESS

#### 3.1 INTRODUCTION

Perhaps one of the most remarkable characteristics of cellulosic fibers is that they contain many hydroxyl groups. The existence of these hydroxyl groups in fibers is essential to papermaking because otherwise fibers would not be dispersible in water and papermaking would be impossible. 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 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 sizing is to make the original hydrophilic fiber surfaces relatively hydrophobic so that a certain degree of water repellency can be achieved. One way to achieve the goal is to apply an amphipathic (polar/nonpolar) material such as rosin size to the fiber surfaces. Ideally, the hydrophilic part of the amphipathic material should bind to the fiber surfaces and its hydrophobic part should extend outwardly (3) to cover the fiber surfaces. When sufficient surface coverage is reached, the paper can have good water repellency.

Apparently to achieve effective sizing, the following requirements must be met (3,6,75):

1. The size precipitate must have high hydrophobicity.
2. The size must be well retained on the fibers.
3. The retained size must be uniformly distributed on fibers to cover the surfaces efficiently.
4. The size precipitate must be strongly bound to the fiber surfaces so that the bonds will not be broke down by fluids( most commonly, water).

The importance of high hydrophobicity, good retention and uniform distribution of size precipitate has been well demonstrated and generally recognized (6,9,18). Applying these basic principles to explain various sizing phenomena and to improve the sizing techniques has also been fruitful(6,8,18).

On the other hand, the importance of bonding strength between size precipitates and fiber surfaces has not been well recognized. Discussions on the relationships between this bonding strength and the effectiveness of sizing can hardly be found in the literature. While the ambiguous word "anchor" has been commonly used to describe the bonding, the types of bonding that may be strong enough to effect sizing, i.e., to keep the size precipitate staying fixed rather than being displaced or overturned when fluids are brought into contact with it, has never been clearly specified. The

strong-bond/weak-bond theory (44) also did not help much in this aspect.

The objective of this chapter is to show the importance of the bonding strength and to clarify the bonding types needed for effective sizing through a thermodynamic analysis of the sizing-desizing process. Since sizing means different things when regarding to different fluid medium and the energetics(interactions involved) is not the same in different sizing system, only rosin soap sizing against water will be discussed.

### 3.2 A THERMODYNAMIC ANALYSIS

Assume all the other requirements for effective sizing have been met and consider only the bonding strength between size molecules and fibers. When the bonding is strong enough, introduction of water molecules onto paper surfaces will not break down the bonding. The orientation of size molecules on fibers will not be disrupted and the surface properties of fibers will keep unchanged during the water penetration. The penetration of water through paper will be a static process during which the surface properties of fibers maintain unchanged and the rate of penetration will be governed by Washburn equation (2):

$$dh/dt = (\gamma R) \cos \theta / 4 \eta h$$

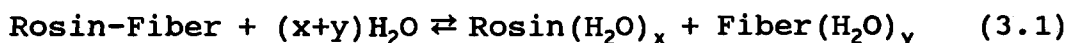
The contact angle  $\theta$  will be a constant here which may be  $90^0$  or greater in a well-sized paper surface. A significant amount of time is needed for water to penetrate through the paper and a high degree of sizing can be observed.

However, if the bonding between the size molecules and fibers is not strong enough, the introduction of water molecules onto paper surfaces will break down the bonds that "anchor" the size on fiber surfaces. The hydrophobic layer on the fiber surfaces formed by the hydrophobic part of the size molecules will be disrupted since the amphipathic size molecules will be dissociated from the fiber surfaces or overturned. The penetration of water through the paper will be a dynamic process during which the surface properties of fibers change gradually. The contact angle  $\theta$  in the Washburn equation will be decreasing and may approach zero quickly. Little sizing can be observed then.

The situation is somewhat more complicated when there are chemical reactions (such as ligand substitution or ester hydrolysis) occurring between the size precipitates and the fluid to which the paper is exposed. The kinetic stability of the system may be able to sufficiently retard the reactions and significant amount of time may be needed to effectively displace or overturn the amphipathic size molecules. A degree of sizing can be observed although the system may not possess thermodynamic stability.

Consider the simpler and the more general situation where water is the only component in the fluid and no

chemical reactions occur. What kind of bonding will be strong enough to resist the attack of water? A desizing process by water molecules can be depicted as following based on the statements made in the previous paragraphs:



The structure "Rosin-Fiber" implies that the rosin size is bound to the fiber by some bonding interactions (direct or indirect bonding via mordants) as in a sized paper sheet. The structures on the right side of the equation (3.1) imply that the bonding between the rosin molecule and the fiber has been broken down by water due to the favorable ion-dipole and/or dipole-dipole interactions between rosin and water molecules and the dipole-dipole (hydrogen bonding) interactions between the hydroxyl group on the fiber and water molecules. The coefficient  $x$  and  $y$  are the numbers of water molecules involved in the interactions and they must be greater than one. No sizing exists in the state depicted in the right side of the equation (3.1). If the change from the left side to the right side of equation (3.1) can proceed spontaneously, the paper is not effectively sized.

Thermodynamics (76) tells us that a process is spontaneous if its Gibbs free energy  $\Delta G$  is negative. Since no chemical reaction is involved, no kinetic stability can retard the desizing process. In other words, effective

sizing can be achieved only when the desizing process described in equation (3.1) meets

$$\Delta G_{\text{desizing}} > 0$$

Thermodynamics (76) also tells us that the greater the  $\Delta G_{\text{desizing}}$ , the smaller the tendency for the desizing process of equation (3.1) to proceed, so the higher the degree of sizing can be.

But 
$$\Delta G_{\text{desizing}} = \Delta H_{\text{desizing}} - T\Delta S_{\text{desizing}}$$

The enthalpy term ( $\Delta H$ ) corresponds to the net change in bonding energy during the desizing process. The entropy term ( $\Delta S$ ) corresponds to the change in randomness during the process.  $T$  is the absolute temperature ( $^{\circ}\text{K}$ ).  $\Delta S$  is always greater than zero for a dissociation process like the desizing process described in equation (3.1) since more species are produced and the system becomes more disordered. However, in most situations the enthalpy term is much larger and more important and the entropy term can be neglected.

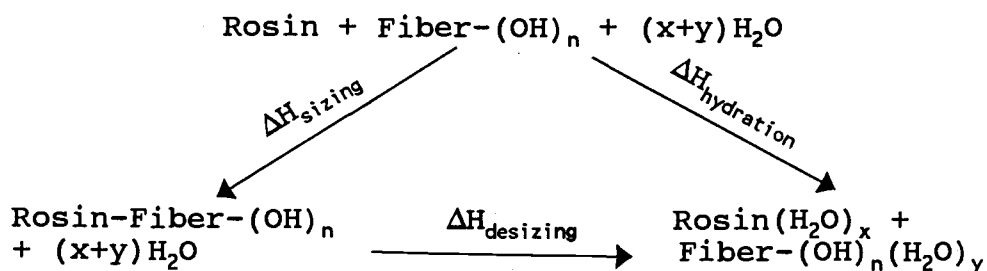
Since 
$$\Delta H_{\text{desizing}} = \Delta G_{\text{desizing}} + T\Delta S_{\text{desizing}}$$

In any case, to achieved effective sizing (to meet  $\Delta G_{\text{desizing}} > 0$ ), there must be

$$\Delta H_{\text{desizing}} > 0$$

and the greater the  $\Delta H_{\text{desizing}}$ , the greater the  $\Delta G_{\text{desizing}}$ , so the higher the degree of sizing of paper.

Considering the following Born-Habel type of cycle (53):



$\Delta H_{\text{sizing}}$  is the enthalpy of bonding interaction (either direct bonding or indirect bonding via a mordant) between one rosin molecule and the fiber, which measures the strength of the size-fiber bond.  $\Delta H_{\text{hydration}}$  equals the summation of the enthalpy of the ion-dipole or dipole-dipole interactions between one rosin molecule and  $x$  water molecules and the enthalpy of the dipole-dipole (hydrogen bonding) interactions between  $n$  hydroxyl groups (exposed from the fiber surface due to the removal of one rosin molecule) on the fiber and  $y$  water molecules, i.e.,

$$\Delta H_{\text{hydration}} = x\Delta H_{\text{ion-dipole}} + ny\Delta H_{\text{dipole-dipole}}$$

According to Hess's law:

$$\Delta H_{\text{hydration}} = \Delta H_{\text{sizing}} + \Delta H_{\text{desizing}}$$

Thus,

$$\begin{aligned} \Delta H_{\text{desizing}} &= \Delta H_{\text{hydration}} - \Delta H_{\text{sizing}} \\ &= x\Delta H_{\text{ion-dipole}} + ny\Delta H_{\text{dipole-dipole}} - \Delta H_{\text{sizing}} \end{aligned} \quad (3.2)$$

All the enthalpy terms in equation (3.2) are negative since all the interactions are exothermic. To ensure  $\Delta H_{\text{desizing}} > 0$ , there must be:

$$|\Delta H_{\text{sizing}}| > |x\Delta H_{\text{ion-dipole}}| + |ny\Delta H_{\text{dipole-dipole}}| \quad (3.3)$$

Since  $|\Delta H_{\text{sizing}}|$  is the measurement of bonding strength between size molecules and fibers, inequality (3.3) means that to achieve effective sizing, the bonding energy between the size molecule and the fiber should be higher than the summation of  $x$  ion-dipole interactions between the rosin soap molecule and water molecules, and  $ny$  dipole-dipole interactions between the hydroxyl groups on the fiber surface and water molecules ( $x$ ,  $y$  and  $n > 1$ , respectively). Otherwise, the desizing process described by equation (3.1) will be a spontaneous process and the paper will not possess effective sizing against water. The importance of the size-fiber bonding strength in determining the effectiveness of sizing is apparent.

The enthalpy of the ion-dipole interaction is proportional to the charge of the ion and the dipole moment of the water molecule and is inversely proportional to the square of the distance between the two species. The enthalpy of dipole-dipole interaction is proportional to the dipole moments of both water molecule and the hydroxyl group on fibers and is inversely proportional to the third-order of the distance between the two species. Since water is a very small molecule with a very large dipole moment (very polar), both the ion-dipole interactions and the dipole-dipole interactions existed in the right side of equation (3.1) is quite strong. To achieve effective sizing, a more stronger bonding interaction between size molecules and fiber is essential.

For a qualitative assessment, the following strength order (53) of various chemical interactions can be helpful:

Covalent bond and ionic bond > ion-dipole > dipole-dipole and hydrogen bonding > ion-induced dipole > dipole-induced dipole > London dispersion energy

The London dispersion energy can be quite high between very large molecules, but this is not the case in rosin soap sizing. Ionic bonds, very strong as they are, usually cannot resist the attack of water molecules since the hydration energy (enthalpy of the ion-dipole interactions) of the ionic species is enormous. It is due to this large

hydration energy that most ionic compounds are soluble in water.

In any case, it is obvious that rosin soap size must be bound to the fibers through primary chemical forces such as covalent bonds to effect sizing. All secondary chemical forces, such as van der Waals forces or hydrogen bonding, are thermodynamically not strong enough to resist the attack of polar water molecules so are unable to contribute to effective sizing against water.

At this point it seems necessary to point out that the metal-ligand bond existed in a coordination complex is a special type of the covalent bond (called dative bonds or coordinate covalent bonds). A dative bond may only be one third to one half as strong as a typical covalent bond in organic compounds (77), but is stronger than ion-dipole or dipole-dipole interactions so could be strong enough to effect sizing.

Equation (3.2) also shows that the greater the  $|\Delta H_{\text{sizing}}|$ , the greater the  $\Delta H_{\text{desizing}}$ , so the higher the degree of sizing can be according to the thermodynamic principles. This is to say that the stronger the bonding between size molecules and fibers is, the higher the degree of sizing of paper can be since  $|\Delta H_{\text{sizing}}|$  is the measurement of the strength of the bonding.

### 3.3 DISCUSSIONS

The bonding pattern between rosin, alum and fibers in rosin soap sizing with alum has been a dispute throughout its application history since 1807. The results of the thermodynamic analysis of the sizing-desizing process strongly support the hypothesis that coordination reactions among rosin, alum and fibers are involved in the mechanism of sizing development, since only dative bond or other types of primary chemical forces can be strong enough to fix the size on fibers and resist the attack of water molecules. The electrostatic force between positive alumina species and negative rosinate anions or fibers can be a very important interaction in the mechanism of size retention, but is less likely a bonding pattern that would contribute to sizing development. Other weak interactions such as hydrogen bonding or van der Waals forces, which have been considered as possible bonding patterns to effect sizing (44), are not strong enough to resist the attack of water molecules. The fact that spraying rosin soap solution on paper and then drying it at room temperature cannot result in sizing is the evidence. In addition, it seems necessary to emphasize that size retention and sizing development are two different processes. The interactions that are important in the mechanism of size retention should be well distinguished from the interactions that are important in the mechanism of sizing development.

Although it is derived from the energetic analysis upon rosin soap sizing system, the conclusion that the bonding strength between size molecules and fibers is a very important factor in the sizing development should be applicable to other sizing systems. The stronger the bonding is, the higher the degree of sizing of paper can be.

Just as the principles about the hydrophobicity, retention and distribution of size molecules can be used to explain many sizing phenomena, the principles about the bonding strength between size molecules and fibers can have the same applications. Fortified rosin size has been known to have superior performance over conventional rosin size. The reason has been thought to be due to its smaller particle size and better size distribution (9). However, the stronger bonding between fortified rosin sizes and fibers is certainly another factor, because the multi-functional groups in it can offer multiple bonding sites. Calcium can retain rosin soap size but cannot induce sizing (21). The poor distribution (14) and low hydrophobicity (4) of calcium rosinate may be the reasons. But the fact that the van der Waals forces which bind the calcium rosinate on fibers are not strong enough to resist the attack of water molecules is also a probable reason. Rosin soap sizing with alum cannot achieve hard sizing on paper but synthetic sizes like AKD can (18). The reason could be that the dative bond which binds the size molecules to fibers in the former is much weaker than the ester linkage that functions equally in

the latter. Many polymers such as protein (18) have been known to be able to improve rosin sizing and no explanation has been given. It seems reasonable to believe now that the reason could be because those polymers can enhance the bonding strength between rosin sizes and fibers. Polymers such as protein contain ligating atoms like nitrogen in their molecular chain which have lone pair of electrons to donate. Therefore, they can join the coordination reactions among rosin, metal ion mordant and fibers so as to strengthen the bonding by increasing the number of bonds.

Just as sizing can be improved by improving the hydrophobicity, retention and distribution of size precipitates, sizing can also be improved by increasing the bonding strength between size molecules and fibers. There are two ways to increase the bonding strength. One is to increase the strength of each bond, and the other is to increase the number of bonds. The former approach will serve as the principle in chapter 4, and the latter approach will serve as the principle in chapter 5.

### 3.4 CONCLUSIONS

Thermodynamic analysis upon a sizing-desizing process shows that the bonding strength between size molecules and fibers is a very important factor in determining the effectiveness of a sizing process. It is as important as the hydrophobicity, retention and distribution of the size

precipitates. Just as the high hydrophobicity, good retention and uniform distribution are always desirable for effective sizing, the stronger the bonding is, the higher the degree of sizing can be. This principle can be used to explain various sizing phenomena and to improve the sizing techniques.

The energetics analysis also shows that rosin soap sizes should be bound to fibers through primary chemical forces to effect sizing against water since the desizing interactions introduced by polar water molecules are moderately strong. Secondary chemical forces such as hydrogen bonding or van der Waals forces, are thermodynamically not strong enough to resist the attack of water molecules so are unable to contribute to effective sizing against water.

## Chapter 4

### ROSIN SOAP SIZING WITH FERRIC AND FERROUS IONS AS MORDANTS

#### 4.1 INTRODUCTION

Papermaker's alum, aluminum sulfate, has been used predominantly as the mordant for rosin size since this sizing technique was developed by Mortiz Illig in 1807. The mechanism of rosin sizing with alum has been a fascinating subject to many researchers. Despite the fact that extensive studies have been made, there is still no universal agreement on the sizing mechanism.

For a variety of reasons, papermaking technology is rapidly shifting from acid to neutral and alkaline conditions. Since rosin soap size was unable to give good sizing under neutral and alkaline conditions, the paper industry went to alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD), the so-called synthetic sizing agents and dispersed rosin size, which are all more expensive and more complicated to use than rosin soap size.

It is now realized that the ineffectiveness of rosin soap sizing with alum under neutral and alkaline conditions is a consequence of the chemistry of alum, not that of rosin. Rosin soap sizing under alkaline condition is possible as long as proper mordants are used (78). Obviously, the understanding of the chemistry involved in rosin soap sizing is crucial if we want to make rosin soap

sizing under neutral to alkaline papermaking conditions commercially applicable.

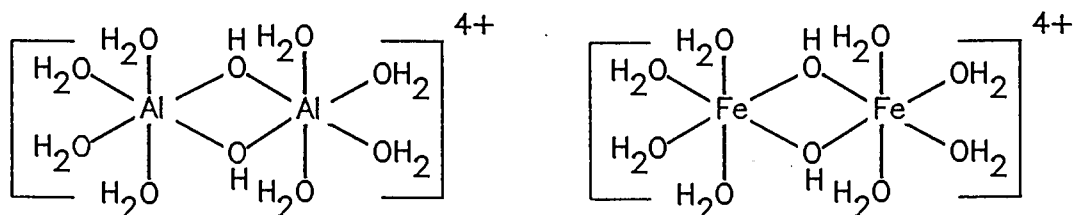
A recent study (21) from our laboratory has looked at the issue closely and the importance of coordination chemistry in the mechanism of rosin sizing development was demonstrated. A series of coordinating metal ions (mostly from lanthanide series) were investigated as mordants for rosin soap sizing and proved efficacious in various pH ranges. Nevertheless, none of them seemed to be as effective as alum.

If the coordination chemistry mechanism is true in rosin soap sizing, we would expect that metal ions with stronger coordination potential may be better mordants of rosin sizing. But why is alum the most effective mordant among all the coordinating metal ions? We know from coordination chemistry that  $Al^{3+}$  is far from the best metal ion as for its coordinating capability with various ligands. Due to the poor shielding of  $d$ -electrons to the nuclei and the existence of empty  $d$ -orbitals, transition metal ions show great potential to coordinate with species having a lone pair of electrons to donate. There should be some ions among the transition metals which might be able to induce better sizing result than a main group metal ion like  $Al^{3+}$  if the coordination mechanism is true.

Based on experiment results and an extensive discussion, two important criteria for an effective mordant of rosin soap size have been pointed out (21,78). First,

the species should be a Lewis acid with the capability of forming coordinate complexes by accepting lone pairs of electrons from rosin and fiber components. Second, the species should be able to form reasonably large complexes with rosin and fiber components. The formation of large complexes is important in that it can increase the stability and hydrophobicity of the three component (rosin, mordant, and fiber) complexes and may also improve the retention of the mordant and rosin size. Alum is able to form large complexes by the formation of hydroxo (Figure 4.1) and oxo bridges, but few other metal ions can do so. This may be the reason why alum is more effective than others.

If a metal ion has a better coordinating capability than  $\text{Al}^{3+}$  and is able to form large complexes in some way as well, we may expect it to be a better mordant for rosin soap sizing than alum. Ferric and ferrous ions may be good



**Figure 4.1** Formation of the hydroxo bridge with aluminum and ferric ions.

candidates from this point of view. They are both transition metal ions and have very good coordinating capability. In addition, the aqueous chemistry (80) of ferric ion is similar to that of  $\text{Al}^{3+}$  in that they are both trivalent cations and ferric ion is also able to form a binuclear species (Figure 4.1) by the formation of a hydroxo bridge, even at very low pH. When the pH is raised above 2-3, more highly condensed species than the dinuclear one can be formed. Ferrous ion is known to be able to form  $\pi$ -complexes with benzenoid aromatics (81) so we may expect it to complex with lignin in pulp and be a good mordant of rosin soap size.

Ferric ion has been studied by Strazdins (19) and Duston (20) to a limited extent and was shown to be a good mordant of rosin sizing in corrugated and newsprint grades. But no results were reported in bleached pulps. No research on using ferrous ion as mordant of rosin sizing was reported in literature either.

## 4.2 RESULTS AND DISCUSSION

### 4.2.1 Sizing in Unbleached Pulp

Ferric chloride was first used as the mordant in rosin soap sizing of unbleached Douglas-fir kraft pulp. All of our results were obtained from standard laboratory handsheets using 0.5% rosin solids (dry pulp basis). As

shown in **Table 4.1**, ferric ion induces better sizing at pH around 3.5 than alum does at its optimal conditions which are pH 4.5 to 5.0 and 1.0% to 2.0% alum dosage. (Remember that higher HST values and lower Cobb size values indicate better sizing, since it takes longer time for ink to penetrate from one side of the paper to the other side and the paper surface will absorb less amount of water within a certain period of the time if the paper is better sized.) Noteworthy is the fact that the HST (Hercules Size Test) values with 1% formic acid (FA) ink are much higher (about 10 times) when ferric chloride is the mordant than that in the case of alum. The HST values with neutral ink are so high that only a few samples were measured.

It is generally thought that divalent cations may not work as well as trivalent cations since the amount of positive charge on metal ions is critical to their retention and the retention of rosin size. In addition, the smaller charge on the divalent metal ion will not be able to draw the ligands as closely as trivalent cations can (53) so the bonding between the metal ion and ligands may be weaker. Surprisingly, the divalent ferrous ion can also induce excellent sizing when used in the same unbleached softwood pulp at pH around 5.5, as shown in **Table 4.1**. Like ferric ion, the HST values of 1% formic acid ink is much higher than in the case of alum, and the HST values of neutral ink are so high that only a few samples were measured as indicators.

**Table 4.1** Sizing results of unbleached Douglas-fir kraft pulp

Mordant	Amount <sup>a</sup> Added(%)	pH of Sizing	Cobb size (g/m <sup>2</sup> /2 min)	HST <sup>b</sup> (S) (Neutral)	HST (S) (1%FA <sup>c</sup> )	Bright- ness(%)
Alum	1.0	3.5	25.3	2400	269	16.8
	1.0	4.5	23.5	3040	325	16.8
	1.0	5.0	25.5	4042	227	16.7
	1.0	6.0	27.8	2200	236	----
	2.0	4.5	23.4	3288	328	----
FeCl <sub>3</sub> ·6H <sub>2</sub> O	1.5	3.5	22.2	7100	2840	14.3
	1.5	4.0	23.1	----	2000	14.6
	1.5	4.5	24.0	----	1940	14.1
	1.5	5.5	30.8	----	712	14.8
	1.5	7.0	36.6	2020	123	15.2
	0.5	4.0	23.9	----	764	15.4
	2.0	4.0	22.7	----	3520	14.2
	3.0	4.0	23.8	----	3060	13.8
	2.0	3.0	22.7	8600	3860	14.5
	2.0	3.5	23.0	8400	3900	14.1
FeCl <sub>2</sub> ·4H <sub>2</sub> O	1.8	4.5	23.8	8200	2950	14.5
	1.8	5.5	23.0	----	3050	14.3
	1.8	6.5	26.5	----	630	14.8
	1.8	7.0	Soaked	----	25	14.9
	1.0	5.5	24.9	----	2630	----
	2.5	5.5	23.0	>12,000 <sup>d</sup>	4500	14.1
	3.0	5.5	23.5	----	3480	14.0
	4.5	5.5	23.5	----	2380	13.9
	2.5	3.0	22.9	----	2700	----
	2.5	3.5	23.0	----	2900	----
	2.5	5.0	23.4	>12,000	4600	14.1

<sup>a</sup>Based on oven-dry pulp.<sup>b</sup>Hercules size test.<sup>c</sup>Formic acid ink.<sup>d</sup>Test terminated at this point.

The effects of pH and the amount of ferric and ferrous ion mordants on rosin sizing results were investigated with the same unbleached pulp with rosin soap size kept at 0.5% on pulp. The results are shown in **Table 4.1** and **Figure 4.2** to **Figure 4.5**. Ferric ion induces optimal sizing at pH around 3 to 4, while sizing results decrease steadily when the pH is increased above that. Ferrous ion induces optimal sizing at pH around 5.5. The sizing efficiency decreases slowly at lower or higher pH but is quite high in the wide pH range of 3 to 6. Like alum, both ferric and ferrous ions work best at an optimal level of addition. Under the experiment conditions, ferric ion induces its optimal sizing at 2.0% dosage (on oven-dry pulp) as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and ferrous ion induces its optimal sizing at 2.5% dosage (on oven-dry pulp) as  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ .

It is well known that aluminum sulfate can induce higher sizing than aluminum chloride since the anions also play some roles. For this reason ferrous sulfate has also been used as the mordant to compare its performance with ferrous chloride. The results are shown in **Figure 4.6** and **Figure 4.7**. Obviously, the sulfate is also very effective, and it seems that the optimal sizing pHs and the optimal ferrous ion dosages are the same for both the sulfate and the chloride. However, no conclusion can be drawn as whether the sulfate or the chloride is superior to the other since their difference is not notable in the experimental ranges when their molar amounts are the same.

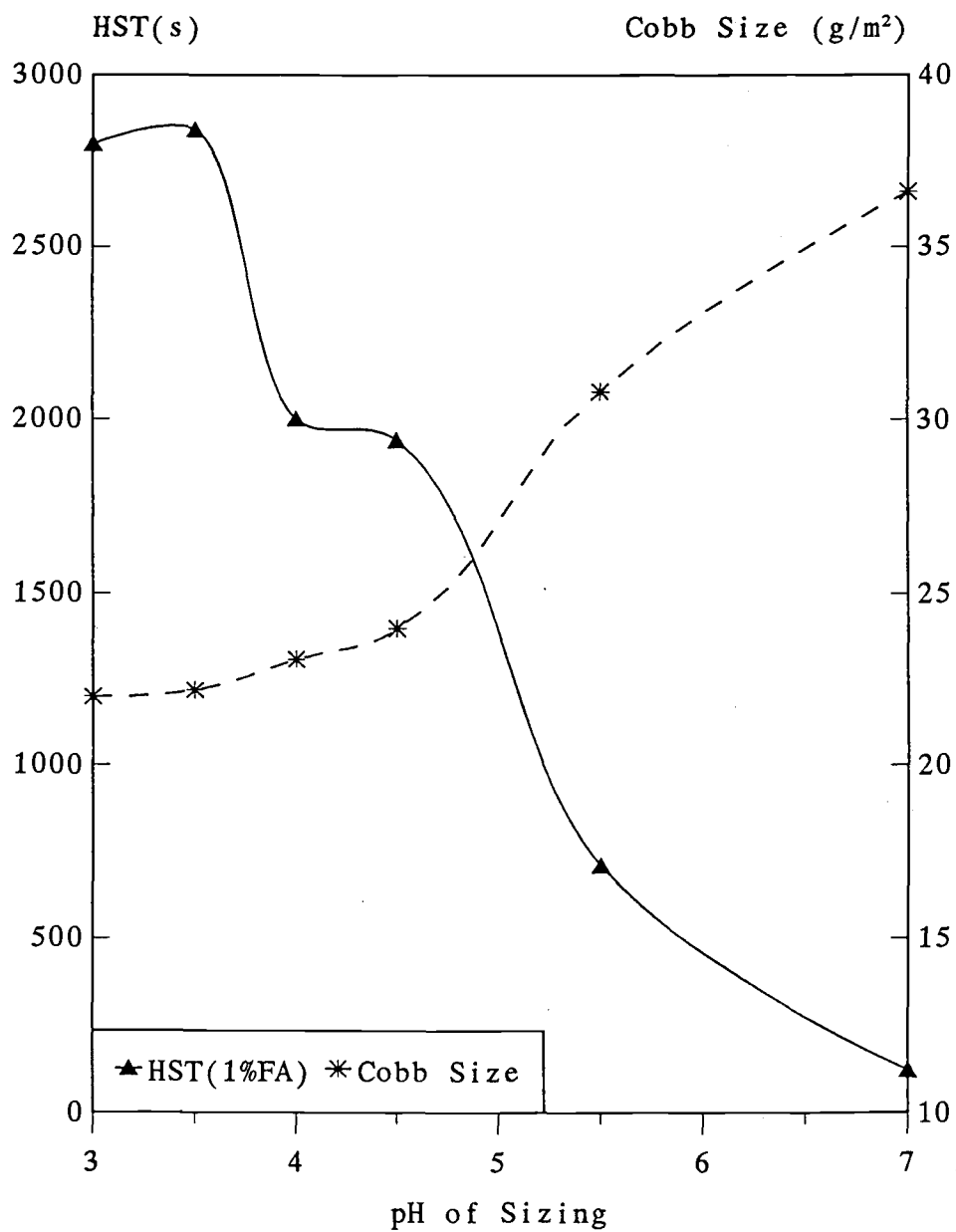


Figure 4.2 Effect of pH on rosin-Fe<sup>3+</sup> sizing. Fe<sup>3+</sup> 1.5%.

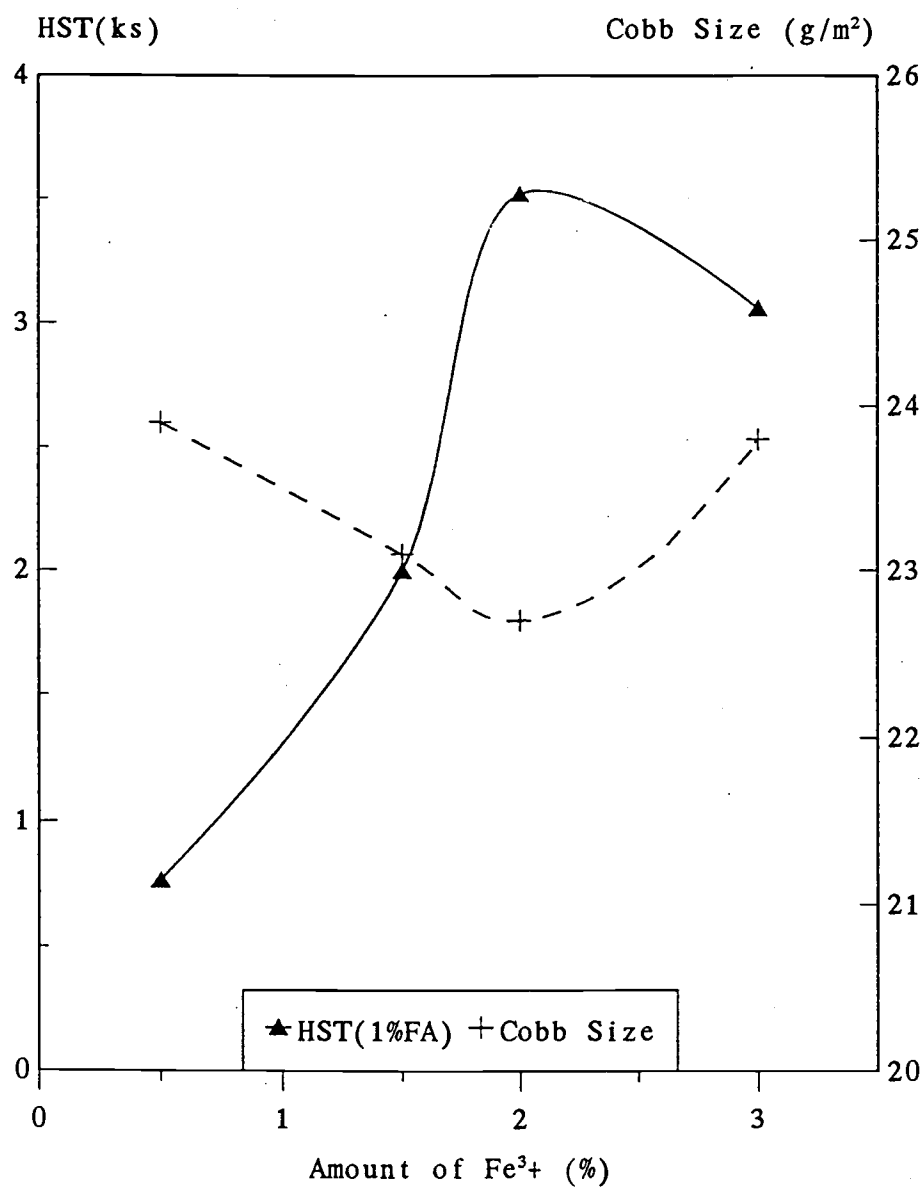


Figure 4.3 Effect of Fe<sup>3+</sup> dosage on rosin-Fe<sup>3+</sup> sizing. pH 4.0.

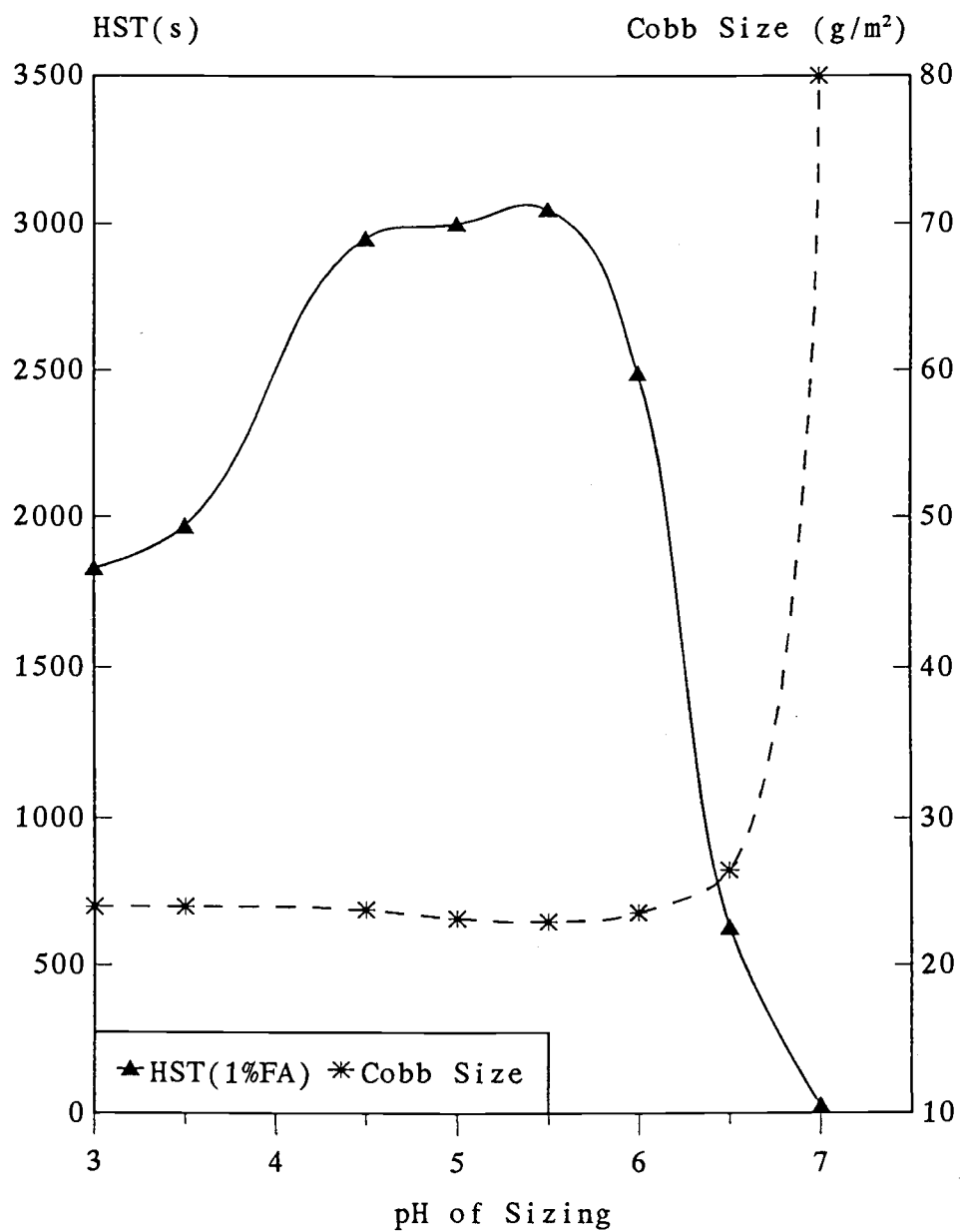
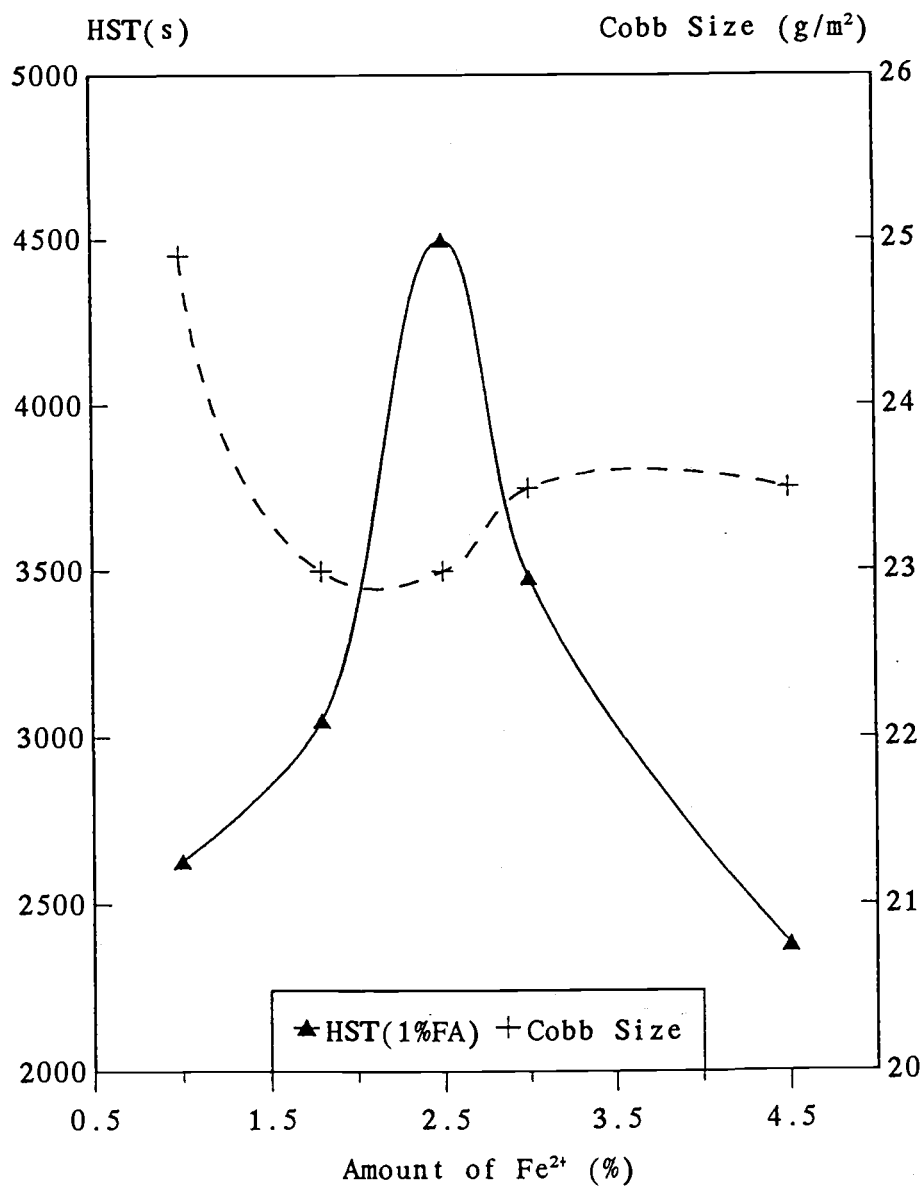
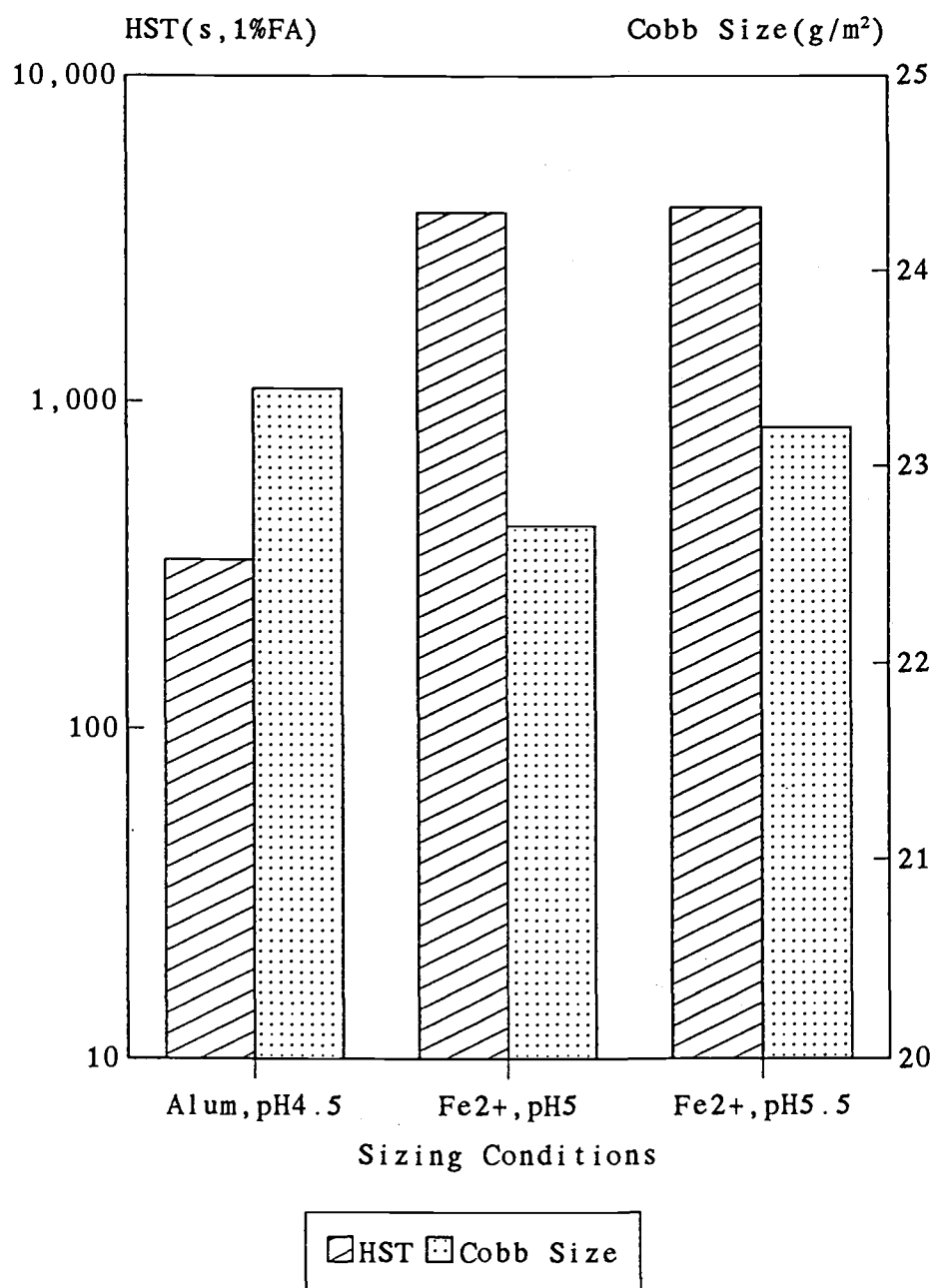


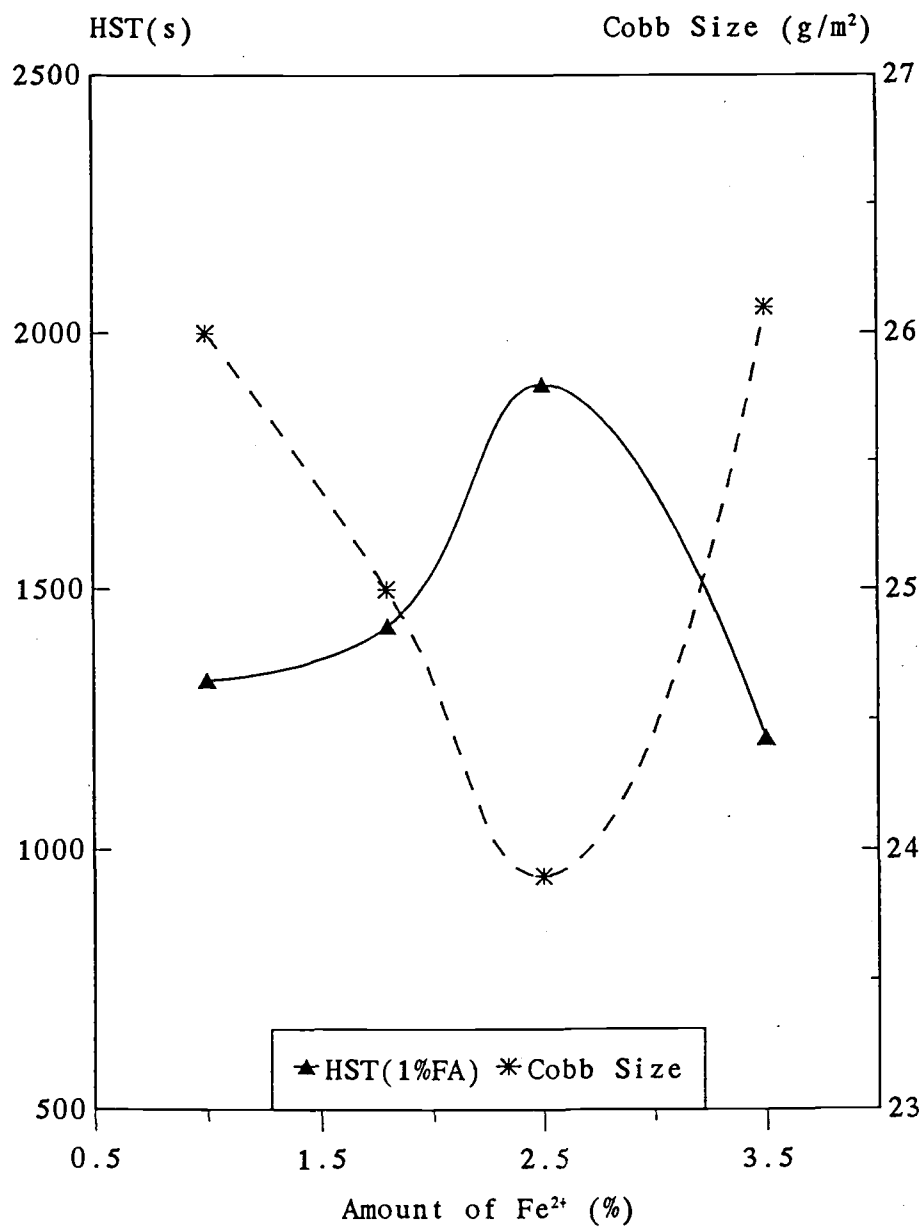
Figure 4.4 Effect of pH on rosin-Fe<sup>2+</sup> sizing. Fe<sup>2+</sup> 1.8%.



**Figure 4.5** Effect of  $\text{Fe}^{2+}$  dosage on rosin- $\text{Fe}^{2+}$  sizing. pH 5.5.



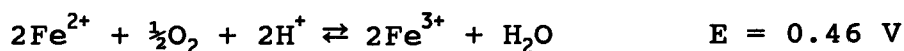
**Figure 4.6** Effectiveness of ferrous sulfate as the mordant. Alum 2.0% and Fe<sup>2+</sup> 2.5%.



**Figure 4.7** Sizing with ferrous sulfate as the mordant. pH 6.0.

The brightness of the handsheets has also been measured, as indicated in **Table 4.1**, too. It is usually lowered by about 2.5 points either when ferric or ferrous ion is used as the mordant instead of alum. It is interesting to notice that the handsheet brightness is not lowered as much in all the conditions where good sizing is not achieved.

One might speculate that ferrous ion can work well as a mordant of rosin size simply because it can be easily oxidized into ferric ion. The potential of the  $\text{Fe}^{3+}\text{-Fe}^{2+}$  electrode is 0.771V, which means that molecular oxygen in water solution can convert ferrous into ferric ion in aqueous solution (80):



Even though this is a thermodynamically favorable reaction, one kinetics study (82) showed that the oxidation rate is extremely low and practically negligible (half-life of many years) at pH below 5.5. **Table 4.1** also show the oxidation reaction should not be significant in the optimal sizing pH range of ferrous ion, since ferrous ion works well in a higher pH range and gives better sizing results than ferric ion does. Ferrous ion should, at most, induce as good sizing result as ferric ion in the same lower pH range (below 4.0, not around 5.5) if it has been oxidized into ferric ion before it can induce sizing. The  $\text{pK}_1$  of metal

ions is believed to be a good indication of the pH of their maximum sizing efficacy. The  $pK_1$  of ferrous ion is 6.74 and that of ferric ion is 2.83, while their pH of maximal sizing efficacy is 5.5 and 3, respectively. This fact is also consistent with the conclusion that ferrous ion is a discrete mordant. The kinetics study (82) also showed that the oxidation rate becomes very rapid when the pH is increased toward neutral or higher values (half-life less than one hour) and this can be the reason why ferrous ion loses its effectiveness rapidly at pH above 6 even though its  $pK_1$  is 6.74.

#### 4.2.2 Sizing in Bleached Pulp

While ferric and ferrous ions are both very effective mordants of rosin soap sizing in unbleached pulp, when they are used as the mordants in bleached Douglas-fir kraft pulp and bleached hardwood chemical pulp, as shown in Table 4.2, they both induce practically no sizing at their optimal sizing conditions for the unbleached pulp. Nevertheless, alum still induces effective sizing.

It is well known (18) that unbleached pulps are easier to size than bleached pulps. The reason is generally attributed to the higher carboxylic acid content (83) and higher levels of "desirable" colloid content such as saccharinic acids or anionic hemicellulose in unbleached pulps (18). Even though this may partly explain the

**Table 4.2** Sizing results of bleached chemical pulps

Mordant	Amount <sup>a</sup> Added(%)	pH of Sizing	Cobb size (g/m/2min)	HST <sup>b</sup> (S) (Neutral)	HST (S) (1% FA <sup>c</sup> )
<u>Bleached Douglas-fir kraft pulp</u>					
Alum	1.0	4.5	25.2	88	47
	2.0	4.5	23.5	136	34
FeCl <sub>3</sub> ·6H <sub>2</sub> O	2.0	3.0	Soaked	1.7	1.4
	2.0	3.5	Soaked	0.6	0.7
	2.0	4.0	Soaked	0.5	0.5
FeCl <sub>2</sub> ·4H <sub>2</sub> O	2.5	5.0	Soaked	2.3	1.2
	2.5	5.5	Soaked	0.8	0.8
	3.5	5.5	Soaked	0.9	0.7
<u>Bleached hardwood Chemical Pulp</u>					
Alum	1.0	3.5	29.7	168	55
	1.0	4.5	24.5	650	209
	1.0	7.0	Soaked	13	4.6
FeCl <sub>3</sub> ·6H <sub>2</sub> O	2.0	3.5	Soaked	5.0	0.8
	2.0	4.0	Soaked	1.9	0.7
	2.0	4.5	Soaked	5.4	0.8
	2.0	5.0	Soaked	1.5	0.6
FeCl <sub>2</sub> ·4H <sub>2</sub> O	2.5	4.5	Soaked	1.8	0.6
	2.5	5.0	Soaked	1.3	0.5
	2.5	5.5	Soaked	2.0	0.6

<sup>a</sup>Based on oven-dry pulp.<sup>b</sup>Hercules size test.<sup>c</sup>Formic acid ink.

different behavior of the two pulps, it can not be the whole story here since alum is effective in both types of the pulp.

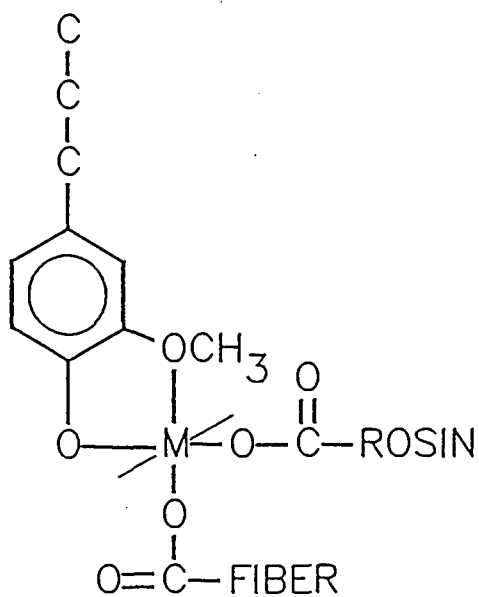
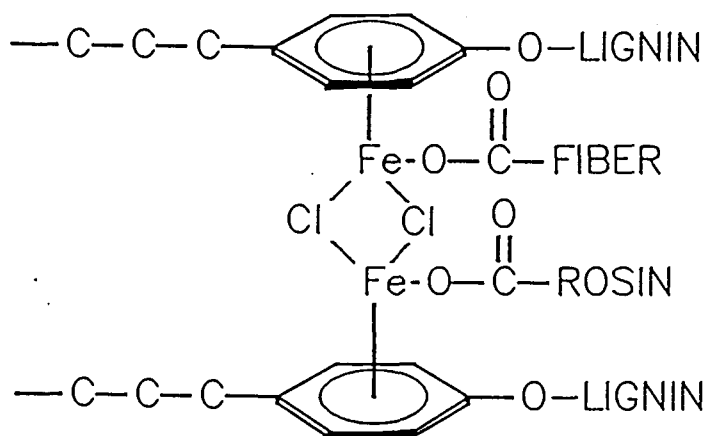
It is believed that ferric and ferrous ions are inducing sizing to paper by a mechanism different from that of alum. The formation of hydroxo bridges to produce large ferric ion polymers in aqueous solution, as shown in **Figure 4.1**, is not significant, if any, to induce sizing. At pH of 5 as much as 90% of the aluminum is in the form of polymers, and at high degrees of hydrolysis the main ion appears to be  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$  (80). But for ferric ion, the major polynuclear species is the dimer  $[Fe_2(OH)_2(H_2O)_8]^{4+}$  and the dimers are only important in relatively concentrated solution (84). That is, even the dimer may have a negligible concentration in dilute solutions as in the case of rosin sizing process.

It is documented (6) that to achieve good sizing, the size precipitate must have: (a) high retention on fibers; (b) uniform distribution and proper orientation on fiber surfaces; (c) high hydrophobicity; and (d) strong bonding to fibers. No sizing can be achieved if any of the above requirements is not met and sizing can be improved by improving one or more of the above factors. What difference can ferrous and ferric ions make between unbleached and bleached pulps? Will they give higher rosin retention in the unbleached pulp than in the bleached pulp? Will they result in more uniform distribution and more proper

orientation of the size precipitates on the unbleached pulp fibers, or will they produce more hydrophobic size precipitates in the unbleached pulp? All of these are very unlikely to happen, and if they do happen at all, the difference would only be on the sizing efficiency rather than on the sizing effectiveness.

It is believed that an effective mordant must be able to form large complexes in some way since the formation of large complexes can enhance the bonding strength between size precipitate and fibers via the mordant. The very different behaviors of iron ions in unbleached and bleached pulps leads us to believe that iron ions are able to form large complexes in some way in the unbleached pulp but are not able to do so in the bleached pulps. In other words, rosin size is able to strongly bind to lignin-rich unbleached fibers via iron ions but is not able to bind to bleached fibers strongly enough to give sizing in the same conditions.

The most obvious difference between the unbleached and bleached chemical pulps is their lignin contents and this could be the reason why iron ions have very different behaviors in the pulps. Based on the principles in coordination chemistry, one can postulate that transition metal ions can form complexes with lignin in the two bonding patterns shown in **Figure 4.8**, especially in the papermaking stages of pressing and drying. The brightness data in **Table 4.1** shows that the handsheets are darkened when ferric or



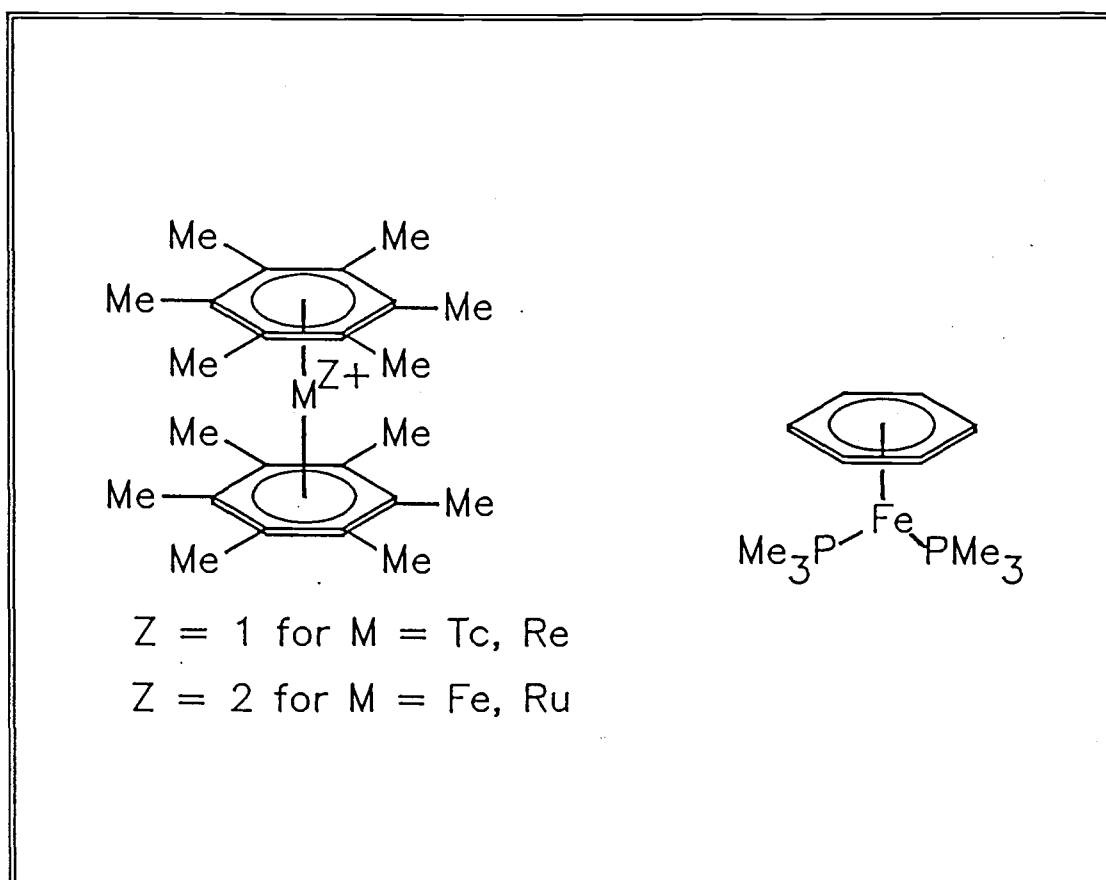
**Figure 4.8** Postulated  $\pi$ -complex and chelating ring formed between lignin and coordinating metal ions.

ferrous ion are used as mordants instead of alum, and it seems whenever good sizing is not achieved, the brightness is not lowered as much. This phenomenon may be a good indication that these two ions do complex with lignin when good sizing occurs. The fact that ferric iron can react with phenolic-like compounds of lignin and produce color reversion during pulp bleaching has been documented (85). Wood extractive tannin can also react with iron and produce blue-black color (86). But we can not expect tannin to exist in a significant amount in pulp after the kraft pulping process since it is very soluble in aqueous sodium hydroxide solution. Tannin, of course, is also a phenolic-like compound like lignin.

The formation of the chelate ring depicted in **Figure 4.8** (bottom) should be possible for all coordinating metal ions, including  $\text{Al}^{3+}$ . The one set of the lone electron pairs in each of the two oxygen atoms on the benzenoid lignin unit are donated to empty metal orbitals. The five-membered chelate rings should greatly enhanced the stability of the complexes. Since bleached chemical pulp has much lower lignin content than unbleached chemical pulp, it is believed that the lignin content also contributes much to the better sizability of unbleached pulp even in rosin sizing with alum.

The basic structure unit of lignin is the phenyl propane, a benzenoid aromatic. We know from organo-transition metal chemistry (81) that benzenoid aromatics can

form  $\pi$ -complex (as indicated in **Figure 4.9**) with virtually all transition metals. There are two kinds of bonding interactions involved in the formation of  $\pi$ -complexes. One is the overlap between empty metal  $d$ -orbitals and filled  $\pi$  orbital system of the benzene ring, in which the arene group usually acts as a six-electron donor, donating six electrons to empty metal  $d$ -orbitals. Bonding between the metal ion and the arene group through all six carbon atoms in the benzenoid ring of the arene group is called a  $\eta^6$  ligand.



**Figure 4.9** Representative  $\pi$ -complexes between arenes and transition metals.

Another interaction is the overlap between the filled metal d-orbitals and the empty benzene ring  $\pi^*$  antibonding orbital, which is usually called backbonding. This backbonding interaction will be enhanced by an electron-rich metal center so it is more common in metals of lower oxidation state. The bond dissociation energy (BDE) values for  $\text{CH}_3\text{-CH}_3$  and  $\text{CH}_3\text{-H}$  bonds are 88 kcal/mol and 104 kcal/mol, respectively. The BDE of metal-ligand bonds from two-electron donors ranges from 25 to 46 kcal/mol, which means the metal-ligand bonds are at most half as strong as the familiar bonds in organic chemistry. But a polyhapto ligands such as  $\eta^6$  arene can form bonds with metal ions which have significantly higher BDE values (81) than that formed by  $\eta^1$  ligands (bonding through one atom in the ligand) with the same metal ions. Iron ion is well known for being able to form  $\pi$ -complexes (Figure 4.9) with arene groups so it is postulated that they can form  $\pi$ -complexes with lignin as shown in Figure 4.8 (upper). The higher BDE of this kind of bonding and the excellent stability of five-membered chelate rings probably explain why the HST values with both neutral ink and 1% formic acid ink are extraordinarily high when iron ions are used as mordants in the sizing of unbleached softwood pulp.

#### 4.2.3 Sizing in Thermomechanical Pulp

It is known that mechanical pulp contains higher lignin content than unbleached pulp and is more difficult to size than chemical pulps. The causes of its poor sizing are not fully understood but are thought to be related to its much larger fiber surface area (so needs more sizing agent to form a hydrophobic layer) and the absence of "desirable" colloid content such as hemicellulosic material on the fiber surface (18). If our hypothesis about the importance of lignin in the sizing mechanism with iron ions is true, we would expect iron ions to be able to induce better sizing than alum in mechanical pulp.

Experimental results show that this is exactly the case. As shown in Table 4.3, ferric ion induces extraordinarily high level of sizing in the pH range from 3.5 to 5.0 when it is used as the mordant for rosin soap size in the thermomechanical pulp. So does ferrous ion at pH 5.5 when an appropriate amount (3.5% to 5.0%  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  on pulp) is added. The Cobb size values are as low as 21  $\text{g/m}^2/2$  min and the HST values with neutral ink are above 10,000 seconds, which is the sizing level alum could never achieve. Since alum is able to induce good sizing while iron ions are not at all effective in bleached chemical pulps, the hypothesis that lignin is involved in the coordination reactions with iron ions in the sizing process is strongly supported.

**Table 4.3** Sizing results of thermomechanical pulp

Mordant	Amount <sup>a</sup> Added(%)	pH of Sizing	Cobb size (g/m <sup>2</sup> /2 min)	HST <sup>b</sup> (S) (Neutral)	HST (S) (1%FA <sup>c</sup> )	Bright- ness(%)
Alum	1.0	4.5	32.1	420	71	52.9
	1.0	5.5	Soaked	31	11	52.8
	2.0	5.0	38.4	393	73	----
FeCl <sub>3</sub> ·6H <sub>2</sub> O	2.0	3.5	21.0	>12,000 <sup>d</sup>	319	35.4
	2.0	4.0	19.8	>15,000	1440	34.6
	2.0	4.5	21.9	>15,000	534	----
	2.0	5.0	24.3	>15,000	270	----
FeCl <sub>2</sub> ·4H <sub>2</sub> O	2.5	5.0	31.9	1400	43	36.2
	2.5	5.5	27.1	5500	125	34.6
	3.0	5.5	24.6	9380	137	----
	3.5	5.5	20.9	>14,000	275	35.2
	4.0	5.5	21.0	>12,000	200	----
	5.0	5.5	22.4	>12,000	165	----
	3.5	5.0	24.3	>12,000	208	----
	3.5	6.0	27.2	1800	38	----

<sup>a</sup>Based on oven-dry pulp<sup>b</sup>Hercules size test.<sup>c</sup>Formic acid ink.<sup>d</sup>Test terminated at this point.

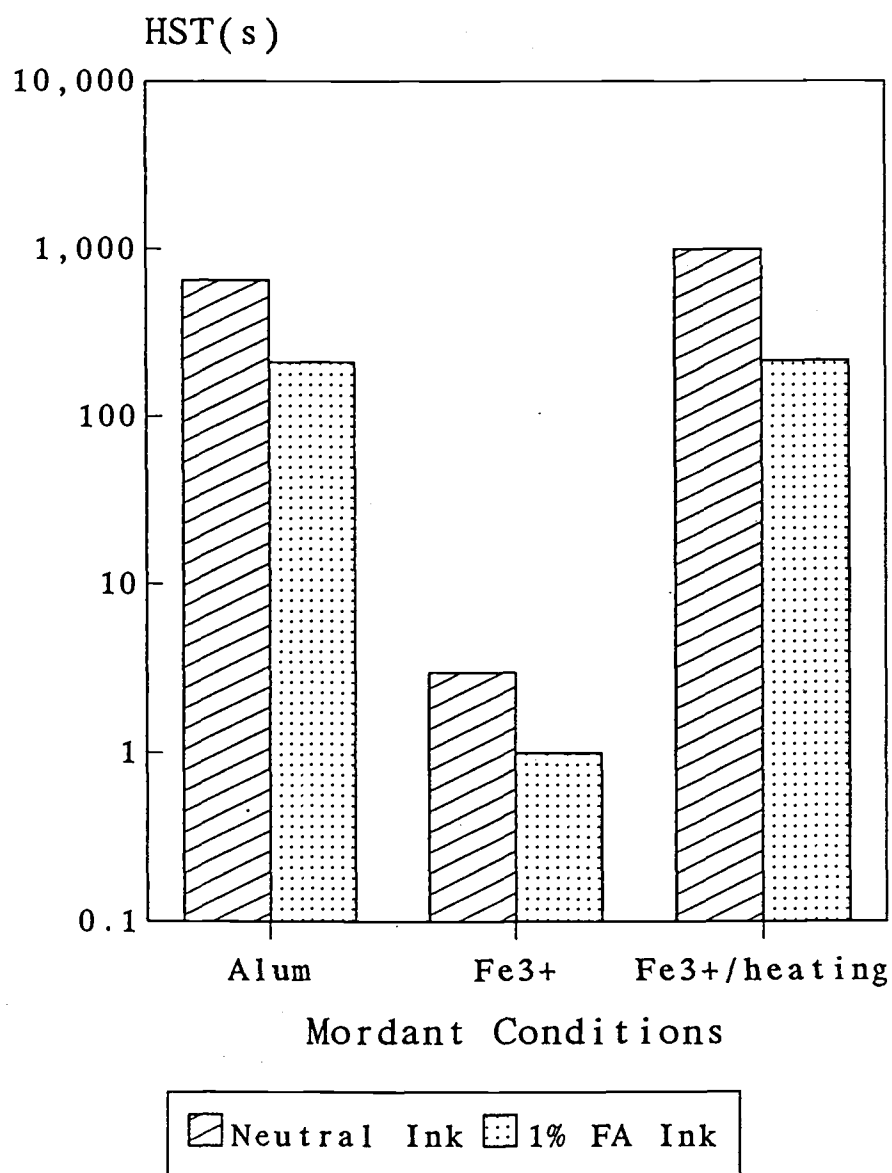
The success of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions in the lignin-rich pulps invoked the attempts to try  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  ions as the mordants in the same pulps since they are also transition metal ions which may possess the same reactivity with lignin as iron ions do but are colorless. Unfortunately, both  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$  shown little effectiveness in either unbleached pulp or thermomechanical pulp when applied in the pH ranges close to their  $\text{pK}_1$  values ( $\text{Zn}^{2+}$  in pH 6 to 8 and  $\text{Mn}^{2+}$  in pH 6.5 to 10). The detail results are omitted since the data is not important.

The handsheet brightness was also measured and the results are shown in Table 4.3, too. It is unfortunate that the brightness is significantly lowered, by as much as 17.5 points when iron ions are used instead of alum, which is not acceptable in most commercial usages of mechanical pulp, such as in the making of newsprint paper. Nevertheless, iron ions might be used as mordants for rosin soap sizing of paper or paperboard where color is not a concern, such as in non-deinked recycled fiber or unbleached pulp grades. Iron based mordants would be effective for dyes in papers such as dark colored construction papers. Ferrous ion with its applicability in a higher pH range than alum and ferric ion can show even more advantages. Achieving sizing at a higher pH and the use of divalent cations in place of alum during papermaking are both expected to lead to increased paper strength (87).

#### 4.2.4 Effect of Heating Treatment on Sizing

As stated in the previous paragraphs, rosin sizing with ferric and ferrous ions as the mordants is not effective in bleached pulps. However, if the same handsheets are put in an oven and treated at a high temperature for a certain period of time, effective sizing can be developed. An example of the heating treatment results is shown in **Figure 4.10**. High level of sizing was observed in the bleached hardwood handsheets sized with rosin- $\text{Fe}^{3+}$  at pH 4 after treating the handsheet at  $160^{\circ}\text{C}$  for 15 minutes, even though no sizing was observed in the same handsheets before the heating treatment and in the blank handsheets (no rosin and mordant added) treated under the same heating conditions.

A detail investigation into the mechanism of the sizing development under heating treatment is certainly an interesting work. Of course, the sizing development can not be attributed to the improvement in size retention since the retention stays the same before and after the heating. One reasonable hypothesis would be that the heating treatment has facilitated the reactions among rosin size, metal ion mordant and fiber components so that rosin size is now able to bind on fiber surfaces strongly enough to resist the attack of water molecules and give sizing. But argument can always be made that the heating treatment could have improved the hydrophobicity or the distribution and



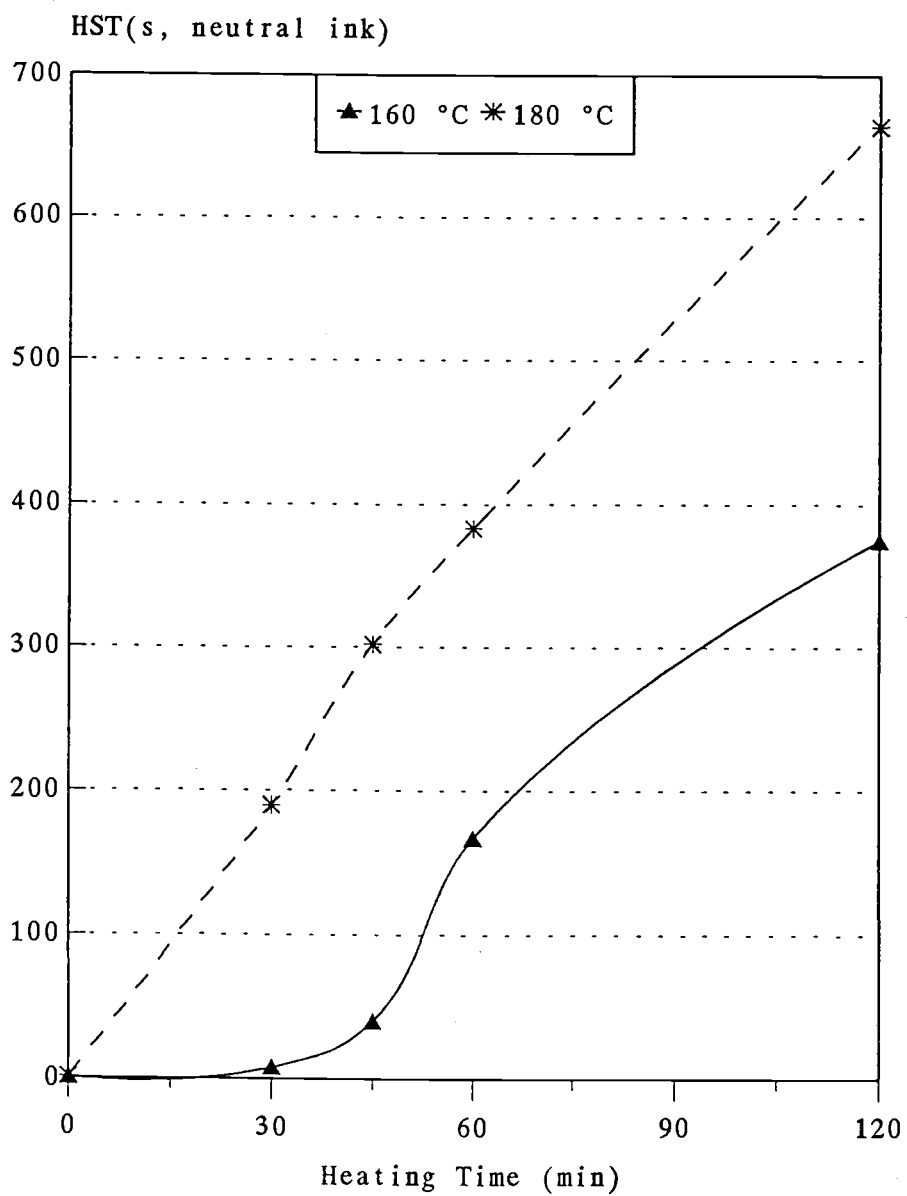
**Figure 4.10** Effect of heating treatment on sizing. Bleached hardwood chemical pulp, Alum 1.0%, pH4.5 and Fe<sup>3+</sup> 1.0%, pH 4.0. Heating condition: 160 °C for 15 min.

orientation of the size precipitates, as often occurred in the literature.

Even more amazing is that effective sizing can be developed in the blank handsheets (nothing is added) made of bleached hardwood chemical pulp if the handsheets are treated at the same ( $160^{\circ}\text{C}$ ) or more severe heating condition for a prolonged period of time, as showed in **Figure 4.11**. Similar sizing development can also be observed in the blank handsheets made of bleached softwood chemical pulp or unbleached softwood kraft pulp, but never in the thermomechanical pulp. Further research is needed to clarify the mechanism.

#### **4.2.5 The Mechanism of HST Test with Formic Acid Ink**

There is still no agreement on why formic acid can accelerate the penetration of ink into paper. Two different mechanisms (73) have been postulated. One attributed the function of formic acid to its lower surface tension. Another stated that the size-fiber bond strength may be an important factor in determining the HST values with formic acid ink. The objective of sizing is to convert the originally high free-energy fiber surfaces to low free-energy ones so that polar (high free-energy) liquid like water will form a large contact angle on the fiber surfaces. A test liquid of lower surface tension (free energy) will form a smaller contact angle on the sized paper so will be



**Figure 4.11** Sizing in blank bleached hardwood handsheet after severe heating treatment.

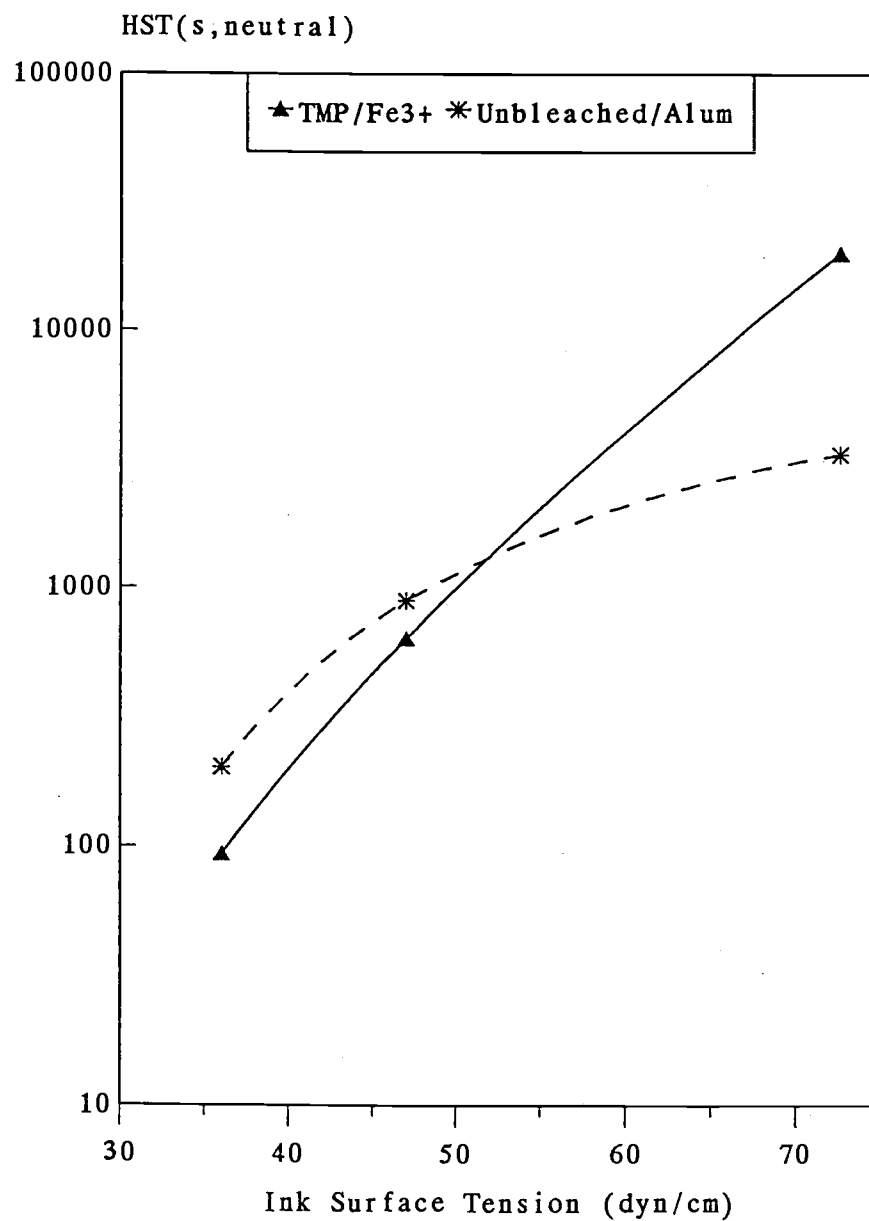
able to penetrate faster via the pores of the paper according to Washburn equation and gives a lower HST value.

Some experiments were carried out to test the theories. The surface tensions of a few ink liquids were measured and the results are shown in **Table 4.4**. It is true that the 1% formic acid ink solution does have a somewhat lower surface tension than the neutral ink. The effect of ink surface tensions on HST values is shown in **Figure 4.12**. 0.025M n-hexanol ink solution (surface tension 47 dyn/cm as reported in reference 88) and 0.05M n-hexanol ink solution (surface tension 36 dyn/cm as reported in reference 88) were used in the tests. Obviously, lowering the surface tension of the neutral ink by adding in the surfactant (n-hexanol) can

**Table 4.4** Surface tension of various aqueous ink solutions

Solution	Distilled water	1% Formic acid	Neutral ink	1% Formic acid ink
Surface tension (dyn/cm)	72.3	70.8	72.6	62.5
Solution	5% Formic acid ink	10%Formic acid ink	0.025M* n-hexanol	0.05M* n-hexanol
Surface tension (dyn/cm)	60.7	60.1	47	36

\* Surface tension data from reference 88.



**Figure 4.12** Effect of ink surface tension on HST measurement. The mechanical pulp was sized with 2.0% Fe<sup>3+</sup> at pH 4.5 and the unbleached pulp was sized with alum 2.5% at pH 4.5.

dramatically reduce the HST values in either rosin-alum/unbleached pulp or rosin- $\text{Fe}^{3+}$  mechanical pulp sizing system. These results support the hypothesis that lower surface tension is a reason that formic acid can accelerate the HST test.

However, the fact that formic acid accelerates the HST test to very different degrees in different sizing systems (e.g, rosin-alum sizing vs. rosin-ferrous ion sizing) and that 5% and 10% formic acid inks have much severe accelerating effects than the 1% formic acid ink (as will be shown in chapter 5) even through their surface tensions are very close shows that the surface tension change is not the only reason. It is believed that ligand substitution reactions are also involved in the HST test with 1% formic acid ink. Formic acid substitutes for carboxylic acids groups in rosin or fiber components (and perhaps other ligands as well) to complex with mordant metal ions so as to dissociate the size molecules from the fiber surfaces and destroy the sizing. If the metal ion mordant has stronger coordination potential with formic acid, the sizing will be destroyed sooner and formic acid will show stronger accelerating effect in the HST tests. If the metal ion mordant has weaker coordination potential with formic acid, the opposite will be true. Thermodynamically, the much higher HST values in rosin-ferric ion sizing system may also mean the bonding among rosin, ferric ion, and fiber complexes is much stronger than that in rosin, alum, and

fiber complexes; therefore, it is more resistant to the attack of the substituting ligand, water and formic acid. Of course, reaction kinetics may also play a role.

#### 4.3 CONCLUSIONS

When used as mordants for rosin soap sizing, ferric ion at pH around 3.5 and ferrous ion at pH around 5.5 can both induce excellent sizing to unbleached softwood kraft pulp, but completely lose their effectiveness toward bleached softwood and hardwood chemical pulps, while alum can induce good sizing to all of these pulps. The reason is believed to be due to the different mechanism of the metal ions in forming large complexes which are important in the sizing process. Alum can form large polymers by the formation of hydroxo and oxo bridges, so it is an effective mordant in both unbleached and bleached chemical pulps. But hydroxo bridging is not significant for iron ions. Iron is able, however, to form complexes with lignin. As a result, iron ions can only act as effective mordants in the sizing of lignin-rich unbleached pulps. This hypothesis is strongly supported by the sizing results in mechanical pulp. While alum can only induce moderate sizing, iron ions in contrast give extraordinarily good sizing results.

Even though sheet darkening is an obstacle to their commercial application, it is strongly recommended that ferrous or ferric ions be used as mordants of rosin soap

sizing instead of alum in unbleached chemical pulp and mechanical pulp in cases where the color of paper or paperboard products are not a major concern, such as in dark colored construction papers. Ferrous ion with its applicability in a higher pH range than alum and ferric ion can show even more advantages.

High level of sizing can be observed in the bleached hardwood handsheets sized with rosin- $\text{Fe}^{3+}$  at pH 4 after treating the handsheet at  $160^{\circ}\text{C}$  for 15 minutes, even though no sizing was observed in the same handsheets before the heating treatment and in the blank handsheets (no rosin and mordant added) treated under the same heating condition. Under prolonged or severer heating conditions, effective sizing can be observed even in the blank handsheets. More research is need to clarify the mechanism.

#### 4.4 EXPERIMENTS

The unbleached Douglas-fir kraft pulp had a Canadian Standard freeness (CSF) of 650 ml and a 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 was Stafor (Westvaco Chemicals) and was used at a level of 0.5% solids on pulp.

Ten grams of pulp was taken and diluted to 650 ml. Then 0.05 grams of rosin soap size in dilute solution of concentration 0.2% was added and stirred for 3 minutes. The appropriate amount of mordant was added and the pH was adjusted with dilute HCl and NaOH solutions with stirring for 5 more minutes. After one or more hours, the stock was then diluted to 5.0 liters with tap water and the pH was readjusted to the appropriate value. 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 standard. The standard press cycle was used, and then the sheets were dried in a sheet dryer at 250°F for 3 min. The sheets were conditioned at 72°F and 50% RH for at least 4 hrs before testing.

Cobb Size values were determined by TAPPI T 441 om-90. Ink resistance was determined on a Hercules Size Tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution (a solution of the same concentration of ink as the 1% formic acid ink made with distilled water instead of 1% formic acid, with an unadjusted pH of about 4).

Six handsheets were made for each trial condition and three of them were used for Cobb Size Test. The other three handsheets were used for the HST tests. Two measurements with both neutral and 1% formic acid ink were made on each handsheet. Since all data were reproducible, they are

simply averaged and reported. Additional verifications, not reported in this study, were also done. For example, most reported experiment results, especially those around each optimal sizing condition, have been repeated at least once.

Surface tension measurement was carried out with a DuNouy Tensiometer (CSC Scientific Company, Fairfax, Virginia) according to the procedures given in the operation manual.

## Chapter 5

### NEUTRAL TO ALKALINE ROSIN SOAP SIZING WITH METAL IONS AND POLYAMINES AS MORDANTS

#### 5.1 INTRODUCTION

Cellulosic paper is very vulnerable to water since it contains many hydroxyl groups; therefore, sizing becomes a necessary process for many paper grades. Rosin soap size has been the most widely used sizing agent since the sizing technique was developed in 1807, because the material is fairly inexpensive and abundant and the sizing process is easy to operate. However, this sizing agent can now be applied only in an acidic pH range since alum has always been the predominant mordant of choice in industry and it is not effective at elevated pH due to its chemical characteristics. Neutral to alkaline papermaking is becoming more and more popular because of its advantages (64) of lower paper cost, higher paper strength, reduced corrosion, improved paper stability on aging and increased paper machine productivity. For example, in wood-free printing and writing papers (64), the grades where the shifting from acidic to neutral or alkaline conditions has been the most successful and profitable, about 80% of the European production and 60% of the North American production was alkaline in 1993, while the corresponding figures in the two regions are expected to be about 100% and 85% by the

turn of this century. But neutral to alkaline papermaking can now be achieved only with emulsified rosin or synthetic sizing agents which are more expensive and more complicated to use than rosin soap size. Rate of cure, surface slip and fugitive sizing problems (89) can also discourage the use of synthetic sizing agents.

It would be a great advance to papermaking if neutral to alkaline sizing could be achieved with rosin soap size. However, this was believed to be theoretically impossible so little research was done in the field. Although many polymers including proteins have long been known to be able to improve rosin sizing (18), no reasonable explanations have been given. Polyamines such as polyvinylcycloamidine (40) and polyethylenimine (PEI) (90) were used with rosin soap size and alum to size paper, and acceptable levels of sizing could be achieved at a pH as high as 8 or 8.5, but again the mechanism of the sizing improvement was not clear.

In our laboratory, various lanthanide metal ions (21) were used as mordants of rosin soap sizing and shown some efficacy up to pH 7.5, even through the sizing was generally not as good as when alum is used under its optimal condition. Polyallylamine (78) was shown to be an effective mordant of rosin soap sizing from pH 3 to pH 10 in bleached hardwood chemical pulp, although its effectiveness in bleached softwood pulp was much lower and it was practically ineffective in thermomechanical pulp.

Further researches in the field are definitely required to make rosin soap sizing under neutral to alkaline papermaking conditions commercially applicable as well as to learn the general principles involved in the sizing process. The objectives of this study are to show that hard sizing can be achieved with rosin soap size at elevated pH in various pulps when mordants with suitable chemistry are used and to verify some hypotheses regarding the sizing process. Although the results here may have limited potential to be used directly in the industry due to the color effect and the cost of the mordants, they should have far-reaching significance in understanding the sizing mechanism and providing guidance to the future efforts in the field.

## 5.2 PRINCIPLES AND HYPOTHESIS

It is generally agreed that to achieve effective sizing, the following requirements must be met (3,5,18,75):

1. The size precipitates must have high hydrophobicity.
2. The size molecules must be well retained on the fibers.
3. The retained size must be uniformly distributed and properly orientated on fibers to cover the surfaces efficiently.
4. The size molecules must be strongly bound to the fiber surfaces.

While the hydrophobicity and the distribution of size on fibers are more related to the inherent properties of the sizing agent, mordants are usually required to retain and anchor the size onto fibers. Rosin-alum sizing cannot be achieved at  $\text{pH} > 6$  was attributed to the lower hydrophobicity or the poorer distribution and orientation (35) of the size precipitates on fibers. It is author's belief that the incapability of alum to bind rosin molecules on fibers strongly at the high pH range is the more probable reason.

Energetic analysis (91) of the rosin sizing process leads one to believe that rosin soap size must be anchored to the fiber surfaces through primary chemical forces such as covalent bonds (dative bonds, which are also called coordinate covalent bonds, are a specific type of covalent bonds) to effect sizing; the stronger the bonding between rosin size and fibers, the better the sizing can be. Secondary chemical forces such as hydrogen bonding or van der Waals forces are not strong enough to resist the attack of polar water molecules so are not effective bonding types. The fact (77) that ferrous and ferric ions cannot induce any sizing in bleached pulps but are very effective mordants of rosin soap size in lignin-rich pulps (unbleached kraft pulp and TMP) shows that even a single dative bond might not be strong enough. Effective bonding between rosin size and fibers should involve multiple dative bonds (via coordinating metal ions) or other types of covalent bonds. The fact (35-37) that rosin-alum sizing is not effective at

pH <3.5 where  $\text{Al}^{3+}$  is the predominant species but is very effective in the pH range of 4 to 5.5 where the polynuclear aluminum species predominate may tell the same story. Heating the no-sizing handsheets made from bleached pulps and sized with rosin-iron ion systems can result in effective sizing could be another supporting evidence for the above hypothesis.

The electrostatic characteristic of alum under various conditions may be important for the retention of rosin size, but should have little effect on the mechanism of sizing development. What is important in the sizing mechanism is the chemical reactivity of various aluminum species. Unfortunately, this property of alum has not received enough attention while its many other properties that are not as important or not important at all to sizing have been studied extensively. The fact that few efforts have been made to achieve neutral to alkaline rosin soap sizing can be attributed to this negligence.

Literature review and some previous studies (21,77,78) from our lab lead me to believe that the most important aspects of  $\text{Al}^{3+}$  chemistry in regard to rosin sizing are:

- (1) Its coordinating capability.

This property enables  $\text{Al}^{3+}$  to anchor rosin size onto fibers through dative bonds and is the basic requirement for a metal ion mordant.

- (2) Its ability to form polynuclear species via hydroxo or oxo bridging.

This property can enhance the bonding strength between rosin size and fibers because of the possibility of multiple bonding and is one of the reasons why alum has been used predominantly as the mordant of rosin sizing. Many metal ions have stronger coordinating capability than alum but cannot form polynuclear species. This is why they are usually not as effective mordants as alum since a single dative bond is often not strong enough. The ineffectiveness of rosin-alum sizing at  $\text{pH} < 3.5$  can also be attributed to this property. At the low pH the concentration of  $\text{OH}^-$  group is too low to enable sufficient amount of polynuclear aluminum species to be formed through the hydroxo or oxo bridging. Ferrous and ferric ions have been shown to be very effective even at pH 3, because they rely on a different mechanism to achieve the necessary strong bonding.

- (3) Its high affinity to hydroxide anions, which is indicated by its low  $\text{pK}_1$  (Figure 5.1) value of 5.01.



$\text{K}_1$  is the equilibrium constant

$$\text{pK}_1 = -\log \text{K}_1$$

M is a trivalent metal ion

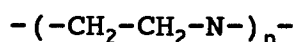
---

**Figure 5.1** The  $\text{pK}_1$  of metal ions

This property is the reason why rosin-alum sizing cannot be achieved at neutral to alkaline conditions because at the high pH, the concentration of  $\text{OH}^-$  is high. With its high affinity to  $\text{OH}^-$  groups, the aluminum ions will only react to  $\text{OH}^-$  groups in the solution and will not be able to react with rosin size and fiber components to accomplish its function as a mordant. In other words, when the concentration of  $\text{OH}^-$  groups is high, the  $\text{OH}^-$  group will dominantly occupy the coordinating sites on aluminum ion so there will be no enough coordinating sites left for rosin size and fiber components. Alum's function as a retention aid of rosin soap size is also poorer at the high pH, but this is not the main reason why sizing can not be achieved since certain amounts of rosin are still retained at the high pH. If the poorer retention is the reason, effective sizing should be achievable by simply increasing the rosin dosage, which we knew is not true.

If the above understanding of the aluminum's chemistry is correct and if there is a species which has very strong coordinating potential and is able to form large complexes with rosin size and fiber components in some way, but has lower affinity to hydroxide anions, we would be able to use the species as an effective mordant of rosin soap sizing even at an elevated pH. This is the reason why the combination of transition metal ions and polyamines was applied in this study. Transition metal ions (10) show greater potential than alum to coordinate with species

having a lone pair of electrons to donate because of the poor shielding of d-electrons to the nuclei and the existence of empty d-orbitals. With their higher  $pK_1$  values than  $Al^{3+}$ , they have much lower affinity for  $OH^-$ . However, they usually cannot form polynuclear species. Polyamines such as polyethylenimine (PEI) contain many nitrogen atoms on their molecular chain, as shown below:



Having a lone pair of electrons around the nucleus, nitrogen atoms in many molecules are excellent ligating atoms (53). The formation of a large complex (Figure 5.2 gives a postulated bonding structure) among rosin, coordinating metal ion, polyamine and fiber components is very possible. The incorporation of polyamine into coordinating metal ions could greatly enhance the bonding strength between rosin molecules and fibers (via metal ions and the polyamine) by increasing the number of bonds if the type of postulated complex can be formed.

In summary, the combination of transition metal ions and polyamines may possess the same chemistry in regards to rosin sizing at neutral to alkaline pH as alum does at acidic pH; therefore, it may be an effective mordant of rosin soap sizing even at elevated pH. On the other hand, if effective rosin soap sizing could be achieved with transition metal ions/polyamines as the mordants, it means

that the above understanding of the aluminum' chemistry is very likely to be true.

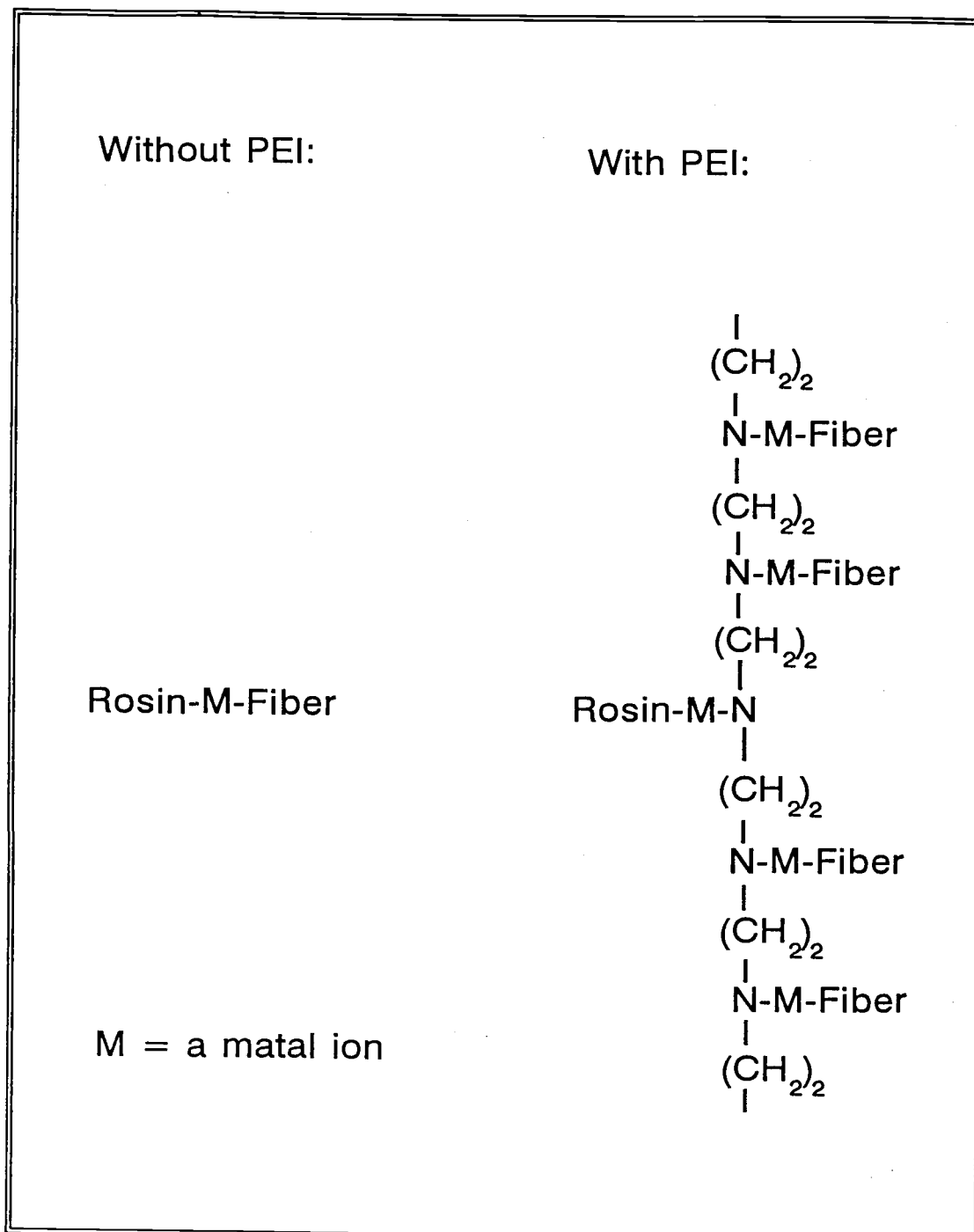


Figure 5.2 Bonding between rosin and fibers

## 5.3 RESULTS AND DISCUSSIONS

### 5.3.1 Sizing in Bleached Hardwood Pulp

Various metal ions were used in combination with PEI as mordants of rosin soap sizing. The sizing results in a bleached hardwood kraft pulp are summarized in **Table 5.1** and some of the data are illustrated in **Figure 5.3**. All the results were obtained from standard laboratory handsheets using 0.5% (on oven-dry pulp) fortified rosin soap size solids except when specifically indicated. Sizing with alum at its optimal conditions is included for comparison. Of course, lower Cobb size and higher HST (Hercules Sizing Tester) values mean better sizing. The applicable pH ranges for various metal ions are chosen based on their  $pK_1$  values since it will be shown that the pH of maximum sizing efficacy of a metal ion is in the vicinity of its  $pK_1$  values.

As shown in **Table 5.1** and/or **Figure 5.3**, PEI alone or with  $Mg^{2+}$  or  $Mn^{2+}$  can not induce any sizing in the reported pH ranges.  $Zn^{2+}$ /PEI can induce moderate sizing at pH 7 to 8, although the sizing is generally not as good as when alum is used at pH 4 to 5. Rosin-alum sizing can be greatly improved with the addition of PEI. Alum/PEI can even induce effective sizing at pH as high as 7, while alum alone can never do the same.  $Fe^{3+}$  and  $Fe^{2+}$  alone were shown to be very effective mordants of rosin soap sizing in lignin-rich

**Table 5.1** Sizing results of bleached hardwood chemical pulp

Mordants	Amount <sup>a</sup> added(%)	pH of sizing	Cobb Size (g/m <sup>2</sup> /2min)	HST <sup>b</sup> (S) (neutral)	HST (S) (1%FA <sup>c</sup> )
Alum	1.0	4.5	24.5	650	209
	1.0	5.0	25.1	585	133
	1.0	7.0	Soaked	13	4.6
PEI	0.5	7.0	Soaked	87	34
	0.7	7.0	Soaked	9	3
	1.5	7.0	Soaked	0.6	0.5
Alum/PEI	1.0/0.3	5.0	23.2	1391	559
	1.0/0.3	7.0	24.8	1153	318
	1.0/0.5	5.0	22.6	2580	520
Mg <sup>2+</sup> /PEI	1.5/0.5	7.0	Soaked	53	42
	1.5/0.5	10.0	Soaked	0.1	0
Mn <sup>2+</sup> /PEI	1.5/0.5	8.0	Soaked	1.0	0.5
	1.5/0.5	10.0	Soaked	0.3	0.1
Fe <sup>3+</sup>	2.0	3.5	Soaked	0.6	0.7
	2.0	4.0	Soaked	0.5	0.5
Fe <sup>3+</sup> /PEI	1.0/0.5	3.5	27.2	1177	709
	1.0/0.5	4.0	27.6	1463	1102
	1.0/0.5	7.0	Soaked	341	97
	0.5/0.3	5.0	26.5	890	516
Fe <sup>2+</sup>	2.5	5.5	Soaked	0.8	0.8
	2.5	7.0	Soaked	0.5	0.3
Fe <sup>2+</sup> /PEI	1.5/0.5	5.5	23.5	2250	2077
	1.5/0.5	6.0	27.0	2065	1855
	1.5/0.5	7.0	24.3	4084	3017
	1.5/0.5	8.0	Soaked	943	47

**Table 5.1** Sizing results of bleached hardwood chemical pulp  
(Continued)

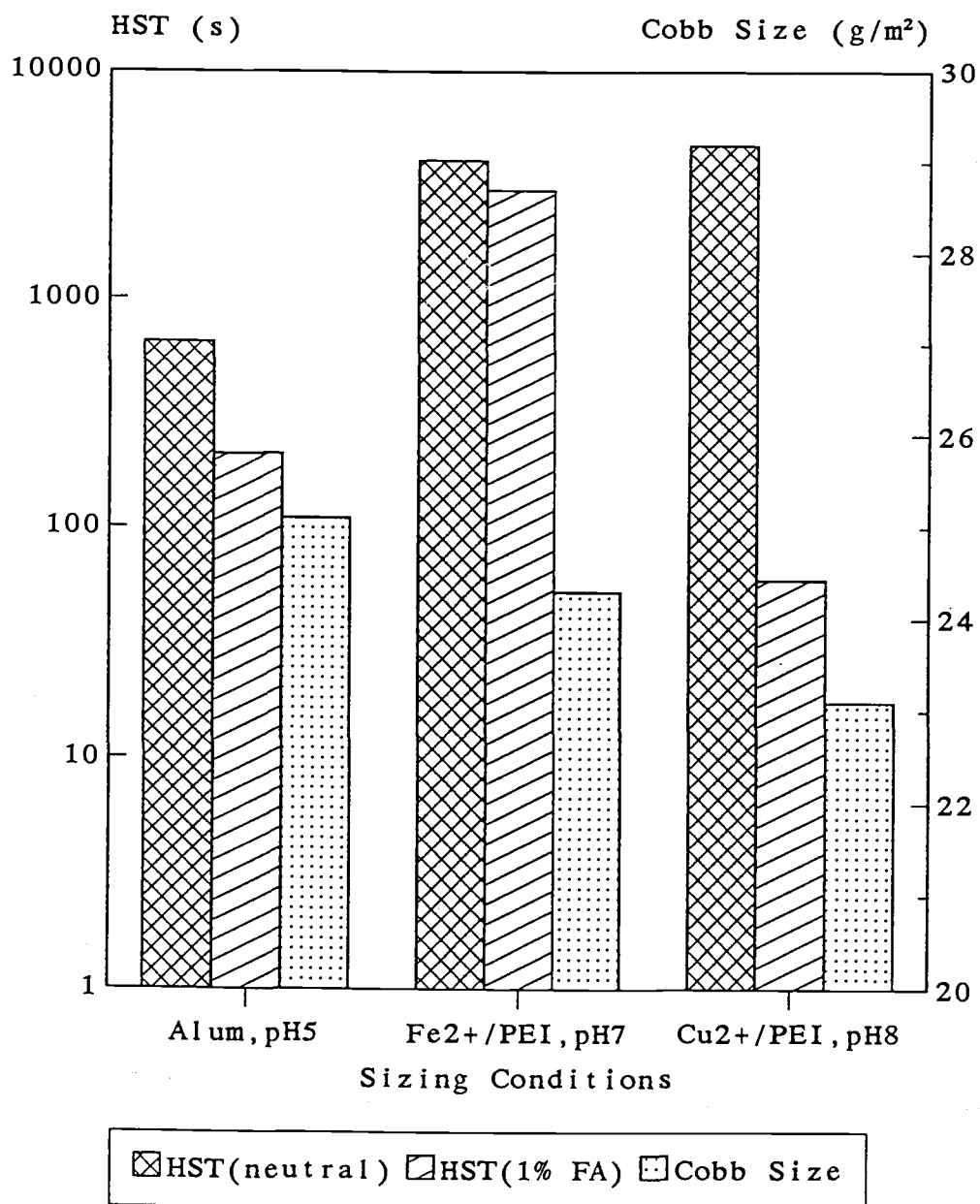
Mordants	Amount <sup>a</sup> added(%)	pH of sizing	Cobb Size (g/m <sup>2</sup> /2min)	HST <sup>b</sup> (S) (neutral)	HST (S) (1%FA <sup>c</sup> )
Cu <sup>2+</sup>	2.5	5.0	Soaked	2.0	1.0
	2.0	7.0	25.8	405	0.6
	2.5	8.0	26.4	372	0.6
	2.5	9.0	Soaked	1.9	0.2
Cu <sup>2+</sup> /PEI	0.5/0.5	7.0	Soaked	835	2.0
	1.8/0.5	7.0	25.0	3791	55
	1.8/0.5	8.0	23.1	3900	67
	1.8/0.5	9.0	25.0	3950	65
	2.5/0.5	7.0	23.5	5110	57
	4.0/0.5	7.0	23.2	6050	144
	2.5/0.5	4.0	50.5	1430	11
	2.5/0.5	6.0	25.2	2780	29
	2.5/0.5	8.0	23.1	4770	59
	2.5/0.5	10.0	28.4	3420	21
	2.5/0.5	10.5	39.0	3390	7.3
Zn <sup>2+</sup>	1.0	7.0	Soaked	0.6	0.4
Zn <sup>2+</sup> /PEI	1.0/0.5	7.0	35.1	987	50
	1.5/0.5	8.0	69.4	320	3.2
	1.0/0.5 <sup>d</sup>	8.0	26.8	1122	533
	2.0/0.5 <sup>d</sup>	8.0	27.0	1020	578

a. Based on oven-dry pulp.

b. Hercules Sizing Tester.

c. Formic acid ink.

d. Rosin soap dosage 1%.



**Figure 5.3** Sizing results in bleached hardwood chemical pulp. Alum 1.0%; Fe<sup>2+</sup> 0.5% and PEI 0.5%; Cu<sup>2+</sup> 2.5% and PEI 0.5%.

unbleached softwood kraft pulp and softwood thermomechanical pulp, but they are not effective at all in bleached softwood and hardwood kraft pulps (77). Table 5.1 and Figure 5.3 shows that with the addition of PEI,  $\text{Fe}^{3+}$  can induce very good sizing at pH 3.5 to 4.0 and  $\text{Fe}^{2+}$  is very effective from pH 5.5 to 7.0 in the bleached hardwood pulp.  $\text{Fe}^{3+}$ /PEI and  $\text{Fe}^{2+}$ /PEI are also very effective mordants in the bleached softwood kraft pulp but the results are not reported here.

Why  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  can not induce any sizing in bleached pulps but are very effective mordants in the same pulps when used in combination with PEI? What is the function of PEI there? Of course, the addition of PEI must have positively affected at least one of the four basic requirements for achieving effective sizing, as summarized in the previous paragraphs. Is it because PEI can improve the hydrophobicity of the size precipitates? Not very likely. The fact that both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions alone can induce high level of sizing in unbleached chemical pulp and mechanical pulp shows that both ferric rosinate and ferrous rosinate must already be hydrophobic enough. Is it because PEI can improve the retention of rosin soap size? It is true that PEI could further improve the retention of rosin size since PEI is a commonly used retention aid. However, the same fact (both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions alone can induce high level of sizing in unbleached chemical pulp and mechanical pulp) as mentioned above shows that  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  alone have the capability of retaining sufficient rosin size. Heating the

handsheets which are made from bleached pulps and sized with rosin-iron ions and which originally have no sizing under moderate heating condition can result in well-sized handsheets, as reported in chapter 4, also shows that iron ions alone can retain sufficient amount of rosin size even in bleached pulps. The further improvement in size retention, if any, is not critical. Can the addition of PEI improve the distribution or orientation of the size precipitates by reducing the particle sizes or lowering the sintering point of the size precipitates, as often argued in the literature in many other situations? Again not likely, and if it is possible at all, the improvement should have only affected the sizing efficiency, not determined the sizing effectiveness.

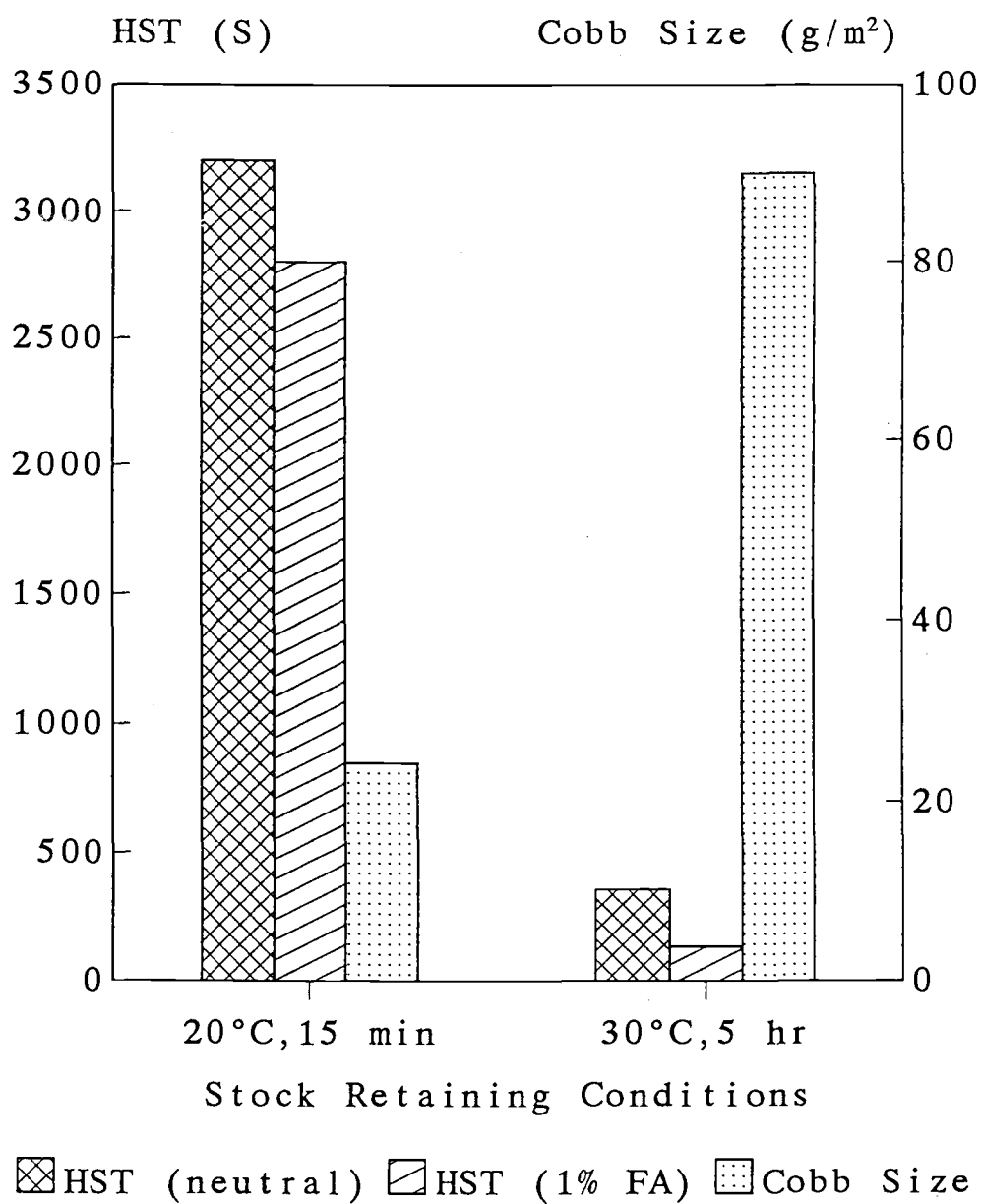
The only other possibility is that the addition of PEI has improved the bonding strength between rosin size and fibers, as depicted in **Figure 5.2**. These results strongly support the hypotheses that the bonding strength between size molecules and fibers is a crucial factor in determining the effectiveness of sizing. A high level of sizing can be achieved when the bonding is through multiple dative bonds or other types of covalent bonds.

The oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  by oxygen molecules in water was discussed extensively in chapter 4. While the oxidation rate is negligible at pH below 5.5, it is quite rapid (half-life less than 1 hour) at pH above 6.5. **Figure 5.4** shows the effect of this oxidation reaction on the

sizing when  $\text{Fe}^{2+}$ /PEI is used as the mordant at pH 7. When the handsheets were made soon after rosin size and the mordant were added, they possessed a high level of sizing. If, however, the stock was kept at 30°C for 5 hours after the rosin size and the mordant were added and before the handsheet were made, the handsheets had practically no sizing. The reason is that most  $\text{Fe}^{2+}$  ions have been oxidized into  $\text{Fe}^{3+}$  ions under the latter condition.  $\text{Fe}^{2+}$  with its  $\text{pK}_1$  of 6.74 can induce good sizing at pH 7 when used with PEI but  $\text{Fe}^{3+}$  with its  $\text{pK}_1$  of 2.83 cannot be an effective mordant at the same pH. Realizing that ferrous ion can be easily oxidized into ferric ion at pH above 6.5 is very important when applying ferrous ion alone or ferrous ion with PEI as the mordant in the high pH range. The stock retaining time after the mordant has been added must be kept as short as possible in order to achieve maximal sizing efficiency.

Table 5.1 shows that  $\text{Cu}^{2+}$  alone can induce some sizing at pH 7 to 8. With the addition of 0.5% PEI, it is very effective throughout a wide pH range from 4.0 to 10.5. The HST values with neutral ink are much higher than when alum is used at its optimal pH. During the experiments it was observed that the stock became bluer when PEI was added after  $\text{Cu}^{2+}$  had been applied. This phenomenon is a strong evidence (53) that PEI reacts with  $\text{Cu}^{2+}$  and forms some coordination complexes during the sizing process.

Formic acid was introduced into the HST test as an accelerator (18) because the HST test with neutral ink takes



**Figure 5.4** The effect of the oxidation of ferrous ions on sizing. Bleached hardwood kraft pulp,  $\text{Fe}^{2+}$  1.5%, PEI 0.5% and pH7.

too long in some well-sized paper grades. An ideal accelerator should speed up the test at the same rate in all circumstances. Unfortunately this is not true for formic acid. **Table 5.1** shows that in the bleached hardwood pulp, while 1% formic acid can do little (usually less than a 50% decrease) in accelerating the HST test when  $\text{Fe}^{2+}$ /PEI is the mordant, it can accelerate the test by more than 100 times when  $\text{Cu}^{2+}$ /PEI is the mordant (and more than 1000 times in TMP pulp). This indicates that there are chemical reactions occurring between formic acid and the rosin/metal ion/PEI/fiber complex. While the bonding among rosin size,  $\text{Fe}^{2+}$ , PEI and fiber components is fairly resistant to formic acid, the same type of bonding when  $\text{Cu}^{2+}$ /PEI is the mordant can be broken down (so the sizing is destroyed) very easily by formic acid. In fact, formic acid is no longer a suitable accelerator when  $\text{Cu}^{2+}$ /PEI is the mordant since the test tells that the paper is poorly sized when Cobb size and HST test with neutral ink have shown that the paper is very well sized. The acidity of formic acid also make it inapplicable in paper grades containing  $\text{CaCO}_3$  filler. As a convenient sizing tester, HST has been more and more widely accepted by the industry. Further investigations into the accelerating mechanism to develop some new accelerators are obviously necessary to accommodate a wide variety of new sizing systems.

### 5.3.2 Coordination Chemistry of Metal Ion Mordants

As introduced in chapter 1, the coordination theory about the function of alum in rosin sizing has been put forth for sixty years. However, it has not been universally accepted, probably because it cannot explain the fact that alum has always been the most effective metal ion mordant and because no direct and convincing evidences about the coordination mechanism have been provided. The discovery and confirmation in chapter 4 that ferrous and ferric ions can be more effective mordants under certain conditions have cleared some of the doubts. Following important observations should provide more convincing proofs.

The first important observation, as shown in **Table 5.2**, is that the  $pK_1$  of a metal ion is a good indication of its pH of maximal sizing efficacy. In all the effective metal

**Table 5.2** Relationship between the  $pK_1$  and pH of maximal sizing efficiency of metal ions

Mordants	$pK_1$ of the metal ion	pH of maximal sizing
Alum/PEI	5.01	4.5-5.0
$Fe^{3+}$ /PEI	2.83	3-3.5
$Fe^{2+}$ /PEI	6.74	6-6.5
$Cu^{2+}$ /PEI	8.00	7-9
$Zn^{2+}$ /PEI	9.00	7-8

ion mordants, such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , the pH values of their optimal sizing are in the vicinity of their  $\text{pK}_1$  values. This phenomenon is easy to explain since the  $\text{pK}_1$  of a metal ion is a measurement of its affinity to hydroxide anions. If a metal ion has a low  $\text{pK}_1$  value, its affinity to hydroxide anions is high. At a certain pH it will have a strong potential to coordinate with hydroxide anions so it is less likely to coordinate with rosin size and fiber components. As a result, it can be an effective mordant of rosin sizing only in a relatively low pH range. If a metal ion has a high  $\text{pK}_1$  value, the opposite will be true. The pH dependence of the rosin-alum sizing system has always been an amazing topic. Many explanations have been developed but none of them is convincing enough. The discovery of the relationship between the  $\text{pK}_1$  values of metal ions and their pHs of maximal sizing efficacy indicates that the pH dependence of rosin soap sizing is closely related to metal ion mordant's affinity to hydroxide anions. This discovery should add another strong evidence to the coordination theory.

Another important phenomenon observed from **Table 5.1** is that the metal ion's performances as the mordants coincide well with a classic rule in coordination chemistry. In the 1950s, Irving and Williams found that (53) for a given ligand, the stability of complexes with dipositive metal ions follows the order:  $\text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ . Similarly, **Table 5.1** shows that when used

with PEI, the metal ion's performances as mordants for rosin sizing follows the order:  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+} < \text{Fe}^{2+}$ ,  $\text{Cu}^{2+} > \text{Zn}^{2+}$ . Both orders are exactly the same. If a metal ion can form a more stable complex with a ligand, that is, if it has a stronger coordinating potential, it is also a better mordant of rosin sizing when used with PEI. This consistency is certainly one of the most strong indications that coordination chemistry is playing a key role in the mechanism of sizing development; it is also an indication that the bond strength (or at least integrity in a given liquid) is of overwhelming importance in developing sizing.

There are two reasons (53) for the Irving-Williams series of stability. One is the decrease in the diameters of the dipositive metal ions across the series due to the increase in the number and the poor shielding of d-electrons. A smaller metal ion can draw the ligands more closely so tends to have stronger attraction to the ligands and form more stable complexes when other factors are the same. Another reason is the ligand field effects. **Table 5.3** shows the crystal field stabilization energy (CFSE) of various dipositive metal ions in a weak ligand field in both octahedral and tetrahedral geometry (53).  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  have significant amount of CFSE, while  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  do not have any. The amount of CFSE is determined by the electronic interaction between the metal ion and ligands so is affected by the d-electron configuration of the metal ion.  $\text{Mg}^{2+}$  has no d-electron,  $\text{Mn}^{2+}$  has 5 d-electrons (half-

**Table 5.3\*** The crystal field stabilization energy (CFSE) in a weak field

Metal ions	No. of <u>d</u> electrons	CFSE (kJ/mol)	
		Octahedral	Tetrahedral
$\text{Mg}^{2+}$	0	0	0
$\text{Mn}^{2+}$	5	0	0
$\text{Fe}^{2+}$	6	47.6	31.4
$\text{Co}^{2+}$	7	71.5	62.7
$\text{Ni}^{2+}$	8	122.4	27.2
$\text{Cu}^{2+}$	9	92.8	27.6
$\text{Zn}^{2+}$	10	0	0

\* Data is from reference 53.

filled d-orbitals) and  $\text{Zn}^{2+}$  has 10 d-electrons (filled d-orbitals). This is the reasons why they have no CFSE. Usually the higher the CFSE, the more stable the complex would be. But this rule of thumb is not always true since CFSE is only a part of, not all of, the stabilization energy involved in the formation of coordination complexes.

### 5.3.3 Sizing in Other Types of Pulp

More sizing experiments were carried out in an unbleached Douglas-fir kraft pulp and a softwood thermomechanical pulp using the mordants which had been

proven to be very effective in the bleached hardwood pulp. The detail results are shown in **Table 5.4** and some is illustrated in **Figure 5.5** and **Figure 5.6**. Sizing with alum as the mordant under its optimal conditions is also given for comparison. It can be seen from **Table 5.4**, **Figure 5.5** and **Figure 5.6** that very high level of sizing can be induced by  $\text{Fe}^{3+}$ /PEI at pH around 4, by  $\text{Fe}^{2+}$ /PEI at pH up to 7, and by  $\text{Cu}^{2+}$ /PEI at pH from 7 to 9 in the two pulps. While reasonable level of sizing in certain types of pulp has been achieved by other researchers with rosin soap size under neutral to alkaline pH ranges, this is the first time it is shown that very high level of sizing can be achieved with rosin soap size in all different types of pulp under neutral to alkaline conditions. Again, the addition of PEI can greatly improve the sizing with alum as the mordant. This sizing improvement can have great practical significance in the sizing of mechanical pulps. As in the bleached pulps, it is again found that formic acid has a much greater accelerating effect when  $\text{Cu}^{2+}$ /PEI is the mordant than when  $\text{Fe}^{2+}$ /PEI is used and it is obvious that the HST test with 1% formic acid ink is not applicable in the  $\text{Cu}^{2+}$ /PEI system. (On the other hand, this sizing system may not be suited to certain liquids.)

**Table 5.4** shows some results which are contradictory to common experiences. When rosin size is compared with synthetic sizing agents such as AKD and ASA, it is said (18) that synthetic sizing agents can give hard sizing to paper

**Table 5.4** Sizing results of unbleached kraft pulp and TMP

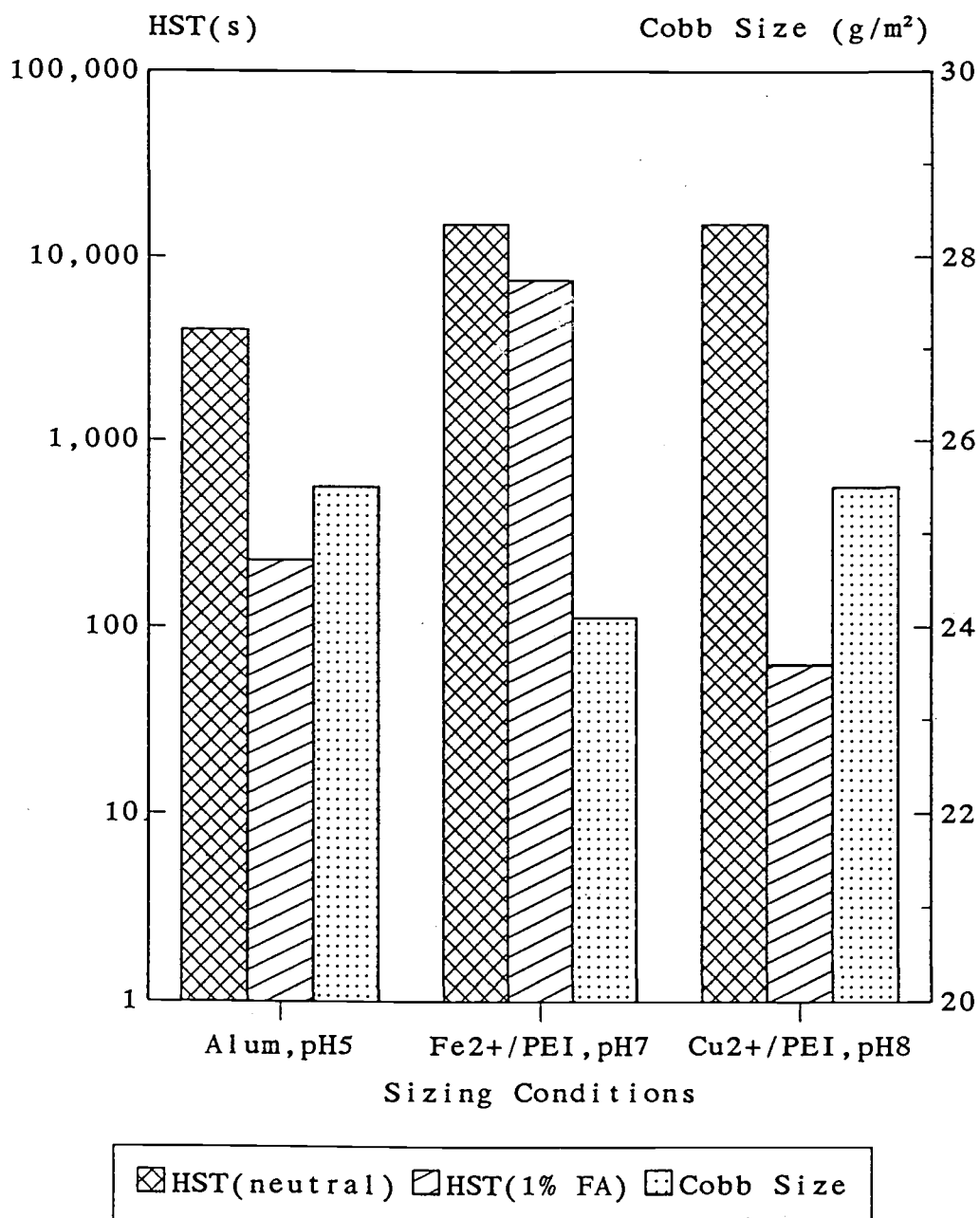
Mordants	Amount <sup>a</sup> added(%)	pH of sizing	Cobb size (g/m <sup>2</sup> /2min)	HST <sup>b</sup> (S) (neutral)	HST (S) (1%FA <sup>c</sup> )
<u>Unbleached Douglas-fir kraft pulp</u>					
Alum	1.0	4.5	23.5	3040	325
	1.0	5.0	25.5	4042	227
Alum/PEI	1.0/0.5	5.0	23.0	8670	1100
	1.0/0.5	7.0	24.9	6022	917
Fe <sup>3+</sup> /PEI	1.0/0.5	4.0	22.8	>10000 <sup>d</sup>	6450
	1.0/0.5	7.0	29.6	2020	500
Fe <sup>2+</sup> /PEI	1.0/0.5	5.5	23.0	>10000	9550
	2.0/0.5	5.5	22.9	>10000	13400
	1.5/0.5	7.0	24.1	>10000	7500
	0.5/0.5	7.5	30.1	3420	2200
	0.5/0.3	6.5	26.3	4890	1380
	0.5/0.65	6.5	24.6	>10000	11700
Cu <sup>2+</sup> /PEI	1.5/0.5	7.0	24.8	>10000	72
	1.7/0.5	8.0	25.5	>10000	63
	2.5/0.5	9.0	27.2	6570	53
<u>Thermomechanical pulp</u>					
Alum	1.0	4.5	32.1	420	71
	2.0	5.0	38.4	393	73
	1.0	5.5	Soaked	31	11
Alum/PEI	1.5/0.1	5.0	25.3	936	125
	1.5/0.25	5.0	22.7	2464	159
	1.0/0.5	5.0	20.7	>10000	207
	1.0/0.5	7.0	22.6	>10000	76
Fe <sup>3+</sup> /PEI	1.0/0.5	4.0	21.8	>10000	395
Fe <sup>2+</sup> /PEI	1.5/0.5	5.5	18.4	>10000	919
	1.5/0.5	7.0	22.1	>10000	1020
Cu <sup>2+</sup> /PEI	1.5/0.5	7.0	22.8	>30000	14
	2.5/0.5	8.0	16.9	>40000	32
	2.5/0.5	9.0	18.3	>40000	36

a. Based on oven-dry pulp.

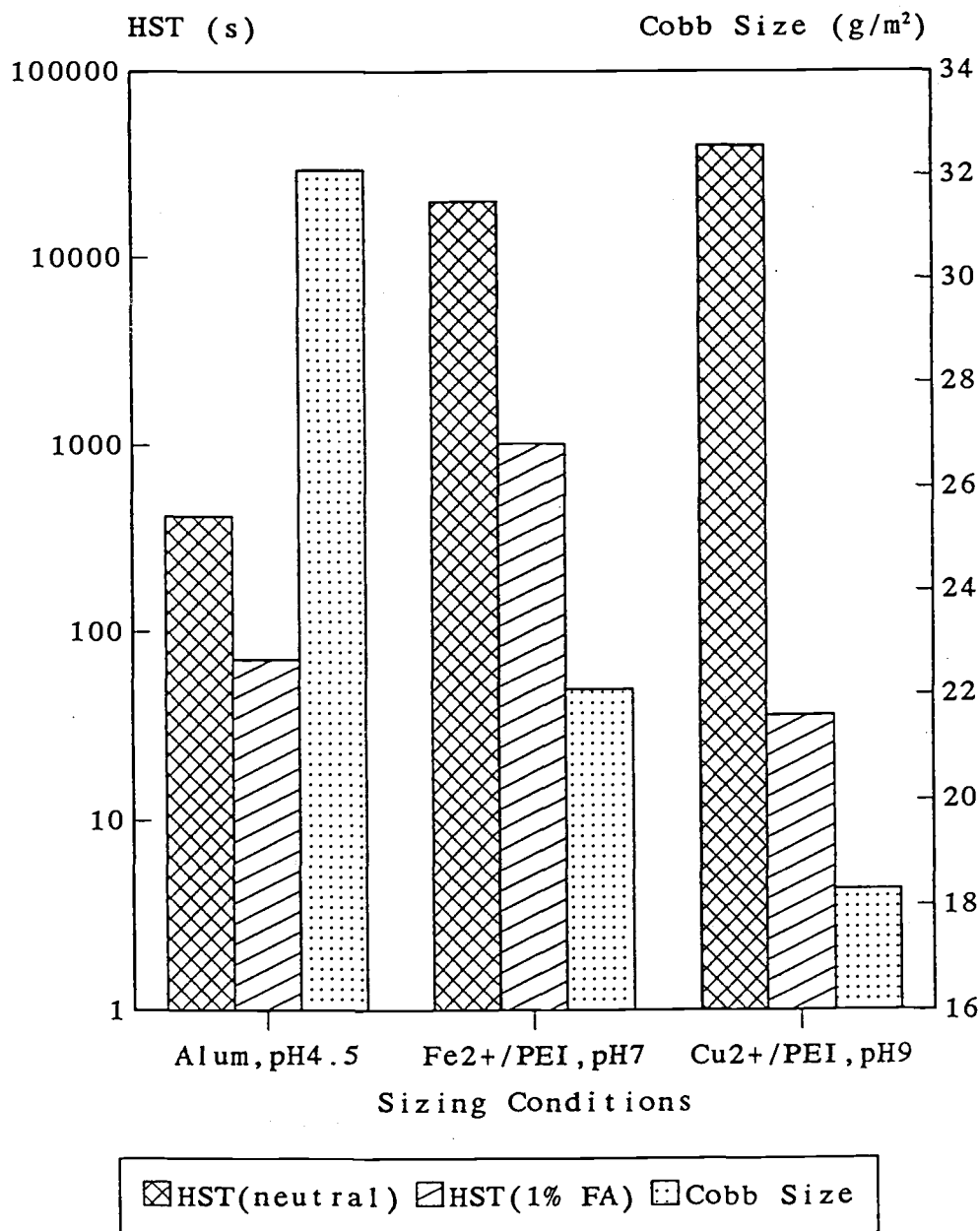
b. Hercules Sizing Tester.

c. Formic acid ink.

d. Test terminated at this point.



**Figure 5.5** Sizing in unbleached softwood kraft pulp. Alum 1.5%, pH 5; Fe<sup>2+</sup> 1.5%, PEI 0.5%, and pH 7; Cu<sup>2+</sup> 2.5%, PEI 0.5%, and pH 8.



**Figure 5.6** Sizing in softwood thermomechanical pulp. Alum 1.0%, pH 4.5; Fe<sup>2+</sup> 1.5%, PEI 0.5%, and pH 7; Cu<sup>2+</sup> 2.5%, PEI 0.5%, and pH 9.

but rosin size cannot. This statement is true when alum is the mordant but is not true here. **Table 5.4** shows that rosin soap size can give very hard sizing when proper mordants are used. Another notable result is that TMP, a pulp which has been well known as being much more difficult to size than chemical pulps (18), is actually easier or much easier to size than the unbleached and bleached chemical pulps when  $\text{Fe}^{3+}/\text{PEI}$ ,  $\text{Fe}^{2+}/\text{PEI}$ , or  $\text{Cu}^{2+}/\text{PEI}$  is the mordant.

#### 5.3.4 Factors Affecting Sizing

Various factors such as the pH of sizing, the amount of metal ions and PEI added (and, of course, the amount of rosin, but it is kept constant at 0.5% throughout this study), the types of polyamines, the anions of the metal salts, and the sheet drying conditions, etc., can all affect the sizing. Some attempts were made to examine their effects.

**Figure 5.7** illustrates the effect of sizing pH when  $\text{Cu}^{2+}/\text{PEI}$  is used as the mordant in the sizing of bleached hardwood chemical pulp.  $\text{Cu}^{2+}$  was added at 2.5% dosage and PEI was added at 0.5% dosage. Sizing is very high throughout the wide pH range from 4 to 10, but the optimal sizing occurs at pH from 7 to 9. **Figure 5.8** illustrate the effect of  $\text{Cu}^{2+}$  amount on the sizing of the same pulp. The sizing pH was kept at 7 and the amount of PEI added was kept

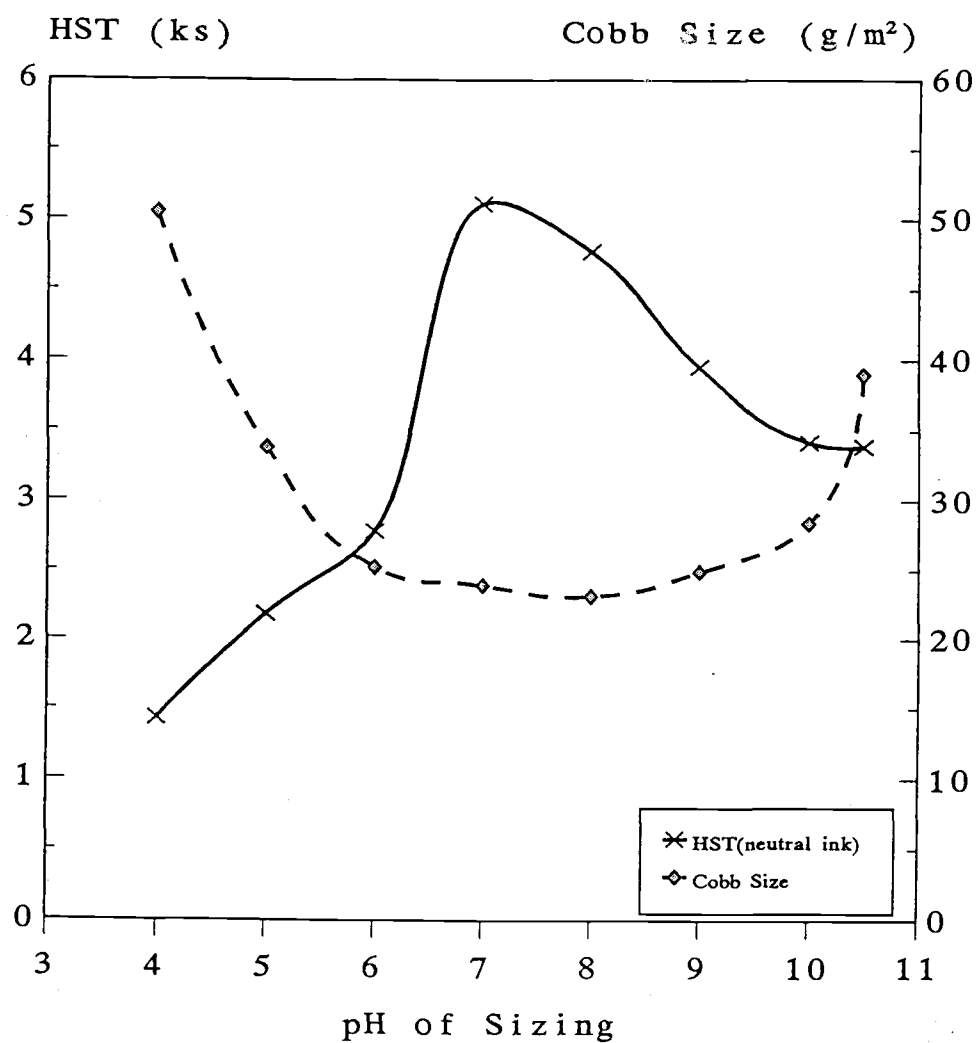
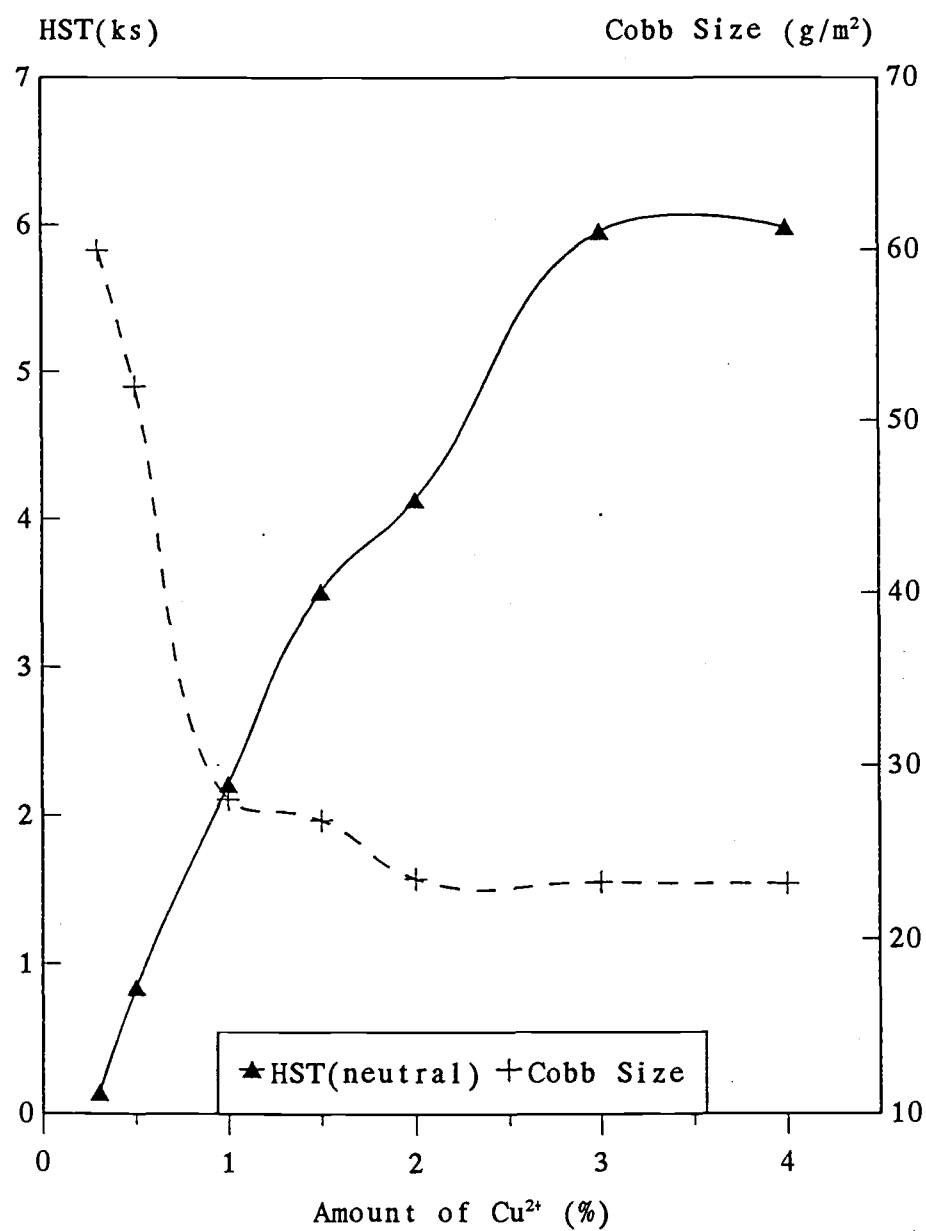


Figure 5.7 Effect of pH on rosin- $\text{Cu}^{2+}$ /PEI sizing. Bleached hardwood chemical pulp,  $\text{Cu}^{2+}$  2.5%, and PEI 0.5%.

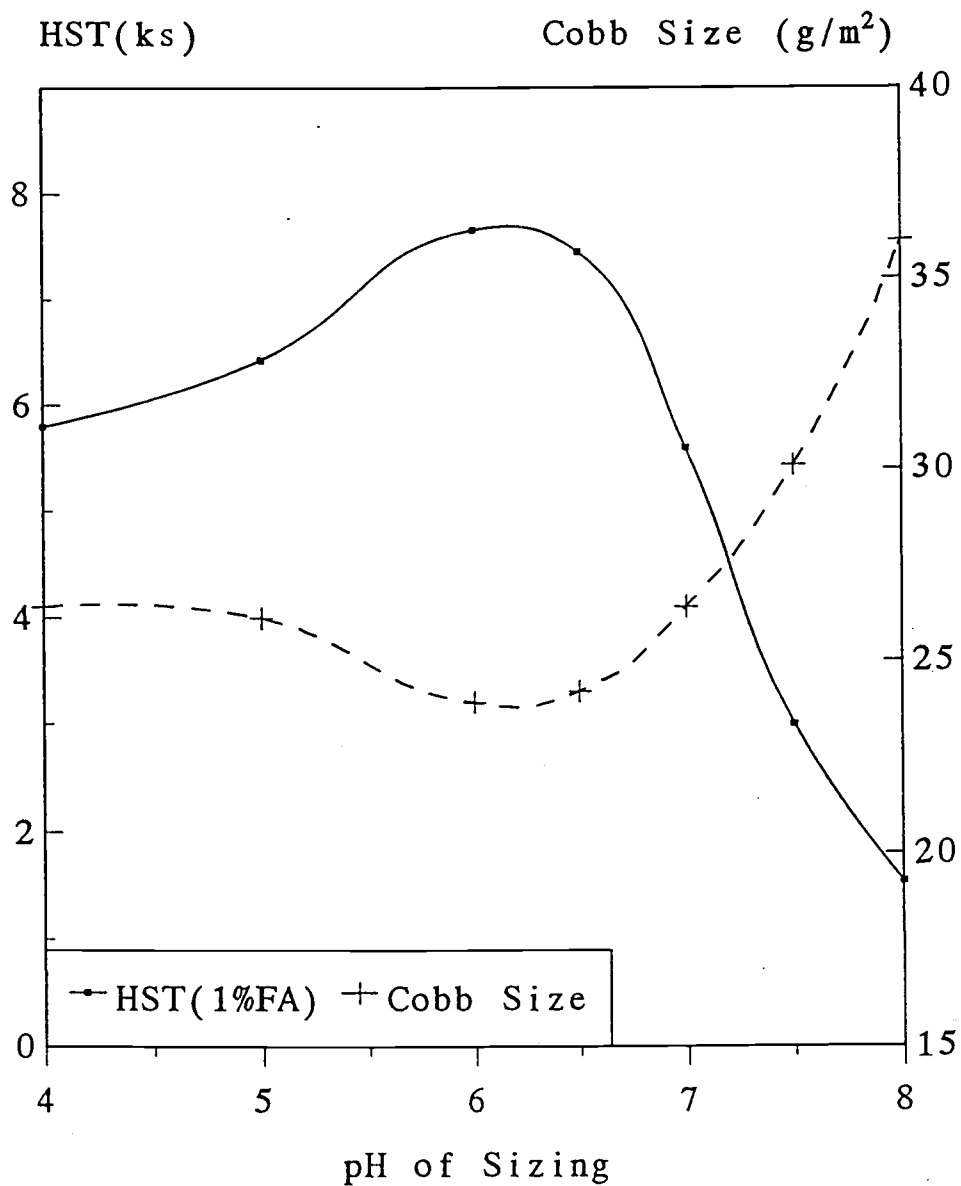


**Figure 5.8** Effect of  $\text{Cu}^{2+}$  dosage on rosin- $\text{Cu}^{2+}$ /PEI sizing. Bleached hardwood chemical pulp, pH 7 and PEI 0.5%.

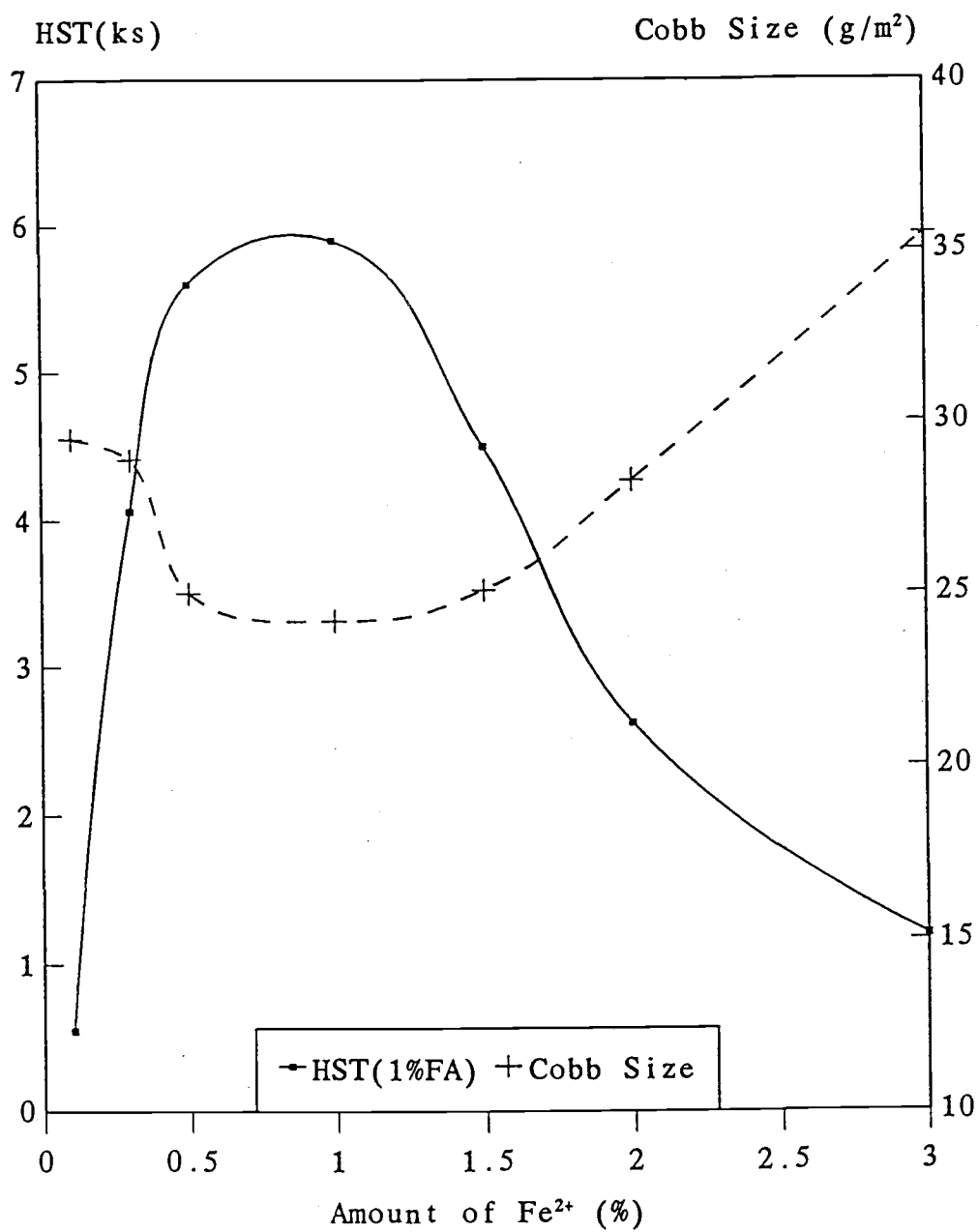
at 0.5%. It can be observed that the sizing is improved steadily with the increase of the  $\text{Cu}^{2+}$  amount under the conditions, but the improvement levels off when the  $\text{Cu}^{2+}$  dosage reaches 3-4%.

The effect of pH on sizing when  $\text{Fe}^{2+}$ /PEI is used as the mordant in the sizing of unbleached softwood kraft pulp is shown in **Figure 5.9**.  $\text{Fe}^{2+}$  and PEI were both kept at 0.5%. It can be observed from **Figure 5.9** that sizing is very effective throughout pH 3 to pH 7, but the optimal sizing occurs at pH 6-6.5. The effect of  $\text{Fe}^{2+}$  amount on sizing in the same pulp was also examined and the results are given in **Figure 5.10**. The sizing pH was kept at 7 and the amount of PEI added was kept at 0.5%. It can be seen from **Figure 5.10** that optimal sizing occurs when the amount of  $\text{Fe}^{2+}$  ion added is at 0.5-1.5%, which is at a much lower level than when  $\text{Fe}^{2+}$  ion alone is used as the mordant, as shown in **Figure 4.5**.

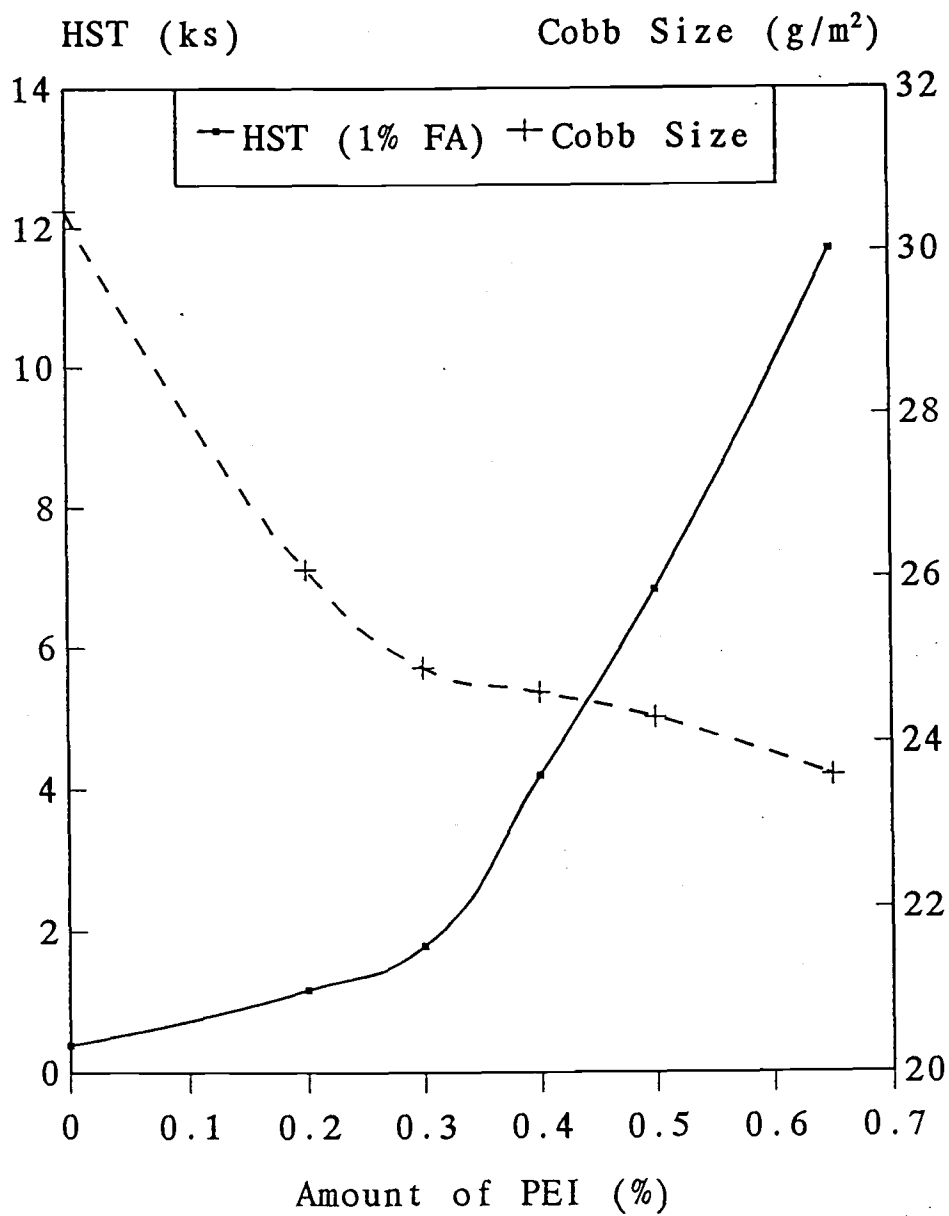
The amount of PEI added has very significant effect on the sizing, too. **Figure 5.11** shows this effect when  $\text{Fe}^{2+}$ /PEI is used as the mordant in the sizing of the same unbleached pulp. The amount of  $\text{Fe}^{2+}$  added was kept at 0.5% and the sizing pH was kept at 6.5. It is found that the more PEI added, the better the sizing when the amount of PEI added is no more than 0.7%. Since PEI is quite expensive and it is unlikely to add more than 0.5% PEI in commercial paper



**Figure 5.9** Effect of pH on rosin-Fe<sup>2+</sup>/PEI sizing. Unbleached softwood kraft pulp, Fe<sup>2+</sup> 0.5%, and PEI 0.5%.



**Figure 5.10** Effect of  $\text{Fe}^{2+}$  dosage on rosin- $\text{Fe}^{2+}$ /PEI sizing. Unbleached softwood kraft pulp, pH 7 and PEI 0.5%.

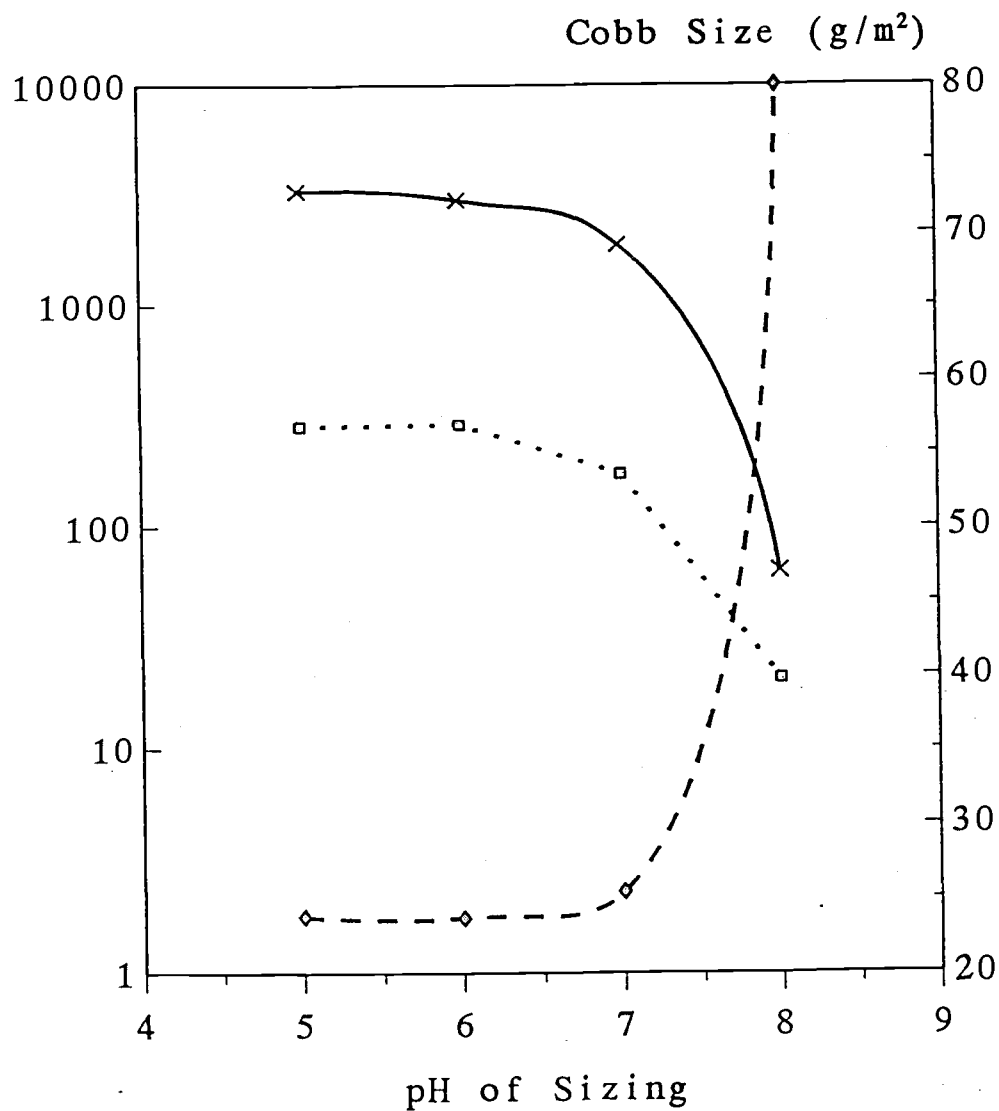


**Figure 5.11** Effect of PEI dosage on rosin-Fe<sup>2+</sup>/PEI sizing. Unbleached softwood kraft pulp, Fe<sup>2+</sup> 0.5%, and pH 6.5.

manufacture, the effect of higher PEI addition levels on sizing was not examined.

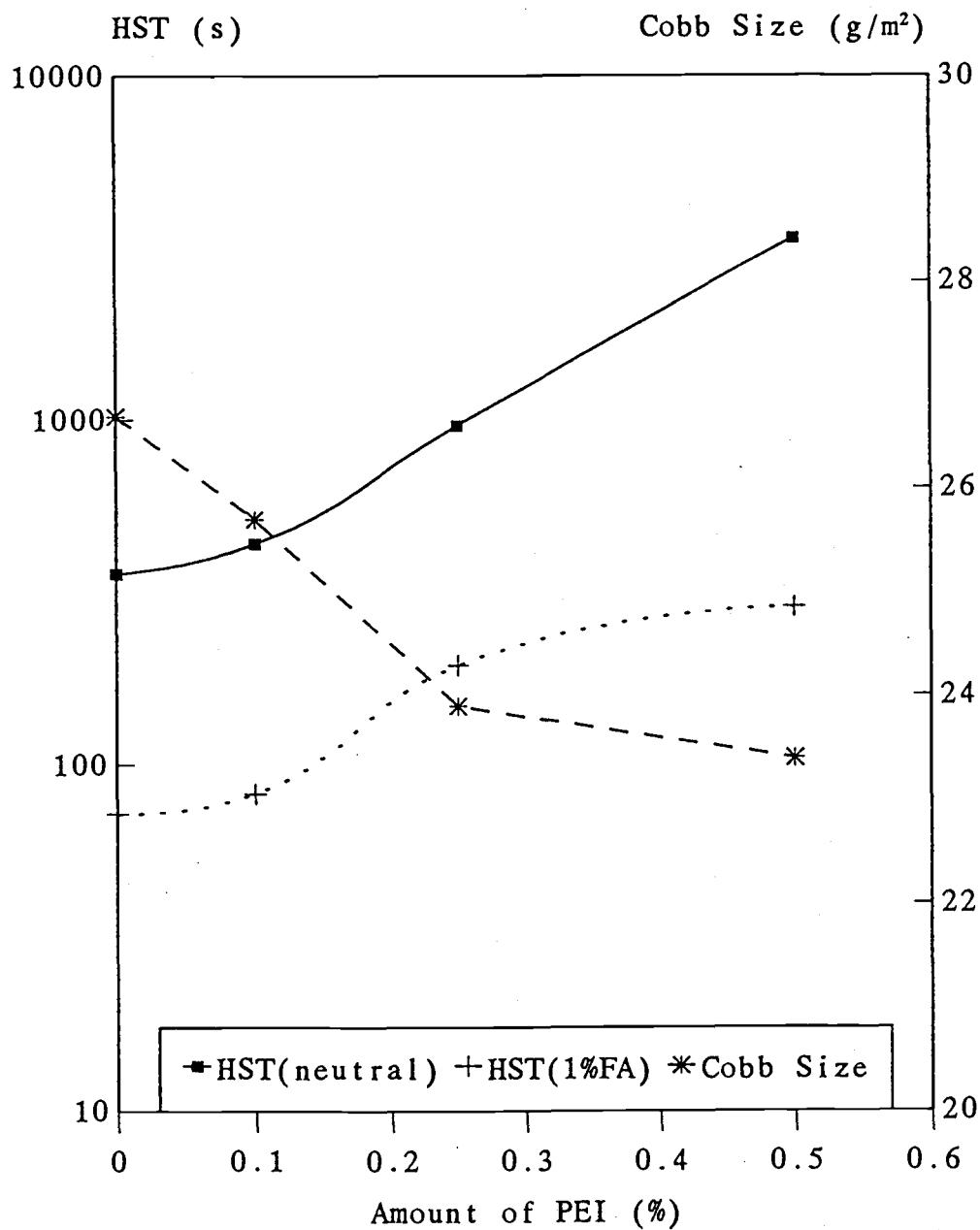
The effect of pH on sizing when alum/PEI is used as the mordant in the sizing of bleached hardwood chemical pulp is shown in **Figure 5.12**. The amount of alum added was kept at 1.5% and that of PEI was kept at 0.5%. It can be seen from **Figure 5.12** that the optimal sizing occurs at pH around 5. Sizing efficiency is quite high from pH 5 to pH 7, but diminishes very quickly after pH 7. The effect of PEI amount on sizing was also investigated when alum/PEI is used as the mordant in the sizing of the same pulp and the results are illustrated in **Figure 5.13**. The amount of alum added was kept at 1.5% and the sizing pH was kept constant at 5. It can be observed from **Figure 5.13** that the sizing efficiency is constantly improved with the increase of PEI addition level in the examined range (PEI less than 0.5%).

Based on the proposed mechanism given in the beginning of this chapter, other polyamines should have the functions similar to that of PEI. Polyamine N634 was used with alum in the sizing of bleached hardwood chemical pulp at pH 7 and the results are shown in **Figure 5.14**. The amount of alum added was kept at 1.5%. It can be noticed from **Figure 5.14** that the sizing efficiency get steadily improved with the increased addition of N634 when the addition level of the

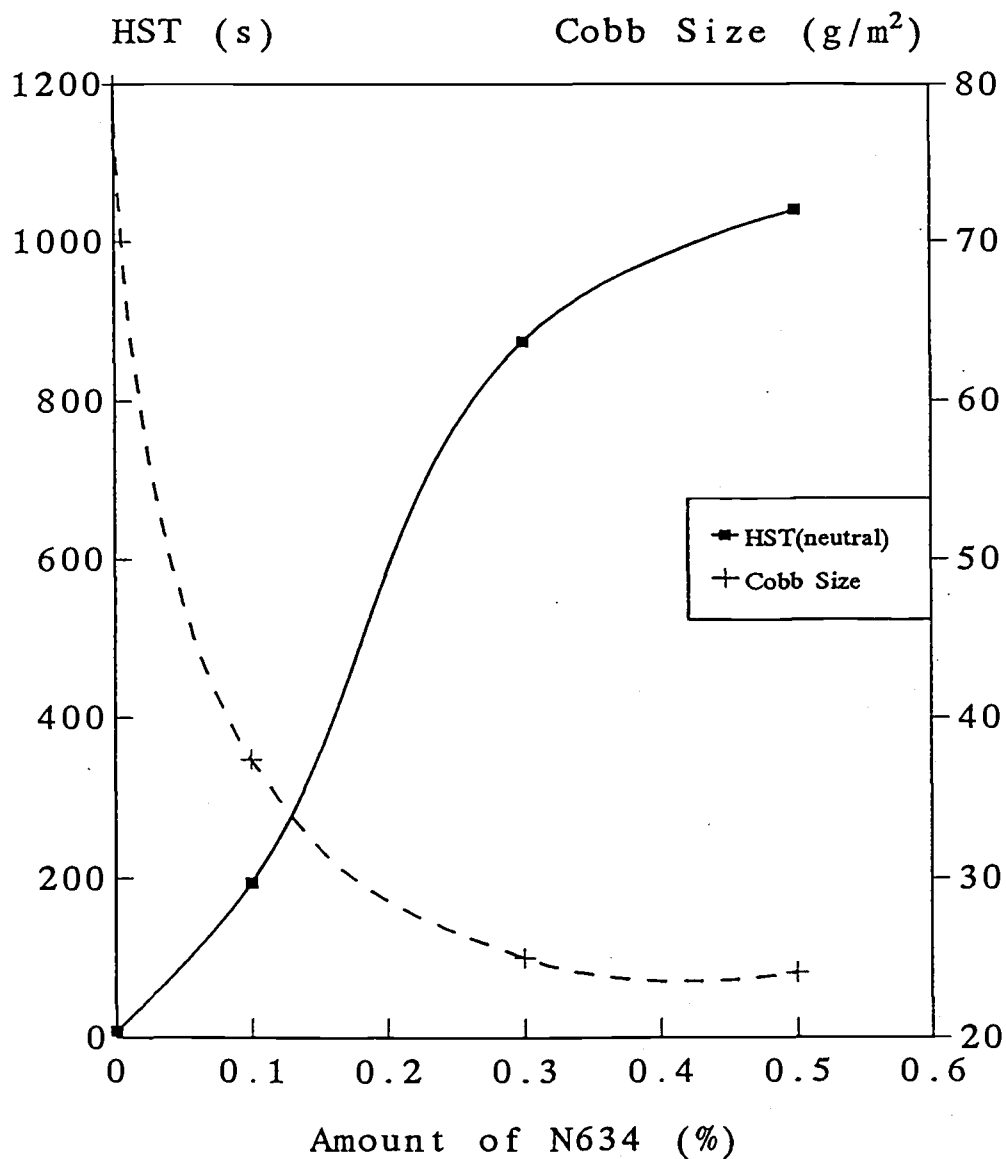


□ HST(1%FA) × HST(neutral) ◇ Cobb Size

**Figure 5.12** Effect of pH on rosin-alum/PEI sizing. Bleached hardwood chemical pulp, alum 1.5%, and PEI 0.5%.



**Figure 5.13** Effect of PEI dosage on rosin-alum/PEI sizing. Bleached hardwood pulp, alum 1.5%, and pH 5.

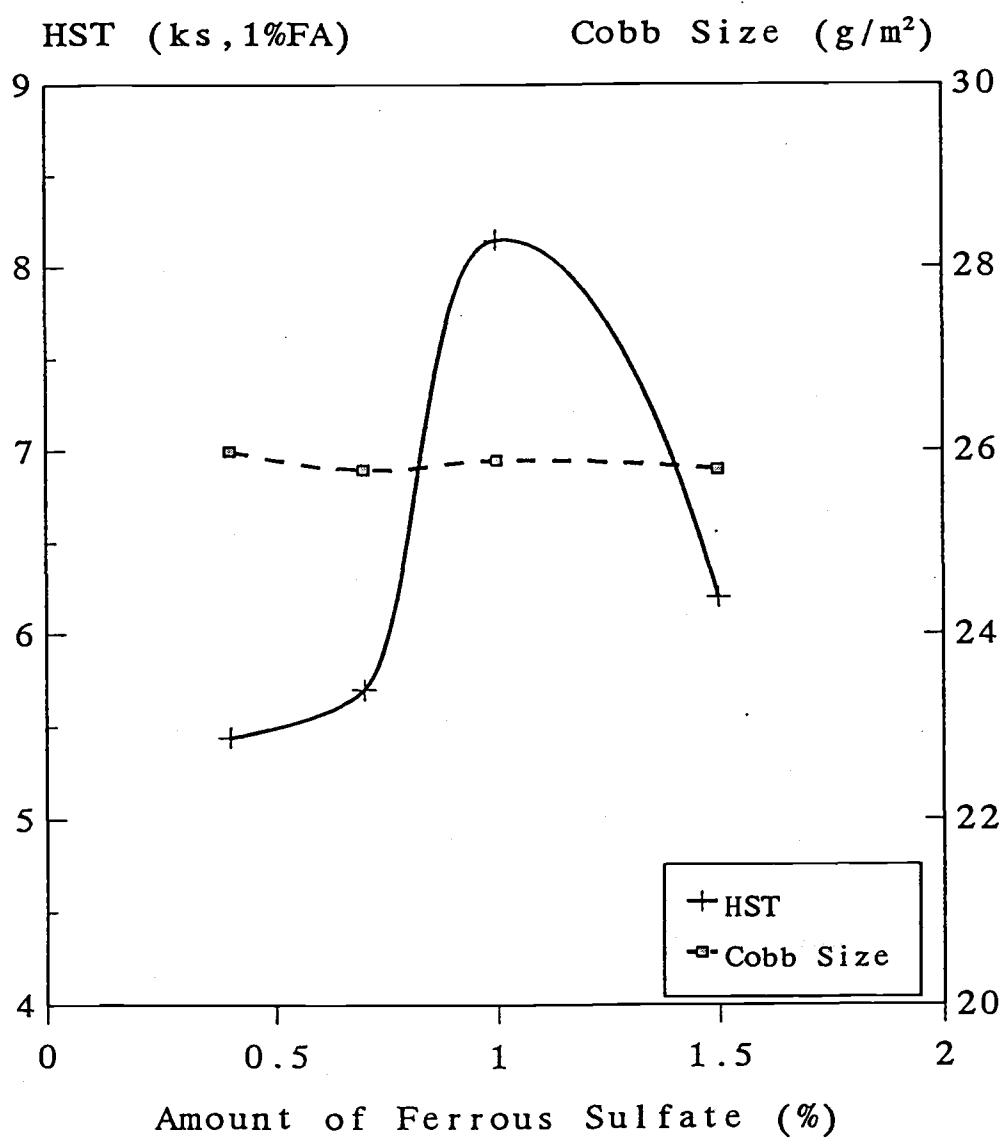


**Figure 5.14** Effectiveness of polyamine N634. Bleached hardwood kraft pulp, alum 1.5%, and pH 7.

polyamine is no more than 0.5%. Without N634, no sizing can be achieved with rosin-alum sizing system at pH 7.

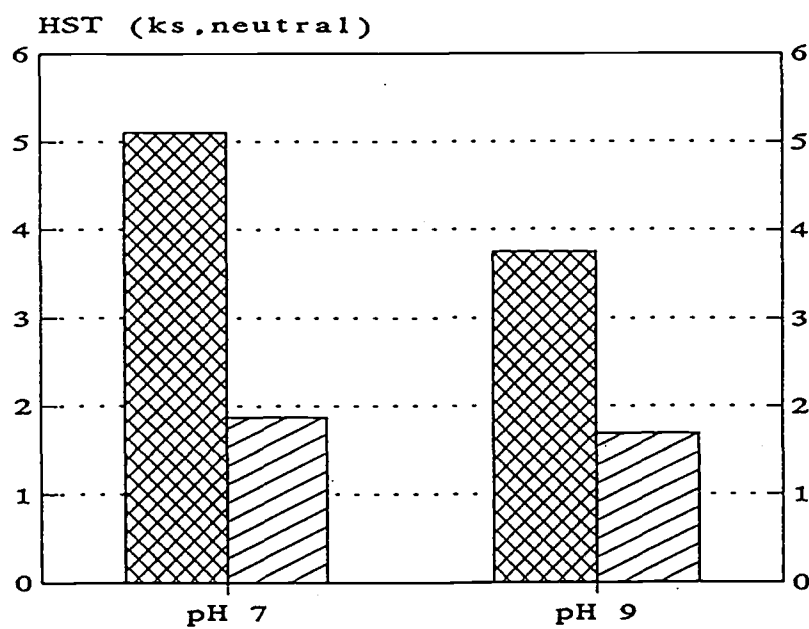
The anion of the metal ions can also affect the sizing performance. Chloride is always used in this study when ferrous ion is used with PEI as the mordant. Can the sulfate be as effective? Figure 5.15 shows the sizing results when ferrous sulfate is used with PEI as the mordant in the sizing of unbleached softwood kraft pulp at pH 6.5. The PEI amount was kept at 0.5% and the ferrous sulfate applied is as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . It can be seen from **Figure 5.15** that ferrous sulfate is also very effective under the conditions. The HST value with 1% formic acid ink can be as high as 8000 seconds, which is a very high level of sizing. As in the case of the chloride, there is an optimal addition level of the metal ion.

Drying condition of the sheets has long been known to have great effect on the development of sizing. The effect of drying condition was also investigated when  $\text{Cu}^{2+}$ /PEI is used as the mordant in the sizing of bleached hardwood chemical pulp at pH 7 and pH 9 and the results are presented in **Figure 5.16**. The amount of  $\text{Cu}^{2+}$  added was 2.5% and that of PEI was 0.5%. It can be observed from **Figure 5.16a** and **Figure 5.16b** that oven-drying always results in a higher level of sizing than air-drying. The sizing improvement upon the drying with heat is believed to be due to the

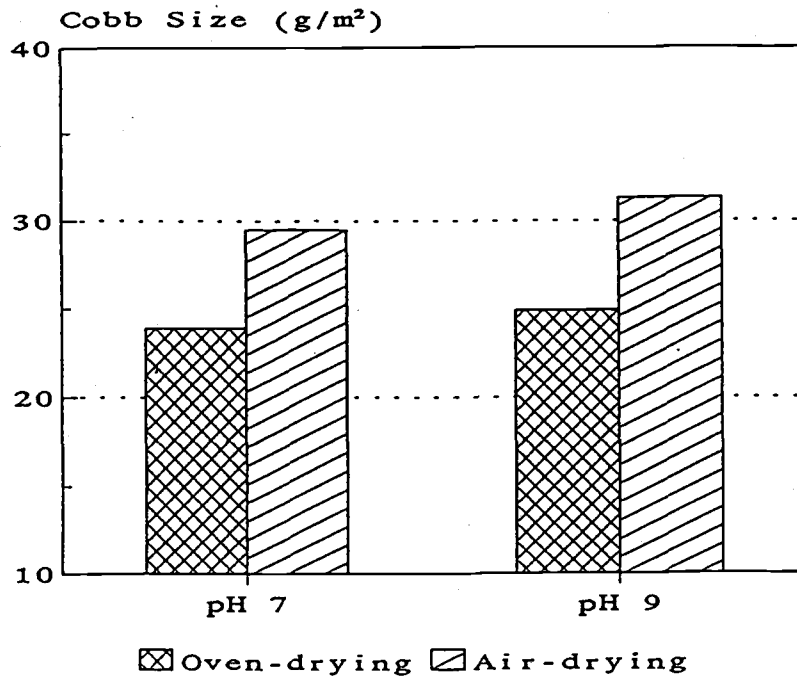


**Figure 5.15** Sizing with ferrous sulfate/PEI as the mordant. Unbleached softwood kraft pulp, PEI 0.5%, and pH 6.5.

A.



B.



**Figure 5.16** Effect of drying condition on sizing. Bleached hardwood chemical pulp, Cu<sup>2+</sup> 2.5%, and PEI 0.5%.

improved size distribution on fibers, while it is more likely that the heat drying has facilitated the reactions among rosin size, mordants and the fiber components so that the bonding between rosin size and fibers has been enhanced.

#### 5.3.5 Strength Improvement in Handsheets

The strength properties of the handsheets were also examined. The detail results are shown in Table 5.5 and some is illustrated in Figure 5.17 where alum is added at the amount of 1.0%,  $\text{Fe}^{2+}$  at 1.5%,  $\text{Cu}^{2+}$  at 2.0% and PEI at 0.5% (all based on oven-dry pulp). Table 5.5 and Figure 5.17 show that in all three pulps, bleached hardwood kraft pulp (HW KP), unbleached softwood (SW) kraft pulp, and softwood TMP, the tensile strength of the handsheets can be increased by 20-30% if either  $\text{Fe}^{2+}$ /PEI or  $\text{Cu}^{2+}$ /PEI is used as the mordant instead of alum. Table 5.5 also shows that the bursting strength of the handsheets exhibited a similar improvement.

The strength improvement is due to the addition of PEI and papermaking at the higher pH. PEI can act as a strength additive since it can enhance the hydrogen bonding between the fibers. Besides, fibers can swell more and become more flexible at higher pH since the acidic groups in the fibers will exist more in the Na-form rather than in the H-form or multivalent metal ion forms (92). As a result, fibers can

**Table 5.5** Strength properties of the handsheets

Mordants	Amount added (%)	pH of sizing	Tensile strength (lb/15mm)	Bursting strength (lb/in <sup>2</sup> )
Bleached hardwood chemical pulp				
Alum	1.0	5.0	8.36	23.8
Fe <sup>2+</sup> /PEI	1.5/0.5	7.0	9.20	28.7
Cu <sup>2+</sup> /PEI	2.0/0.5	7.0	9.45	30.6
Cu <sup>2+</sup> /PEI	2.0/0.5	8.0	9.66	31.0
Unbleached Douglas-fir kraft pulp				
Alum	1.0	5.0	7.52	31.1
Fe <sup>2+</sup> /PEI	0.5/0.5	7.0	10.1	42.3
Fe <sup>2+</sup> /PEI	1.5/0.5	7.0	9.70	40.4
Cu <sup>2+</sup> /PEI	1.7/0.5	7.0	10.7	41.2
Softwood thermomechanical pulp				
Alum	1.0	4.5	2.70	---
Fe <sup>2+</sup> /PEI	1.5/0.5	7.0	3.26	---
Cu <sup>2+</sup> /PEI	1.7/0.5	7.0	3.49	---

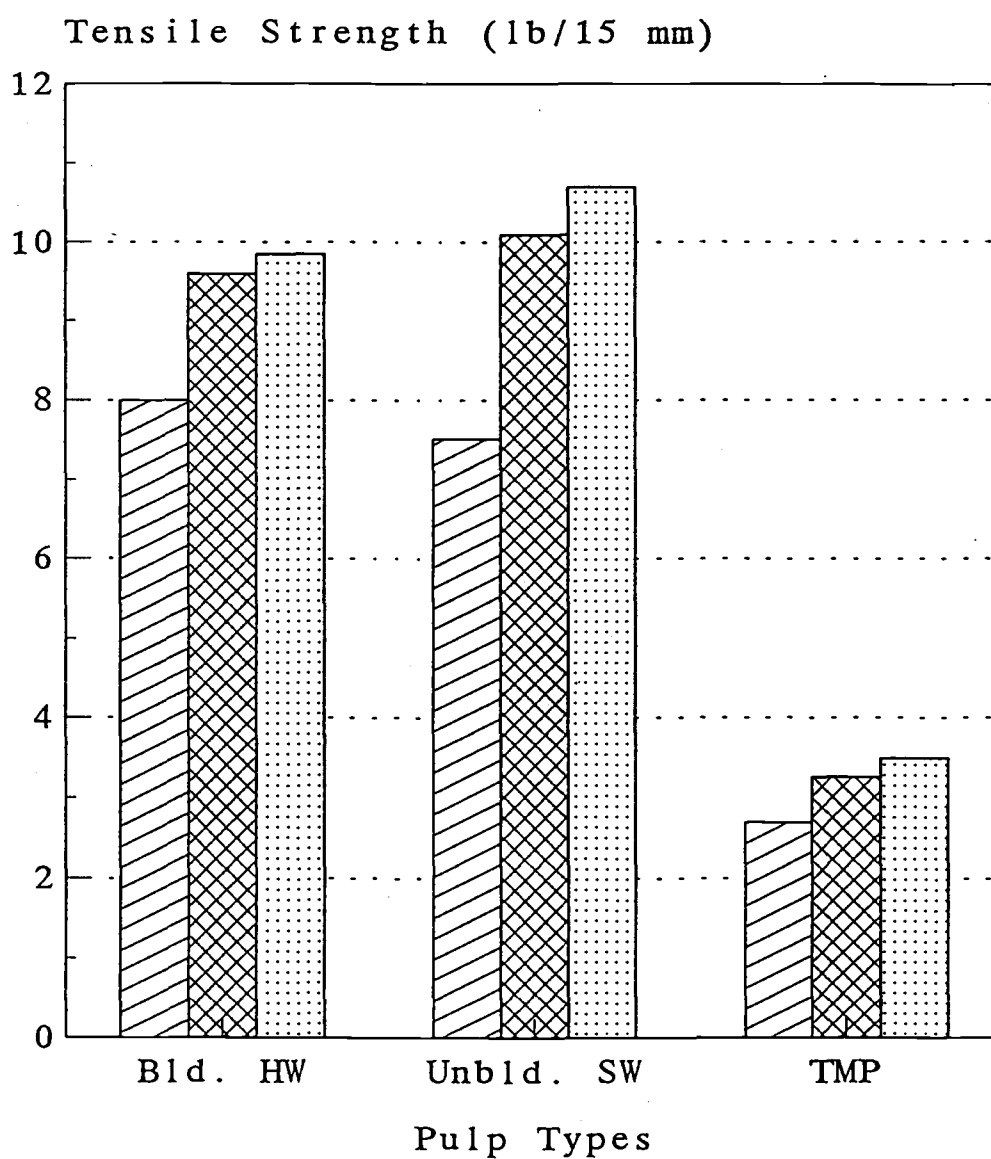


Figure 5.17 Tensile strength of handsheets

come into a closer contact under the same pressure and bonding between fibers is stronger, resulting in a higher paper strength.

#### 5.3.6 HST Tests with Different Inks

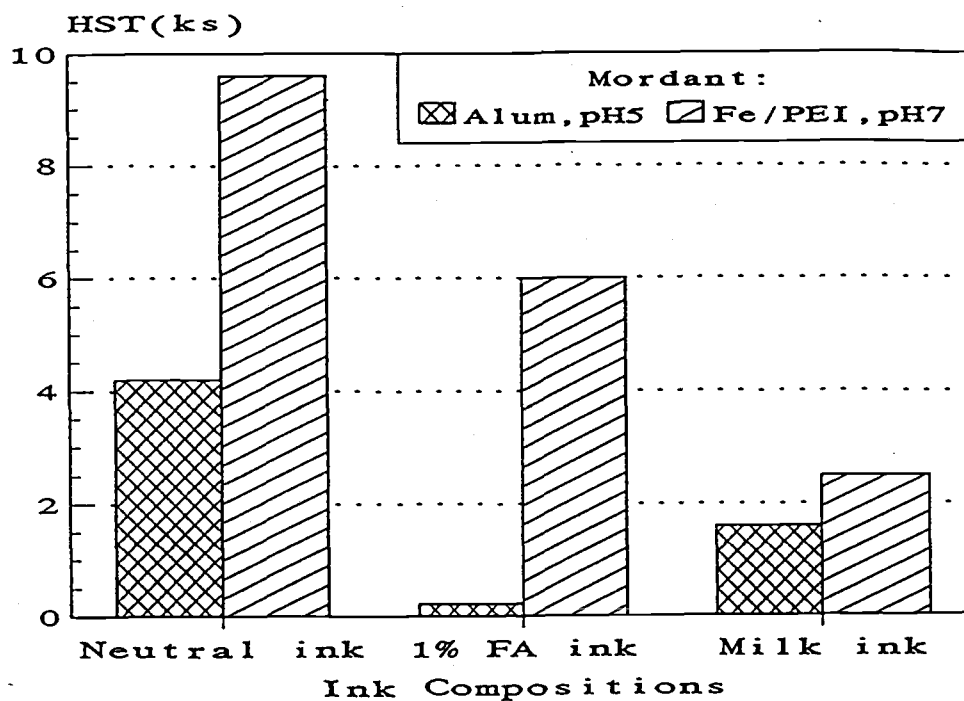
As discussed before, sizing has meanings only when the liquid with which paper is put in contact is specified. The composition of the testing liquid can have overwhelming effect on the testing results obtained. It is well known (6) that rosin-alum sized paper is not resistant to both acids and alkali. People have customarily regarded these inferior performance as the inherent property of rosin size without a good understanding of the reasons. This study shows that rosin-alum sized paper is not resistant to both acids and alkali mostly because of the chemical reactivity of alum, not that of rosin size. The resistance to acids and alkali could be improved when a different mordant is used.

Because rosin-alum sized paper has low resistance to lactic acid, synthetic sizing agent such as AKD or ASA must be used in the sizing of certain grades of paper such as milk carton (6). Rosin-Fe<sup>2+</sup>/PEI sized paper has been shown to be very resistant to 1% formic acid ink. Can it be resistant to milk or ink of higher formic acid concentration so that rosin-Fe<sup>2+</sup>/PEI sizing might be applied in the

manufacture of milk carton? **Figure 5.18** demonstrate the effect of ink compositions on the HST testing results. It can be seen from **Figure 18a** and **Figure 18b** that although rosin- $\text{Fe}^{2+}$ /PEI sized paper has extremely high resistance to neutral ink and 1% formic acid ink, its resistance to milk ink (the mixture of half neutral ink and half grocery store 2% milk) and 5% formic acid ink is not impressive. Rosin- $\text{Fe}^{2+}$ /PEI sized paper has even lower resistance to 1%  $\text{NH}_3$  ink. Aqueous  $\text{NH}_3$  solution contains ligands  $\text{OH}^-$  (the alkalinity) and  $\text{NH}_3$ . The possible ligand substitution reactions ( $\text{OH}^-$  and  $\text{NH}_3$  replace rosin, PEI and fiber components to complex with  $\text{Fe}^{2+}$  so as to dissociate rosin from the fiber surfaces and destroy the sizing) are believe to be the reasons.

**Figure 19** compares the resistance of rosin-alum/PEI sized paper and rosin- $\text{Cu}^{2+}$ /PEI sized paper to alkaline inks. Both handsheets are made from mechanical pulp and they both have extremely high HST values against the neutral ink. However, when the pH of the testing ink increases, the ink resistance (HST value) of rosin-alum/PEI sized paper drops dramatically, while that of rosin- $\text{Cu}^{2+}$ /PEI sized paper decreases much slowly. The reason is obviously due to  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  ion's very different affinity to hydroxide anions. Rosin sized paper can have an improved resistance to alkaline solutions if the metal ion mordant applied has a low affinity to hydroxide anions.

A.



B.

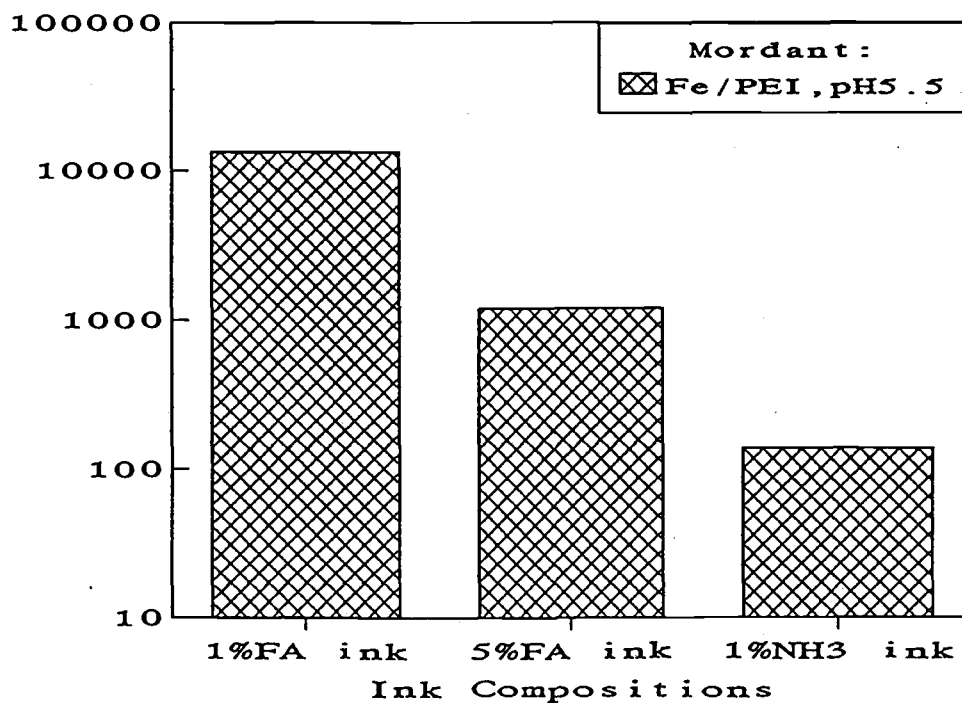
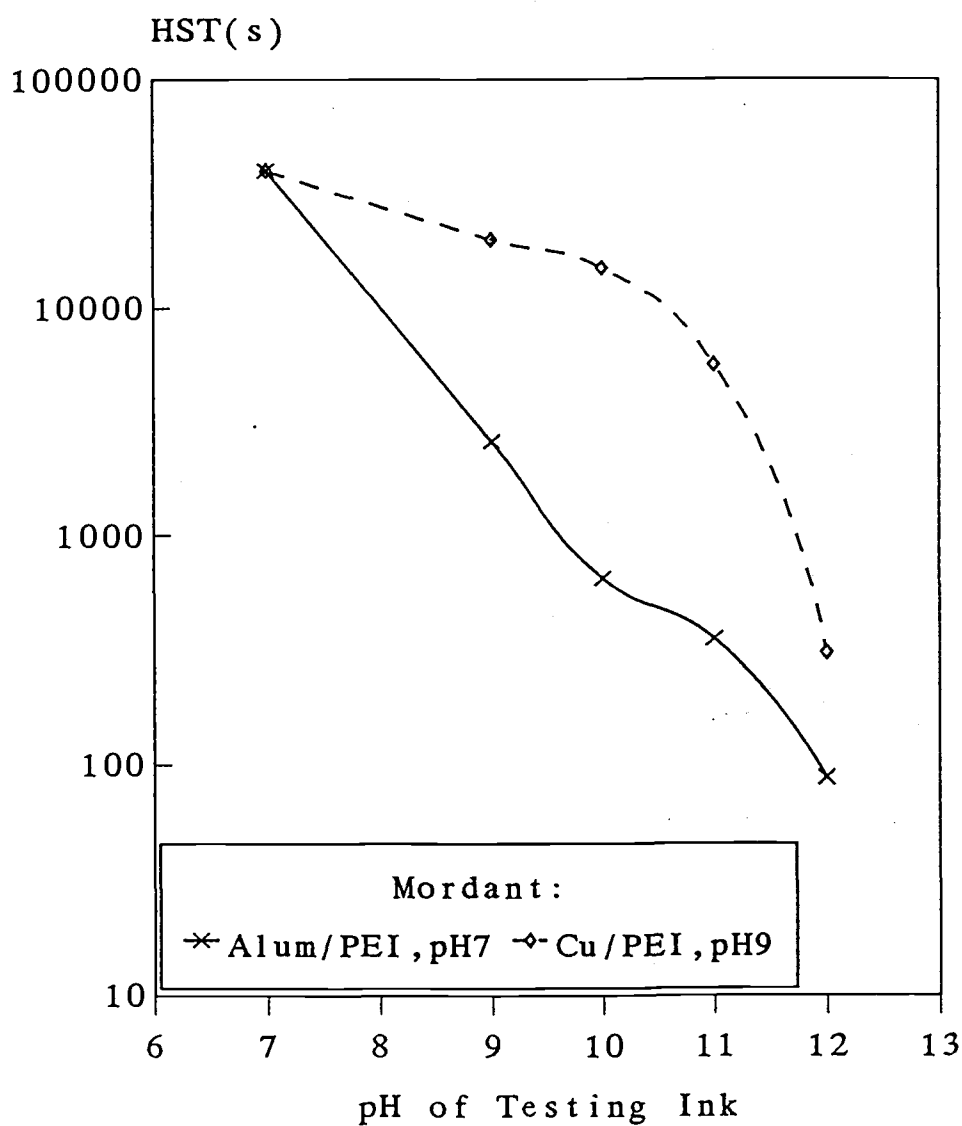


Figure 5.18 Effect of ink compositions on HST measurement



**Figure 5.19** Effect of ink pH on HST measurement. Mechanical pulp, PEI 0.5%. Alum 1.0%;  $\text{Cu}^{2+}$  2.5%.

#### 5.4 CONCLUSIONS

Various metal ions,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  were used in combination with PEI as mordants of rosin soap sizing in bleached hardwood and unbleached softwood kraft pulps and TMP. It is shown that:

1. Very high levels of sizing can be achieved with rosin soap size in all three pulps under neutral to alkaline conditions when proper mordants are used.  $Fe^{2+}$ /PEI is a very effective mordant up to pH 7, and  $Cu^{2+}$ /PEI is very effective from pH 7 to pH 9.  $Zn^{2+}$ /PEI can also induce moderate sizing at pH 7 to pH 8, but  $Fe^{3+}$ /PEI is only effective at pH around 4.  $Mg^{2+}$ /PEI and  $Mn^{2+}$ /PEI are not effective mordants.

2. The  $pK_1$  value of a metal ion is a good indication of its pH of maximum sizing efficacy. The direct relationship between the  $pK_1$  values of metal ions and their pH of maximal sizing efficiency indicates that the pH dependence of rosin sizing is related to, and probably only to, the mordant's affinity to hydroxide anions.

3. The metal ion's performances as mordants are consistent with the Irving-Williams Effect, which describes the general trends in the stability of metal complexes. This consistency is a strong indication that coordination chemistry is playing a key role in the mechanism of sizing development and that the integrity (strength under a certain set of conditions) of the rosin-mordant-fiber complex is of

central importance in sizing development.

4. Chemical reactions are involved in the mechanism of the HST test with formic acid ink. To discuss sizing without specifying the properties of the solution against which sizing is tested is meaningless since these properties affect the stability of the size-mordant-fiber complex.

5. The tensile and bursting strength of the handsheets can be increased by 20-30% in the three pulps if either  $\text{Fe}^{2+}/\text{PEI}$  or  $\text{Cu}^{2+}/\text{PEI}$  is used as the mordant instead of alum.

While these results might have limited commercial applicability due to the color effects and the cost of the mordants, the principles discovered should improve our understanding of the sizing mechanism and provide valuable guidance for further efforts in the field.

## 5.5 EXPERIMENTS

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 was Stafor (Westvaco Chemicals) and was used at a level of 0.5% solids on pulp throughout the study.

All metal ions were from reagent grade chemicals. The

percentages are to the weight of oven-dry pulp. Alum is as  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ ,  $\text{Mg}^{2+}$  is as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}^{2+}$  is as  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}^{3+}$  is as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}^{2+}$  is as  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}^{2+}$  is as  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{Zn}^{2+}$  is as  $\text{ZnCl}_2$ . For example, 2.0%  $\text{Fe}^{2+}$  as referred in this paper is actually 2.0%  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . The PEI (Aldrich, Milwaukee, WI) is 50,000-60,000 average molecular weight, with 40-50% primary amines, 25-30% secondary amines, and 25-30% tertiary amines.

Ten grams of pulp were taken and diluted to 650 ml. Then 0.05 grams of rosin soap size in dilute solution (concentration 0.2%) were added and the stock was stirred for 3 minutes. The appropriate amount of metal ions was added, following by the addition of polyamine after 1 minute. Then the pH of the stock was adjusted with dilute HCl and NaOH solutions with stirring for 5 more minutes. After one or more hours (unless otherwise specified), the stock was diluted to 5.0 liters with tap water and the pH was readjusted to the appropriate value.

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 sheets were dried in a sheet dryer at 250°F for 3 min. The sheets were conditioned at 72°F and 50% RH for at least 4 hrs before testing.

Cobb Size values were determined by TAPPI T 441 om-90. Ink resistance was determined on a Hercules Sizing Tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution (a solution of the same concentration of ink as the 1% formic acid ink made with distilled water instead of 2% formic acid, with an unadjusted pH of about 6.5).

Six handsheets were made for each trial condition and three of them were used for Cobb Size Test. The other three handsheets were used for the HST tests. Two measurements with both neutral and 1% formic acid ink were made on each handsheet. Since variances within a specific mordant condition are usually far smaller than the differences among different mordant conditions, the results were simply averaged and reported. Most reported experiment results, especially those around each optimal sizing pH and those from which specific inferences have been drawn, have been repeated at least once with good reproducibility.

## REFERENCES

1. Casey, J. P., Pulp and Paper: Chemistry and Chemical Technology, 3rd edn., John Wiley & Sons, New York, 1981.
2. Hiemenz, P. C., Principles of Colloid and Surface Chemistry, 2nd edn., Marcel Dekker, Inc., New York, 1986, p338.
3. Davison, R. W., Tappi 58(3):48(1975).
4. Ekwall, P. and Bruun, H. H., Tappi 37(7):303(1954).
5. Griggs, W. H. and Crouse, B. W., Tappi 63(6):49(1980).
6. Strazdins, E., Tappi 64(1):31(1981).
7. Cobb, R. M. K. and Lope, D. V., Tappi 38(2):49(1955).
8. Marton J. and Marton T., Tappi J. 65(11):105(1982).
9. Strazdins, E., Tappi 60(10):102(1977).
10. Strazdins, E., Tappi 48(3):157(1965).
11. Marton J. and Kurrle, F. L., J. of Pulp & Paper Sci. 13(1):J5-J9(1987).
12. Davison, R. W., J. of Pulp & Paper Sci. 14(6):J151 (1988).
13. Davison, R. W., Tappi 47(10):609(1964).
14. Kaltenbach, J., Das Papier 8(19/20):409(1954).
15. Vandenberg, E. J. and Spurlin, H. M., Tappi 50(5):209 (1967).
16. Churchill, R. K. and Martin, N. L., Pulp Paper Mag. Can. Convention Issue, 237(1956).
17. Robinson, S. J., Paper Trade J. 103(7):130(1936).
18. Reynolds, W. F., The Sizing of Paper, 2nd edn., TAPPI PRESS, Atlanta, 1989.
19. Strazdins, E., Tappi 46(7):432(1963).

20. Duston, H. E., Tech. Assoc. Papers, 25:475(1942).
21. Subrahmanyam, S. and Biermann, C. J., Tappi J. 75(3): 223(1992).
22. Turner, R. C., Can. J. Chem. 54:1528 and 1910(1976).
23. DeBruyn, P. L., DeHek, H., and Stol, R. J., J. Colloid Interface Sci., 51(3):449.
24. Turner, R. C., Can. J. Chem. 53:2811(1975).
25. Brosset, C., Biedermann, G., and Sillen, L., G., Acta Chem. Scand. 8:1917(1954).
26. Biedermann, G., Svensk. Kem. Tidskr. 76:362(1962).
27. Grunwald, E., and Fong, D., J. Phys. Chem. 73:650 (1969).
28. Aveston, J., J. Chem. Soc.:4438(1965).
29. Arnson, T. R., Tappi 65(3):125(1982).
30. Arnson, T. R. and Stratton R. A., Tappi J. 66(12):72 (1983).
31. Jaycock, M. J. and Pearson, J. L., Svensk Papperstid. 78(5): 167(1975).
32. Jaycock, M. J. and Pearson, J. L., Svensk Papperstid. 78(8):289(1975).
33. Reynolds, W. F. and Linke, W. F., Tappi 46(7): 410 (1963).
34. Linke, W. F., Tappi 45(4):326(1962).
35. Strazdins, E., Tappi J., 67(4):110(1984).
36. Strazdins, E., Tappi J., 69(4):111(1986).
37. Marton J. and Kurrle, F. L., 1985 Papermaking Conference Proceedings, TAPPI PRESS, Atlanta, GA, p.197.
38. Matijevic, E., Janauer, G. E., and Kerker, M., J. Colloid Sci. 19:333(1964).
39. Matijevic, E., J. Colloid Interface Sci. 43(2):217 (1973).

40. Strazdins, E., Can. pat. 1,008,609 (1977).
41. Marton, J., 1985 Advanced Topics in Wet End Chemistry Seminar, TAPPI PRESS, Atalanta, GA, p.29.
42. Marton, J., Nordic Pulp & Paper Research J. No.2:77 (1989).
43. Marton, J. and Jarrell, D. D., 1987 TAPPI Sizing Short Course, Atalanta, GA, p.53.
44. Gess, J. M., Tappi J. 72(7):77(1989).
45. Thomas, A. W., Tech. Assoc. Papers 18:242-245(1935).
46. Wilson, W. S., Tappi 32(9):429-432(1949).
47. Wilson, W. S. and Duston, H. E., Tech. Assoc. Papers, 27:673-678(1944).
48. Price, D., Ind. Eng. Chem. 39:1143-1147(1947).
49. Price, D., Analyst. Chem. 20(5):444-449(1948).
50. Price, D. and Cameron, D. D., Pulp Paper Mag. Canada 40:142-148(1946).
51. Duston, H. E., Tech. Assoc. Papers 25:475-478(1942).
52. Porter, E. N. and Lane, W., Tappi 32(10):465(1949).
53. Huheey, J. E., Inorganic Chemistry, Principles of Structure and Reactivity, Happer & Row Publishers, New York, 3rd edn., 1983. p.381, etc.
54. Weisgerber, C. A., Davis, J. W., and Roberson, W. H., Tappi 39(12):21(1956).
55. Wurzbeg, O. B. and Mazzarella, E. D., US pat. 3,102,064 (Aug. 27, 1963).
56. Davidson, R. R., Paper Technology 8(4):370(1967).
57. Wortley, B., PIMA Magazine 71(2):44(1989).
58. Rohringer, P., Bernheim, M., and Wertheman, D. P., Tappi J. 68(1):83(1985).
59. Isogai, A., Taniguchi, R., Onabe, F. and Usuda, M., Nordic Pulp & Paper Research J. 7(4):193(1992).

60. Bottorff, K. J., Tappi J. 77(4):105(1994).
61. Odberg, L., Lindstrom, T., Liedberg, B., and Gustavsson, J., Tappi J. 70(4):135(1987).
62. Lindstrom, T. and Soderberg, G., Nordic Pulp & Paper Res. J. 1(2):31(1986) and 1(1):26(1986).
63. Dumas, D. H. and Evans, D. B., 1986 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, GA, p.31.
64. Burke D. J., Tappi J., 76(4):40A(1993).
65. Dumas, D. H., TAPPI Sizing Short Course, TAPPI PRESS, 1980, p.47.
66. Abell, S., 1985 Alkaline Papermaking Conference Proceedings, TAPPI PRESS, Atlanta, GA, p31.
67. Wiley, T., Pulp & Paper 62(12):43(1989).
68. Gess J. M., Tappi J. 75(4):79(1992).
69. Crouse, B. W., and Wimer, D. G., Tappi J. 74(7):152 (1991).
70. Hennessy, T. J., Southern Pulp & Paper, No.4:18(1983).
71. Scalfarotto, R. E., Pulp & Paper 58(4):126(1985).
72. Chen, G. C., Belgard, W. E., and Olson. C. R., 1987 Papermakers Conference Proceedings, TAPPI PRESS, Atlanta, GA, p.133.
73. Gess, J. M., Tappi 64(1):35(1981).
74. Kurrel, F. L., 1987 Sizing Short Course, TAPPI PRSEE, Atlanta, GA, p.9.
75. Guide, R. G., Tappi 42(9):740(1959).
76. Atkins, P. W., Physical Chemistry, 4th edn., W. H. Freeman and Company, New York, 1990, p104.
77. Zhuang, J. & Biermann, C. J., Tappi J. 76(12):141(1993).
78. Biermann, C. J., Tappi J. 75(5):166(1992).

79. Zhuang, J. & Biermann, C. J., unpublished work.
80. Cotton, F. A. and Wilkinson, G., Advanced Inorganic Chemistry, Interscience Publisher, New York, 4th edition, 1980.
81. Collman, J. P., Hegedus, L. S., Norton, J. R., and Finke, R. G., Principles and Application of Organo Transition Metal Chemistry, University Science Books, 1987. p. 158-168, 239, 149.
82. Weast, R. C., CRC Handbook of Chemistry and Physics, CRC Press, Inc., Florida, 67th edition, 1986:p.F-31.
83. Snoeyink, V. L. and Jenkins, D., Water Chemistry, John Wiley and Sons, New York, 1980, p.384.
84. Lindstrom, T., Svensk Papperstidn. 85(3):R14(1982).
85. Pankow, J. F., Aquatic Chemistry Concepts, Lewis Publishers, Michigan, 1991: p369.
86. Singh, R. P., The Bleaching of pulp, TAPPI Press, 3rd edition, 1979:p.263.
87. Zabel, R. A. and Morrell, J. J., Wood Microbiology, Decay and Its Prevention, Academic Press, San Diego, CA, 1992:p.331.
88. Biermann, C. J., Essentials of Pulping and Papermaking, Academic Press, San Diego, CA, 1993, p.156.
89. Herner, B., Pulp & Paper. 64(1):141(1990).
90. Chizhov, G. I., et. al., Mezhevuz. Sb. Nauch. Tr., Khim. Tekhnol, Drev. Tsellyul. (Nepenin, Y. N., Ed.), 1983, p17.
91. Zhuang, J. and Biermann, C. J., A Thermodynamic Analysis of the Rosin Sizing Process, unpublished.
92. Zhuang, J., Liu, R., and Cao, G., China Pulp and Paper, No.6: (1986).