

AN ABSTRACT OF THE THESIS OF

Sriram Subrahmanyam for the degree of Master of Science in Forest Products presented on July 8, 1991.

Title : Studies on Rosin Soap Size Interaction with Selected Coordinating Metal Elements in the Sizing of Paper.

Abstract approved : Signature redacted for privacy.

Christopher J. Biermann

Several chemical additives are used in papermaking to impart paper the property to resist penetration of aqueous liquids. The most common additive used for this purpose is rosin size. The rosin is fixed onto the pulp fibers with the help of certain metal salts like papermaker's alum (aluminum sulfate). Several publications have come out in the past on the sizing of paper with rosin. Even though rosin is widely used, the type of interaction in rosin soap sizing has not been clearly understood.

Rosin sizing, with a variety of coordinating elements, was predicted to occur based on coordination chemistry principles. The purpose of this study was to highlight the importance of coordinate reactions taking place in rosin sizing. The effectiveness of selected coordinating elements as sizing mordants was observed with alum as the control. There are several advantages with extending the use of rosin soap size beyond the pH range of 4-6, the range currently

being employed. Some of the benefits, especially in the alkaline range, are higher paper strength, use of inexpensive calcium carbonate fillers, lower corrosion rates of the papermaking system, and improved permanence of the paper.

Sizing studies with rosin soap size and several metal salts were carried out. The metal elements were mainly chosen from the lanthanide series (Ce, Er, Eu, Dy, Ga and La). As expected, the degree of sizing was pH dependent, and sizing results obtained with alum (as a mordant), were generally better than with the other elements used in this study. However, these element complexes were effective at pH ranges where the aluminum rosinate complex is ineffective as a sizing mordant. Different mordants used in this study gave maximum sizing, as measured by the Hercules sizing test with neutral ink and reported in seconds, as follows: alum 585 (pH=5.0), cerium chloride 310 (pH=7.0), cerium sulfate 257 (pH=7.0), dysprosium chloride 342 (pH=7.0), dysprosium sulfate 320 (pH=7.0), erbium chloride 436 (pH=7.0), erbium sulfate 350 (pH=7.0), europium sulfate 325 (pH=7.0), gallium sulfate 280 (pH=4.0), lanthanum chloride 235 (pH=7.0) and lanthanum sulfate 113 (pH=6.5).

The effectiveness of any metal ion as a sizing mordant was dependent on the first acid ionization constant, K_1 . The peak value of its effectiveness was at a pH in the vicinity of the pK_1 value of the metal ion. This allows one to predict the ideal pH to use with any suitable mordant in sizing.

The results suggest that rosin soap size can be used in

neutral and alkaline conditions. These results, besides enhancing our current knowledge, give a better perspective of the mechanism involved in the rosin soap sizing process.

Studies on Rosin Soap Size Interaction with Selected
Coordinating Metal Elements in the Sizing of Paper

by

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STUDIES ON ROSIN SOAP SIZE INTERACTION WITH SELECTED COORDINATING METAL ELEMENTS IN THE SIZING OF PAPER

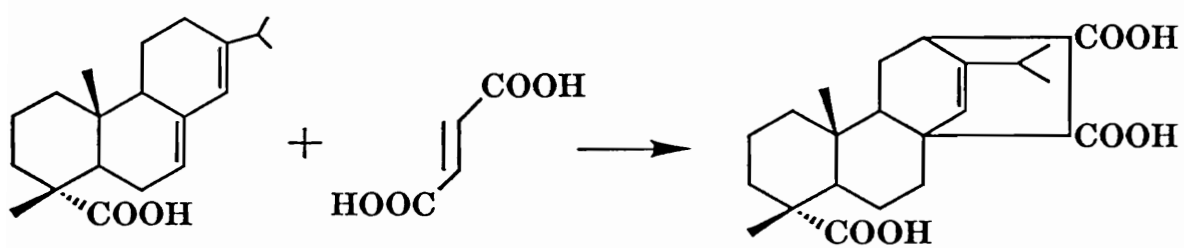
I. INTRODUCTION

Sizing is the property of paper to resist the penetration of aqueous liquids through it. Sizing of paper is usually subdivided into two types - internal and external or surface sizing. This study is restricted to internal sizing. The property of internal sizing, is extremely important for most grades of paper, especially printing and structural grades. This property is imparted by reacting the pulp fibers as a dilute aqueous suspension with molecules which have both hydrophobic and hydrophilic moieties. The hydrophobic moiety resists wetting while the hydrophilic moiety make these compounds water dispersible and provides a reacting site to anchor the molecules onto the fibers. Once these compounds have reacted with the cellulosic fibers, they make the fiber surface hydrophobic. To fix the rosin molecules onto the fibers, metal salts like alum are used as intermediatories.

These types of intermediate fixing agents have been termed mordants. In the textile industry a mordant is a substance that fixes colored dyes to the fabric material. A mordant works by combining with the oxygen or nitrogen atom of the dye to form an insoluble complex that attaches onto the fibers. Due to the similar characteristic of the size fixing intermediate compound, the use of the word mordant seems appropriate to describe the effect in rosin sizing. In

fact alum is a common mordant in textile dyeing. Sizing with rosin dates back to 1807, when rosin was fixed to the fibers with papermaker's alum (aluminum sulfate). Traditionally, rosin sizing was the common method to size paper. However, in modern formulations, to improve the reactivity of the rosin molecule, rosin is fortified through its reaction with maleic or fumaric acids yielding a tricarboxylic acid. The rosin fortification reaction is shown in Figure 1.

There are basically two categories of rosin sizes - soap size and dispersed phase size. In soap size the rosin acid is in the salt form and is water soluble. On the other hand, in the dispersed phase size the rosin acid is dispersed as an emulsion in an aqueous medium. Rosin soap size is effective only when sizing is carried out in the pH range of 4-5.5, whereas the dispersed phase sizes are effective at a slightly higher pH range. There has been substantial research work done on sizing, in spite of these efforts, the type of interaction taking place in rosin soap sizing still remains unclear. The focus of this study was to determine the probable mechanism of rosin soap sizing based on coordination chemistry principles. Extending the use of rosin soap size beyond the pH range of 4-6 and especially into the alkaline range, has numerous benefits. Some benefits obtained with this change are: higher paper strength, use of inexpensive calcium carbonate as an inorganic filler, higher filler percentages, less corrosion of papermaking system, and

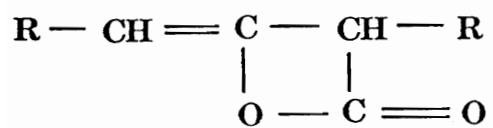


Abietic acid

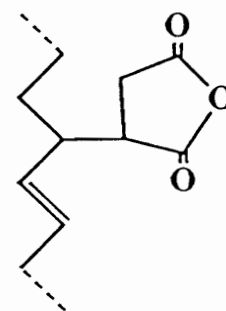
Fumaric acid

Fumaropimaric acid

Figure 1. Rosin fortification reaction.



Alkyl Ketene Dimer



Alkenyl Succinic Acid

Figure 2: Synthetic sizes.

improved permanence of the paper.

The improved quality and economy added to the paper, has driven the paper industry to switch from an acid to an alkaline papermaking system. While less than 20 % of paper was made under alkaline conditions just a few years ago, the percentage is expected to be over 60 % a few years from now. With the search for new sizing agents that are effective in alkaline conditions, new ideas have been added to our current knowledge. This has resulted in the use of sizing agents like alkenyl succinic anhydride (ASA), alkyl ketene dimer (AKD), stearic acid, etc. However, these synthetic sizing agents are expensive and difficult to use. The structures of synthetic sizes are shown in Figure 2.

To find a simpler approach to this problem and to gain a clearer insight into the interaction of rosin sizes, this study has looked into the possibility of using the inexpensive and readily available rosin soap size. A variety of coordinating metal elements were chosen to get a better understanding of the type of interaction taking place with the metal salts added as mordants. To achieve this objective selected metals, especially from the lanthanide series, were taken for this study due to their coordinating ability. Sizing studies were carried out with the chosen elements to look at their effectiveness as a sizing mordant in different pH ranges.

II. LITERATURE REVIEW

A. Theory of metal-size interaction

To understand clearly the nature of interaction between different ions in the sizing process, the past and present views on sizing must be reviewed. The importance of coordination chemistry of these ions involved must be clearly understood.

The view on coordination interaction of metal ions in sizing process started in 1935, with Arthur W. Thomas of Columbia University (1). He was of the view that aluminum could coordinately bind with different anions and at the same time with cellulose. To confirm his findings considerable work was done later by Wilson on aluminum bonds (2), by Price (3) and by Price and Cameron on acid, alum, and the alum-rosin precipitate (4), by Duston (5) and by Porter and lane (6) on the use of aluminum chloride. Considerable experimental verifications were done by electrophoretic mobility of rosin-aluminum sulfate complex by Collins, Davis and Rowland (7) and by Thode, Gorham and Atwood (8). However, this view has not predominated the views on sizing and the importance of this hypothesis has been undermined by the later hypotheses put forth.

To reassert the coordination interaction in rosin sizing, this study was undertaken and considerable sizing

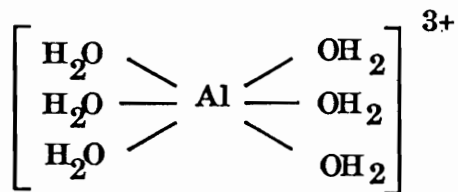
studies carried out. Several coordinating metal ions like cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gallium (Ga) and lanthanum (La) were used in this study besides aluminum.

Rossotti (9) has defined a complex as a species formed by the association of two or more simpler species each capable of independent existence. According to coordination chemistry the number of neutral or anionic species coordinately attached to a central cation is termed the coordination number. This number is determined by the size of the cation and the number of molecular orbitals present in it. Thus small cations like Beryllium in aqueous solutions coordinate with four water molecules at the corners of a tetrahedron, forming $[\text{Be}(\text{OH}_2)_4]^{2+}$. While larger molecules like aluminum coordinate with six water molecules at the corners of an octahedron, to give $[\text{Al}(\text{OH}_2)_6]^{3+}$, as they have additional empty "d" orbitals (10,11). A closer look of how the bond is formed, with alum in consideration, will give us a better understanding on coordination interaction. Coordination complexes are formed upon the reaction of Lewis acids, compounds which accept electron pairs, with Lewis bases, compounds which donate electron pairs. The term ligand denotes the species donating the electron pair. Because of steric hinderance, generally only one pair of electrons from one atom is donated to a particular atom. Thus, while the oxygen atom of water has two free electron pairs, only one

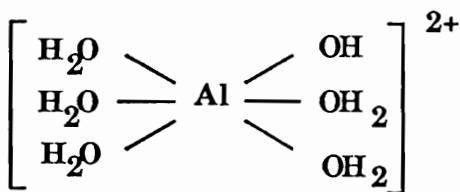
pair act with a particular aluminum cation. The oxygen atom of the OH^- ion, which has three unshared electron pairs, shares only one pair of electrons with a particular aluminum cation. However, the oxygen atom of the OH^- group is known to form coordinate bonds with two different coordinating cations and, thereby, forming a bridge. The bridging of two aluminum cations in aqueous solution is shown in Figure 4. These bridges are crucial to rosin sizing with alum as they increase the size of the aluminum-rosin complex and decrease water solubility. Complexes involving 2-8 or more aluminum ions in aqueous solutions are well known (11). Dimers of ferric ions complexed with OH^- are well known at pH 2-3, while highly condensed species occur at higher pH's (11a).

Over the years, alum has been widely used in the sizing of paper. Therefore it is more likely that a study on the interaction of alum as an example would clearly explain the behavior of other coordinating elements added as a sizing mordant. Thomas explained the peculiarities of aluminum salts based on the theory of polymerization known as olation, put forth by Werner and Pfeiffer (1). According to Pfeiffer the hydrolysis of the hydrated aluminum complex takes place as shown in Figure 3.

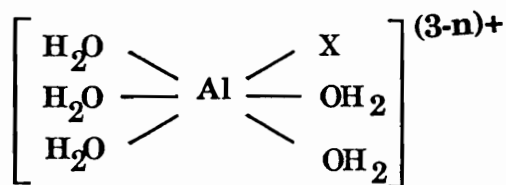
The extent of dissociation has been found to depend upon the nature of the anion that coordinates with the cation, concentration, temperature and basicity of the solution (1). Basicity plays a vital role in influencing the extent of



Hexa-aquo-alumini ion



Penta-aquo-hydroxo ion



Penta-aquo-X ion

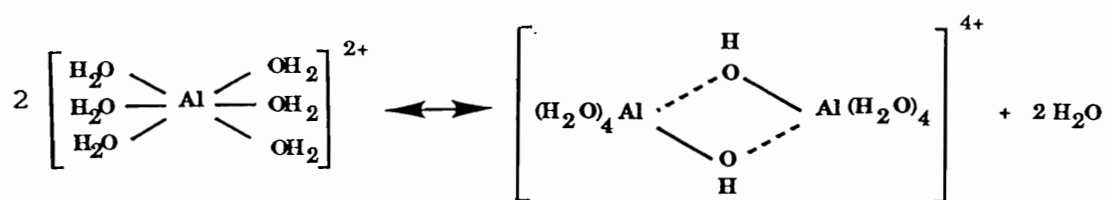
X^{n-} = Any ligand

Figure 3. Typical aluminum complex in aqueous solutions.

dissociation because added hydroxide ion removes one of the products formed, namely a proton and promotes further hydrolysis. Upon addition of alkali, the OH^- groups successively substitute the water molecules in the complex and promote polymerization by bridging with a different cationic complex.

In 1902, Pfeiffer (1) suggested the possibility of a coordinative bond of each of two metal atoms being shared by one hydroxyl group which Werner termed them as *ol* compounds.

A schematic representation of the dimerized aluminum complex would be



Penta aquo hydroxo
aluminum ion

Octa aquo
dialuminum ion *ol* complex

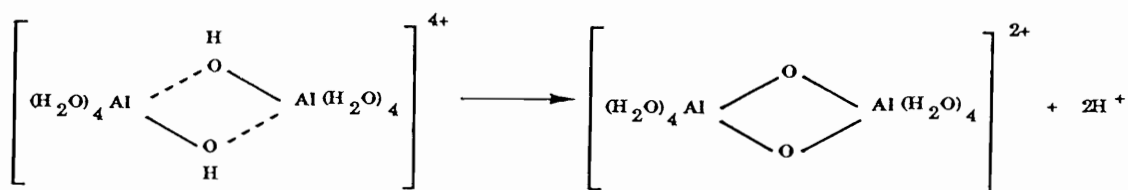
Figure 4. Polymerization (*olation*) of metal complexes.

This polymerization is favored by elevation in temperature and increase in concentration (1). The polymerized aluminum complex is stable and does not easily revert back either on cooling or on dilution. From the above mechanism, it is evident that *olation*, by virtue of removal of one of the

products, favors the reaction to the right.

The addition of an alkali to a solution of an aluminum salt, which results in the formation of more hydroxyl groups in the complex around the metallic atom, greatly increases the process of olation. Besides, as the acidity of the solution is neutralized, not only is the rate of formation of ol compounds increased, but also the reaction will involve more nuclei to form polynuclear compounds through bridging.

Stiasny (1), in 1926, revived interest in the process of olation and after noticing that solutions containing analogous complexes of chromium becoming very acidic and producing refractory chromic complexes on heating, he suggested that the hydrogen atom of the hydroxyl group bridging the two metal complex is lost as a proton. Such conversion of ol bridges to oxygen bridges, is called oxalation. Oxo compounds are very resistant to the action of hydrogen ion. Thus once the reaction to the right has been effected, its reversal is exceedingly slow.



Octa aquo dialumini
diol complex

Octa aquo dialumini
dioxo complex

Figure 5. Conversion of ol to oxo complex.

Unlike aluminum, lanthanide group elements do not have a tendency to form oxo complexes. Therefore the tendency for lanthanide elements to form stable complexes is expected to be less than aluminum (11). In other words the level of sizing would be expected to be less than with aluminum. Upon hydrolysis of any of the water molecules shown in Figure 4, it is seen how coordination with other similar nuclei may result through the hydroxyl groups thus formed, producing larger complexes. With the dissociation of a water molecule, a hydrogen ion leaves the complex thereby reducing the charge on the complex. When the charge of nuclei is reduced, so is the stability in solution (11b). It is well-known that addition of alkali causes precipitation of the dispersed phase of "hydroxide" sols (1).

Reactions in dilute aqueous solution during rosin sizing have been the key focus in the past, but it should be realized that the equilibrium mixtures of the coordinating species increase with the decrease in water content in web in the papermaking process. Thus many coordination complexes will form in the press and dryer sections, where the concentrations of the species involved are somewhat high as is the temperature of the system. Higher temperatures are not required. Furthermore higher temperatures increase the reaction rate of the slow coordination reactions. This explains why heat setting of the rosin size is important. It has been observed that heating of paper at 250⁰F for

approximately two minutes is necessary to develop fully surface sizing with zirconyl acetate (12). Chemistry in dilute aqueous solutions is important principally as a means of dispersing the size and salt mixtures for better interaction.

Rosin sizing with mordants, with alum as an example, can be considered to occur in hypothetically three distinct steps. First, aluminum in alum complexes with neutral and anionic ligands such as water, rosinate ion, hydroxyl ion, sulfate ions and other groups which may be present in the solution to form a relatively large complex of complicated structure called the aluminum-rosinate complex, which is depicted hypothetically in Figure 6.

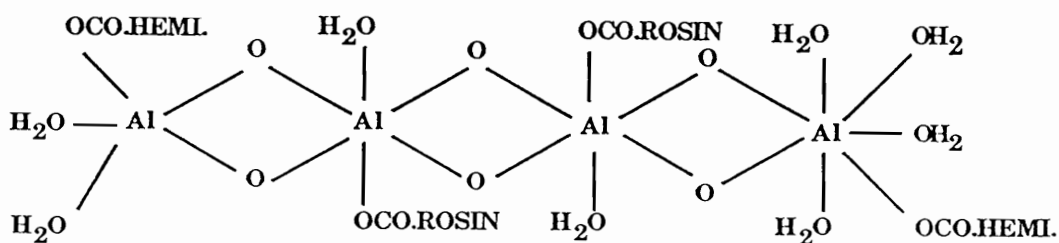


Figure 6. Hypothetical structure of aluminum-rosin complex.

As already mentioned, the type of complex formed depends on the nature and concentration of the reacting species (ligands), basicity and temperature. Thus, it is essential to keep in mind, however, that the aluminum-rosinate complex contains more than just aluminum and rosinate anion, and the

effectiveness with which the type of complex formed needs careful control of different variables mentioned above. The aluminum-rosin complex must have limited water solubility. If the complex is too stable in water, the equilibrium with fiber complexing will be small and the rosin will not be retained. Alum at pH below 4 has very little sizing ability because the Al^{3+} ions have not complexed with OH^- species. Therefore, it has a high solubility. While rosinate certainly coordinates with aluminum at pH of 4, the complex is not retained on the fiber as it is at higher pH's.

In the second step water is removed from the web with the retention of the aluminum-rosin complex. Finally, in the third step, the remainder of the water is removed and the temperature increased in the dryer section. This allows new stronger bonds to form that are not possible in dilute, aqueous solutions. Elevated temperatures enhance the speed of the coordination reaction (1). As the concentration of the aluminum rosin complex increases, additional coordinate bonds are allowed to form with cellulose fibers provided the pH is not too high. At high pH, OH^- groups, which have higher affinities to coordinate, occupy most of the available sites that might otherwise complex with functional groups of the cellulose fiber. The reason that the emulsion sizes are so effective at higher whitewater pH's is probably because they can effectively lower the pH during the drying of the paper near the aluminum-rosinate complexes.

Carboxylate groups of the hemicelluloses on the surface of fibers, being anionic, would allow the formation of strong coordinate bonds with the aluminum-rosinate complex. The origin of the carboxyl group, which is the main constituent group to render the fibers negatively charged, can be traced to the non-cellulosic polysaccharides of the native wood. Although, there are no carboxyl groups present in cellulose, the non-cellulosic polysaccharides, namely hemicellulose, lignin, etc., are closely associated with the fiber structure and are present even after the pulping process. Most of the carboxyl groups are present in the xylan backbone of the hemicellulose (13). Besides carboxylate groups, other functional groups, though to a much lesser extent, available as ligand on the surface of the fiber are hydroxyl, phenolic and alcoholic groups. Phenolic hydroxyl groups, being weakly acidic, need a rather high pH to ionize. The alcoholic groups are far less acidic than phenolic groups and require strong alkali to ionize. It should, however, be mentioned that because of the inductive effect of certain groups attached to the structure can strongly influence the ionization of phenolic and alcoholic hydroxyl groups. But, under papermaking conditions the carboxylate groups mainly influence the sizing process due to their reactivity than the other groups. It is well known that pulps with higher concentrations of carboxylate groups are more effectively sized than pulps with lower concentrations or without

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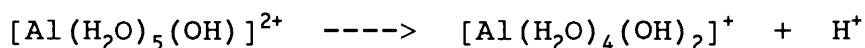
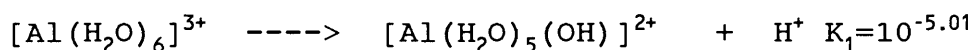
carboxylate groups (14).

Over the years, many publications have tried to explain the mechanism of rosin sizing. Few of them have stressed the coordination aspect of interaction resulting in conflicting view points. The common explanations are that the type of interaction taking place is ionic interaction of aluminum and rosinate ions resulting in ionic compound with resultant positive charge. These charged compounds eventually are held by ionic forces. Furthermore, heating of the sheet should have very little to do with sizing efficacy if this is true. Also the failure of quaternary amines to act as a mordant argues that this is not so. Finally, ionic bonds due to their high polarity are easily destroyed by highly polar solvents like water, where as coordinate bonds are more non-polar.

In the sizing process the pH is a vital variable, which influences the performance of a particular type of mordant used. Unlike, the earlier held view about soap size being able to be employed only between a narrow pH range of 4-6, it has been shown that depending on the type of mordant used the range could be extended beyond this range. For example sizing with ferric ion is possible well below the pH of 4 where aluminum cannot be employed (15) and the present study has demonstrated rosin soap size can also be employed above pH of 7.5 in the presence of an appropriate mordant. Let us investigate the characteristic of a variety of candidate

mordants for rosin sizing of paper in terms of coordinate chemistry.

Substitution reactions occur when one ligand is replaced by another, such as when a water molecule is replaced by a rosinate ion, sulfate anion, etc. Metallic complexes of water may undergo hydrolysis, a type of substitution reaction that is equivalent to acid dissociation. For aluminum the first two acid dissociations are as follows:



The value of the second dissociation constant has little practical significance because of formation of the polyaluminum complexes mentioned previously. It is useful to know that when the pH of a solution is equal to the pK_a of an acid, then both the acid and the conjugate base are present in equal amounts. This is a consequence of the Henderson-Hasselbalch equation. Thus in the case of acetic acid, which has a pK_a of 4.75 for the acid ionization, an aqueous solution of acetic acid at pH of 4.75 has equal concentrations of acetic acid and acetate ion species. With aluminum and other highly coordinating species the chemistry is more complex. The pK_1 for the first ionization of aluminum is 5.01. Due to the complex formation with OH^- ions from

solution the pH of the solution drops. Thus 0.5 equivalents of OH^- is expected to neutralize this drop in pH. It has been observed that as much as 2.5 equivalents of OH^- per equivalent of aluminum is required to bring the pH back to 5.01. The reason is that competing reactions involving higher substitutions and polyaluminum complex occur. It has been observed that maximum sizing occurs at a pH near the pK_1 of the aluminum ion. So, the first acid dissociation constant, pK_1 , of a variety of coordinating metallic ions will be used to predict their mordant action in rosin sizing as a function of pH.

Earlier work with different metal ions besides aluminum as mordants have been studied with rosin soap size. Some of these elements were Cr^{3+} , Fe^{3+} , Ca^{2+} , Cu^{2+} and Mg^{2+} (15). Ferric ion has been known to be used in U. S. during World War II when the availability of alum was limited. The Fe^{3+} ($\text{pK}_1 = 2.83$) gave effective sizing at pH 3.6 and Cu^{2+} ($\text{pK}_1 = 8.0$) at pH 6.9. The reason for effective sizing with ferric ion at lower pH is due to the higher affinity for OH^- ions by Fe^{3+} ions. On the other hand cupric ion has a maximum sizing efficiency at a higher pH due to their low affinity for OH^- ions when compared with Fe^{3+} .

III. EXPERIMENTAL PROCEDURE

A. Wood Pulp Characteristics

Bleached kraft hardwood pulp was used for the complete set of experiments. The pulp sheets were defibered in a pulper and refined in a disk refiner. The following conditions were maintained.

Consistency : 2.5 %

CSF : 360

The refined pulp was stored in plastic containers at a consistency of 10 % in cold storage. Portions of this thickened pulp was diluted to 1.5 % consistency before use.

B. Preparation of size solution

Potassium resinate (5.0 g), (Stafor liquid 50 %, Westvaco) was dissolved in 1 liter of distilled water (pH = 9.25). The size solution was prepared fresh everyday to prevent any variability in results.

C. Preparation of mordant solution

1. Alum : Hydrated aluminum sulfate (8.0 g), ($\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$, reagent grade 98-102 %, Aldrich Chemical Co.) was dissolved in 1 liter of distilled water (pH = 2.8).

2. Lanthanide group elements and gallium : The procedure followed in preparing the solutions was similar to the one followed for alum. The respective amounts of different metal salts used is given in Table 1. The amounts of different

metal salts used for each set of sizing experiments were based on the molar amount of alum corresponding to 40 lb/ton (2 %) of hydrated alum. For example 0.024 grams hydrated alum (per 1.2 g handsheet) with formula weight of 666.41 is equal to 0.072 milliequivalents (meq) of Al^{3+} ; 0.072 meq of cerium (III) chloride heptahydrate (formula weight of 372.59) is 0.0268 g per handsheet.

D. Preparation of Ink

1. Neutral Ink : Equal volumes of the 2.5 % green naphtha dye (Hercules Inkpak, Hercules Inc.) and distilled water were mixed (pH = 3.87). The shelf life of this mixture is 1 week.

2. 1% Formic Acid Ink (#2 Ink) : Equal volumes of 2 % formic acid and 2.5 % green naphtha dye (Hercules Inkpak, Hercules Inc.) were mixed (pH = 1.9). The shelf life of this mixture is 6 weeks.

E. pH Measurements

All pH measurements were made with a Orion Research 601A digital ionalyzer equipped with a general purpose combination glass electrode (Corning Cat. No. 476531). Prior to the pH measurements, the glass electrode was calibrated with standard pH buffers (Mallinckrodt Chemical Works) 4.00, 7.00 or 10.00. The electrodes were rinsed with distilled deionized water after each measurement. Measurement were corrected to a temperature of 25⁰C

Table 1 : Amounts and pH of mordant solutions

Component	Amount (g/L)	pH
Cerium(III)chloride heptahydrate	8.80	4.85
Cerium(III)sulfate anhydrous	6.85	3.75
Dysprosium(III)chloride hexahydrate	8.82	4.82
Dysprosium(III)sulfate octahydrate	8.86	3.74
Erbium(III)chloride hexahydrate	8.93	5.03
Erbium(III)sulfate octahydrate	8.96	3.90
Europium(III)sulfate octahydrate	8.61	4.00
Gallium(III)sulfate	5.00	2.35
Lanthanum(III)chloride hexahydrate	8.62	5.09
Lanthanum(III)sulfate octahydrate	8.31	3.50

F. Procedure

A weight of 10 g (O.D basis) of the refined pulp was used for each experiment. The pulp sheets were repulped in a repulper and then refined in a disk refiner at a pulp consistency of 2.5 %. The pulp was refined to an average freeness of 360 CSF was obtained. The freeness of the pulp was measured according to the Tappi standards (T227 om-85). The pulp at a consistency of 1.5 % was taken in a plastic beaker was stirred continuously to keep the fibers from settling. The rosin size solution (50 mL) was added to the pulp stock and allowed to mix completely. At the end of 5 minutes the mordant solution (50 mL) was added to this stock

stock and left stirred for one hour. Thereafter, the pulp was diluted to a consistency of 0.25 % with tap water with the pH adjusted to that of the stock. A 500 mL of this dilute stock was taken and a sample handsheet formed on the British Sheet Mold. The sheet was pressed in a hydraulic press and dried in a speed drier (Emerson Speed Dryer, Emerson Apparatus Co.). The sheet was weighed and based on its weight the volume of stock corrected for the remaining handsheet such that the amount of OD pulp is equal to 1.2 g per handsheet (equivalent to 60 gsm). The handsheets were then made on a British Sheet Mold in accordance with Tappi standards (T205 om-88). The handsheets were pressed in a standard Tappi Press and then dried at 250⁰F on Emerson speed dryer for 3 minutes. The handsheets were placed in a Tappi standard room (72⁰F and 50 % RH) for 10 minutes before testing the extent of sizing by Cobb and Hercules sizing test. The following conditions were maintained for Cobb and HST tests.

Cobb test:

Duration of the test : 120 seconds

HST :

End point reflectance : 80 %

In order to duplicate the results, six handsheets were made. One of each sample used for HST with different inks and two sheets for Cobb sizing. As a result of testing four HST tests on only one handsheet for the particular

conditions of the type of mordant used, pH and retention time, statistical methods to find the error due to variations in different samples could not be done.

Testing of pulp and handsheet properties

The following TAPPI Test methods (17) were used for testing of pulp and handsheets.

- T205 om-88 : Forming handsheets for physical tests of pulp.
- T227 om-85 : Freeness of pulp.
- T441 om-90 : Water absorptiveness of sized (non-bibulous) paper and paperboard (Cobb test).
- T530 pm-89 : Size test for paper by ink resistance (Hercules Method).

IV. RESULTS AND DISCUSSION

With the hypothesis of coordination interaction of mordants in rosin soap sizing, it should be easy to use a variety of coordinating elements to get effective sizing. In the formation of a coordinate complex, if the formation constants with different ligands for a particular cation is known, the development of a sizing complex can be easily predicted. Thus, coordinating elements with appropriate pK_1 values can be used for effective sizing in different pH ranges, particularly in the alkaline range.

Although the use of lanthanides is not commercially viable, some important generalization about mordants in sizing can be drawn by their use in our study. Some of the characteristics of candidate mordants, including elements used in this study, are given in Table 2. In a set of experiments, a variety of elements were tested as mordants and gave good sizing. The results of sizing with 12.5 lbs of potassium rosinate soap solids and the molar equivalent of aluminum ion, as 40 lb aluminum sulfate hydrate per ton of hardwood pulp, of mordant have been summarized in Table 3, Table 4 and Table 5 and are also shown from Figure 7 to Figure 16. The higher values for the HST and lower values for the Cobb sizing tests reflect better sizing. The weight of handsheet made for the sizing tests were 60 g/m².

In the experiments conducted, alum seems to work better,

as a sizing mordant, than all the lanthanide group metals and gallium. The reason for this improved performance is hypothesized to the formation of a dioxo complex (Figure 5) by losing two protons from each diol bridges between metal atoms. Besides, with the loss of protons from the diol complex the charge on the complex decreases thereby making these complexes less polar, more stable and less soluble in aqueous solutions. Gallium forms such oxo complexes but with longer retention times. With lanthanide group elements the formation of any dioxo complexes are not reported in the literature. The obvious reason for this could be due to the lanthanide elements in aqueous solutions undergoing hydrolysis to a much smaller extent than aluminum or even gallium (11). Hydrolysis increases with increasing atomic number of the lanthanide. For e.g., Ce^{3+} is believed to exist in equilibrium as:



With such a lower level of hydrolysis the oxo bridging of the lanthanides is not likely under the conditions of rosin sizing. The oxo complexes are known to be much more stable than the hydroxo complexes. Thus it supports the fact that while alum and gallium show greater stability towards 1% formic acid, the lanthanides lose their sizing ability. Therefore, it is obvious that the mordant action by the

Table 2 : Properties of candidate species as mordants in rosin sizing in water at 25⁰C

Elements	Cation	pK ₁	SO ₄ ²⁻	Cl ⁻	AcO ⁻
Trivalent ion					
Aluminum	Al ³⁺	5.01	-	-	-
Cerium	Ce ³⁺	9.00	43	3	123
Chromium	Cr ³⁺	4.00	58	-	63
Dysprosium	Dy ³⁺	8.10	-	-	107
Erbium	Er ³⁺	7.99	-	-	102
Europium	Eu ³⁺	8.30	35	-	204
Ferric	Fe ³⁺	2.83	170	6	1580
Gallium	Ga ³⁺	3.40	-	-	-
Lanthanum	La ³⁺	9.03	28	-	105
Yttrium	Y ³⁺	8.34	100	-	93
Divalent ion					
Calcium	Ca ²⁺	12.8	200	-	17
Copper	Cu ²⁺	8.0	10	9.6	47
Magnesium	Mg ²⁺	11.4	178	-	18
Manganese	Mn ²⁺	10.6	200	3.9	25
Tetravalent ion					
Thorium	Th ⁴⁺	3.9	2100	1.7	-

Table 3 : A summary of sizing results with various sizing mordants

Mordant	pH	COBB (g/m ² /2 min)	HST(N) (sec)	HST(FA) (sec)
Aluminum sulfate	4.5	24.5	410	120
	5.0	25.1	585	133
	5.5	24.1	382	101
	6.0	25.1	340	-
	6.5	26.4	200	84
	7.0	No sizing	12	6.5
Cerium chloride	6.0	28.4	100	3.4
	6.5	25.8	300	3.0
	7.0	25.8	310	2.0
	7.5	32.9	100	0.9
Cerium sulfate	6.0	31.3	73	2.2
	6.5	26.1	260	2.4
	7.0	28.5	257	1.3
	7.5	30.1	177	1.1
	8.0	No sizing	2	0.7

HST(N): Hercules sizing test with neutral ink.

HST(FA): Hercules sizing test with 1% formic acid ink.

Table 4 : A summary of sizing results with various sizing mordants

Mordant	pH	COBB (g/m ² /2min)	HST(N) (sec)	HST(FA) (sec)
Dysprosium chloride	5.5	29.8	116	3.2
	6.0	28.0	95	2.9
	6.5	24.5	284	2.8
	7.0	24.4	342	1.9
	7.5	25.5	300	1.7
	8.0	34.7	75	1.0
Erbium chloride	6.5	28.1	200	4.6
	7.0	23.1	436	5.0
	7.5	25.0	366	2.8
Erbium sulfate	6.0	27.7	165	5.1
	6.5	26.3	172	5.3
	7.0	23.2	350	3.8
	7.5	25.3	285	3.1
	8.0	25.3	273	2.3
Europium sulfate	6.5	25.4	205	4.2
	7.0	25.3	325	2.8
	7.5	29.0	235	1.4
	8.0	No sizing	7	0.8

HST(N): Hercules sizing test with neutral ink.

HST(FA): Hercules sizing test with 1% formic acid ink.

Table 5 : A summary of sizing results with various sizing mordants

Mordant	pH	COBB (g/m ² /2 min)	HST(N) (sec)	HST(FA) (sec)
Gallium sulfate	3.0	42.3	62	7.9
	3.5	32.4	155	9.8
	4.0	27.2	280	12.5
	4.5	42.6	150	3.2
	5.0	43.2	135	4.6
Lanthanum chloride	6.0	31.1	53	2.4
	6.5	29.97	136	2.5
	7.0	28.4	235	1.7
	7.5	35.4	100	1.1
Lanthanum sulfate	5.0	36.3	55	1.6
	5.5	31.0	75	2.8
	6.0	33.4	61	2.5
	6.5	28.0	113	2.5
	7.0	No sizing	25	1.1

HST(N): Hercules sizing test with neutral ink.

HST(FA): Hercules sizing test with 1% formic acid ink.

Table 6 : A comparison of sizing results between sulfate and chloride salts of various mordant cations

Component	pH	HST(N) (sec)	COBB (g/m ² /2 min)
Cerium chloride	7.0	334	25.90
Cerium sulfate	6.5	99	29.00
Dysprosium chloride	7.0	362	24.37
Dysprosium sulfate	7.0	321	24.91
Erbium chloride	7.0	458	23.07
Erbium sulfate	7.0	334	23.69

HST(N): Hercules sizing test with neutral ink.

Table 7 : Sizing results when H₂SO₄ and HCl were used for pH adjustments in the experiments

Component	pH	COBB* (g/m ² /2 min)	COBB** (g/m ² /2 min)
Alum	5.0	25.57	23.34
Cerium chloride	7.0	27.57	26.38
Cerium sulfate	6.5	29.60	29.39
Dysprosium chloride	7.0	26.37	25.19
Erbium chloride	7.0	24.44	23.51
Erbium sulfate	7.0	24.05	24.48
Europium sulfate	7.0	27.19	25.28
Gallium sulfate	4.0	32.37	26.98
Lanthanum sulfate	6.5	30.58	29.40

* Dilute H₂SO₄

** Dilute HCl

Table 8 : Sizing results when H₂SO₄ and HCl were used for pH adjustments in the experiments

Component	pH	HST(N)* (sec)	HST(N)** (sec)
Alum	5.0	409	650
Cerium chloride	7.0	313	334
Dysprosium chloride	7.0	342	362
Erbium chloride	7.0	436	458
Erbium sulfate	7.0	348	334
Europium sulfate	7.0	331	379
Gallium sulfate	4.0	280	294
Lanthanum sulfate	6.5	113.7	120

* Dilute H₂SO₄

** Dilute HCl

HST(N): Hercules sizing test with neutral ink.

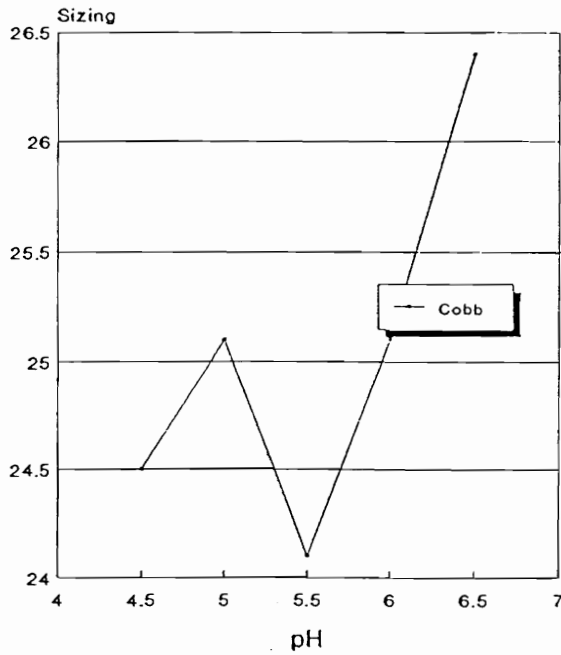
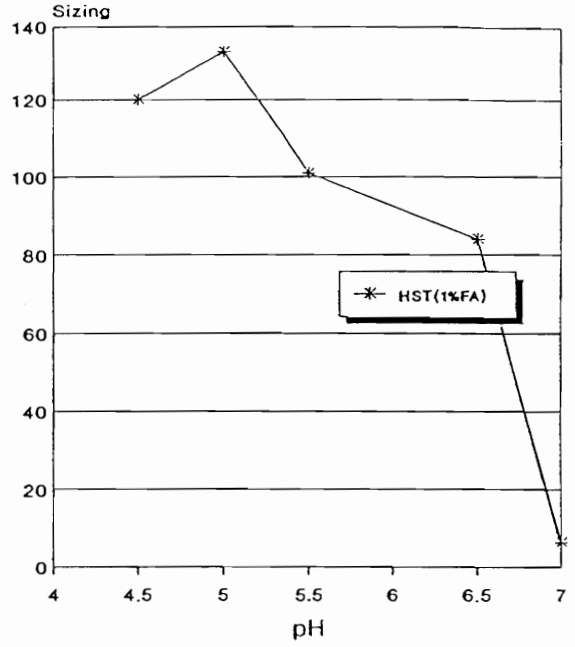
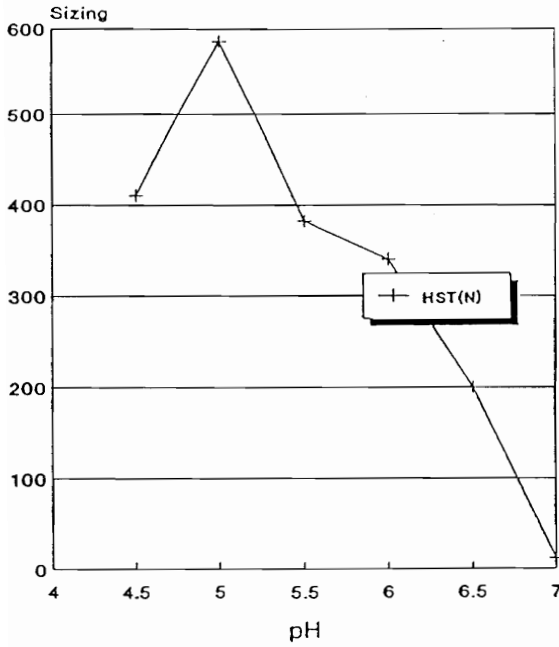


FIGURE 7: Degree of sizing at different pHs with rosin soap and alum shown by three different tests.

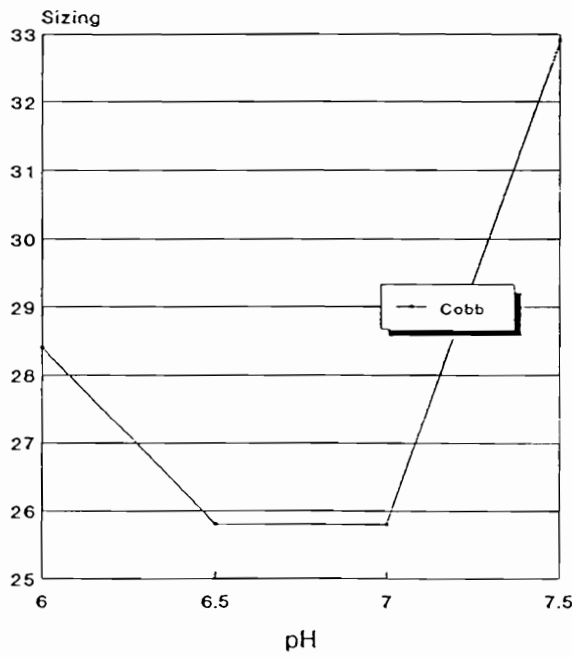
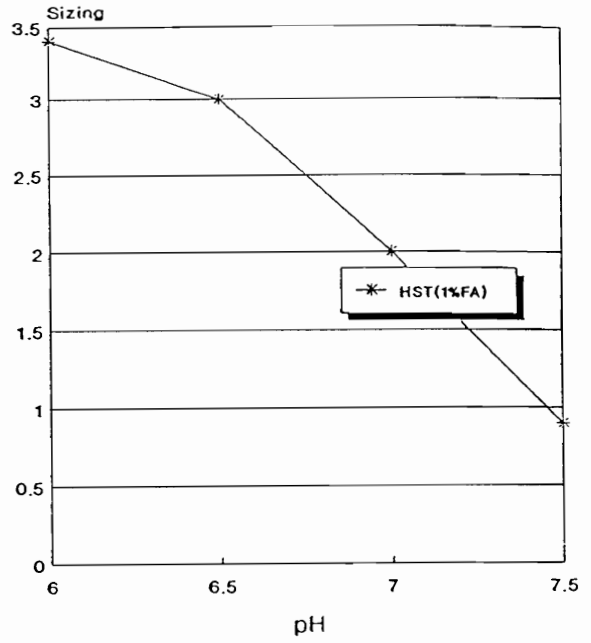
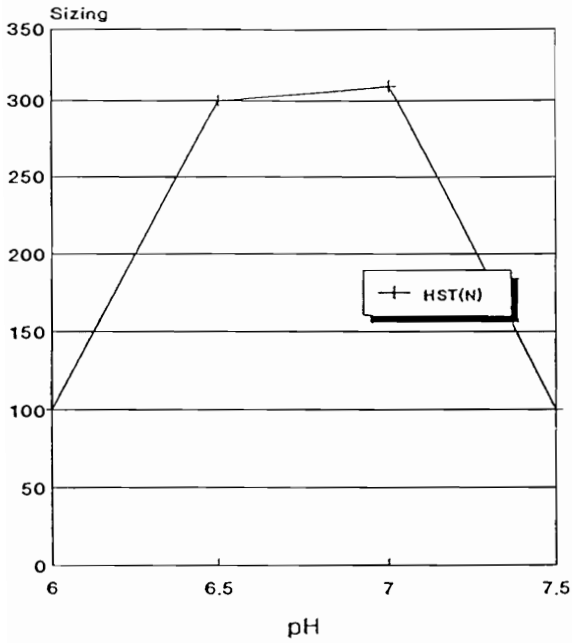


FIGURE 8: Degree of sizing at different pHs with rosin soap and cerium chloride shown by three different tests.

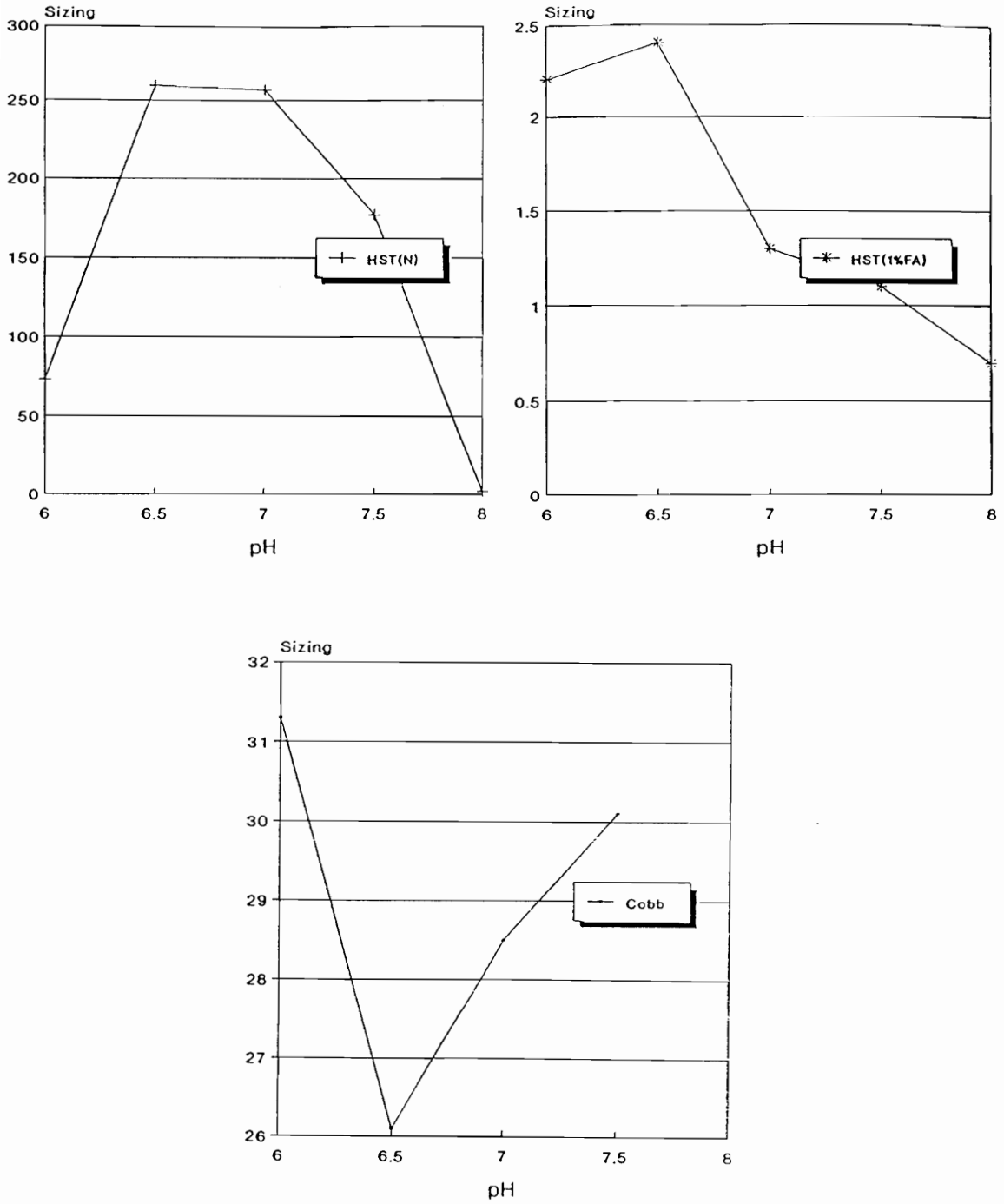


FIGURE 9: Degree of sizing at different pHs with rosin soap and cerium sulfate shown by three different tests.

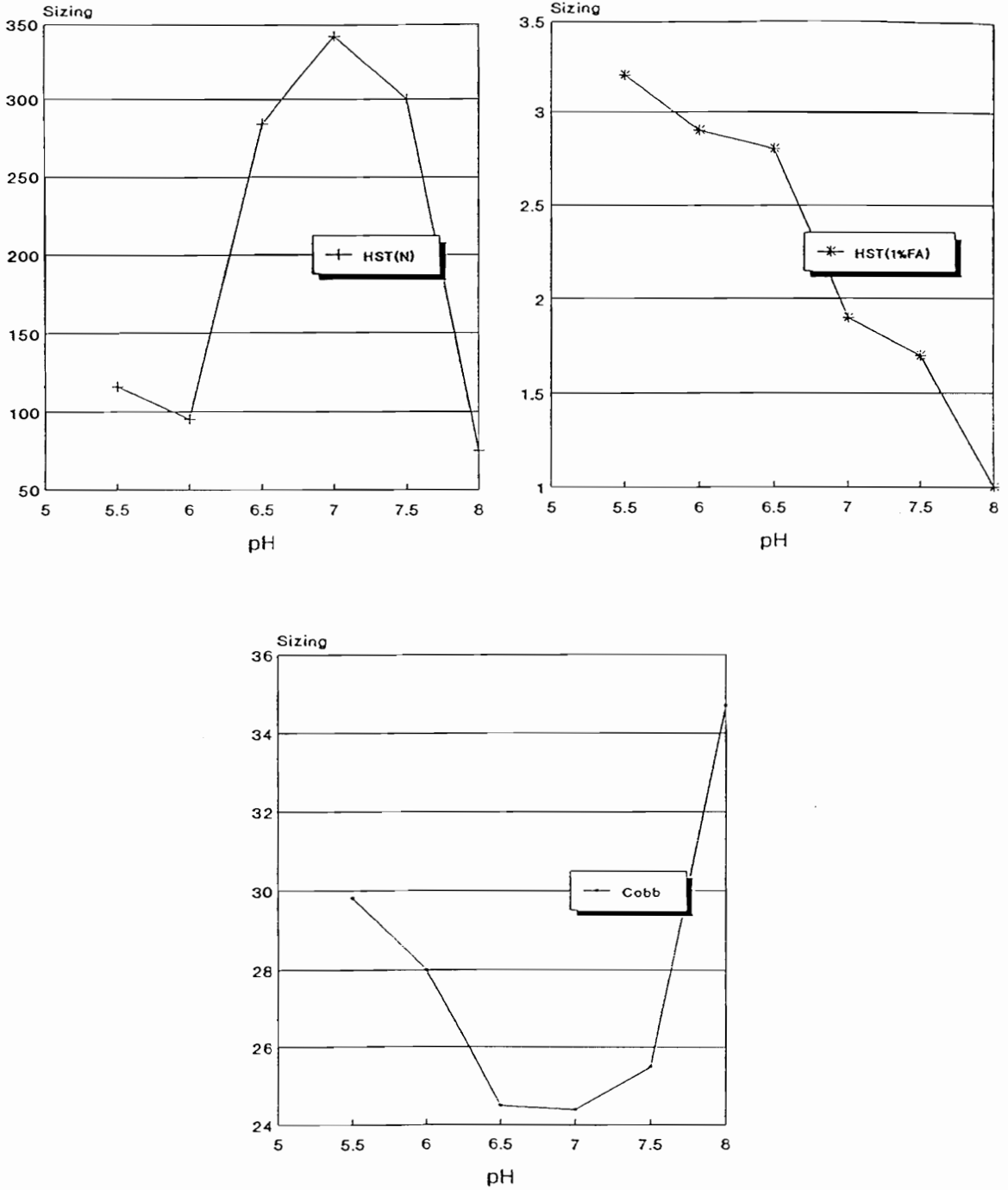


FIGURE 10: Degree of sizing at different pHs with rosin soap and dysprosium chloride shown by three different tests.

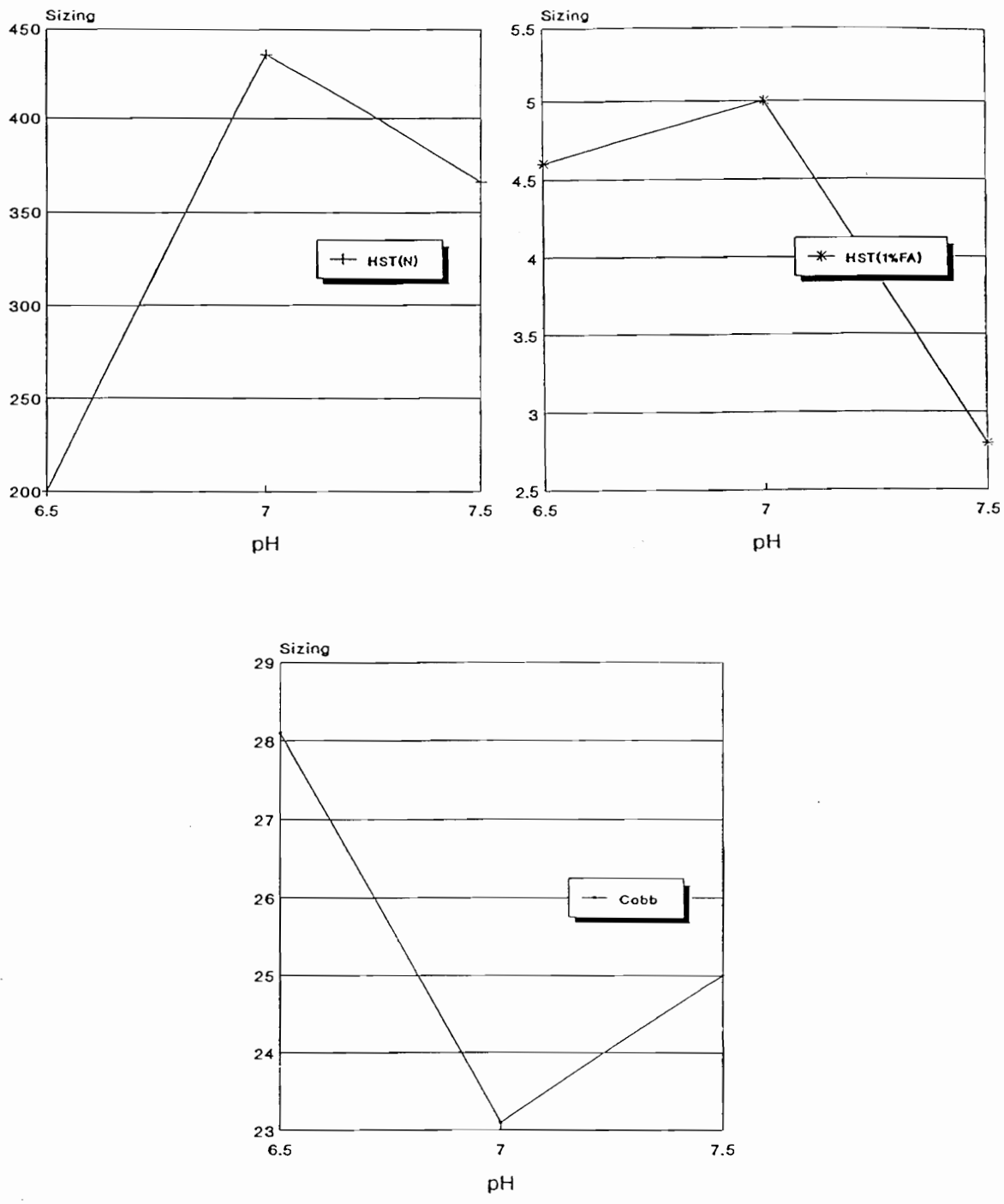


FIGURE 11: Degree of sizing at different pHs with rosin soap and erbium chloride shown by three different tests.

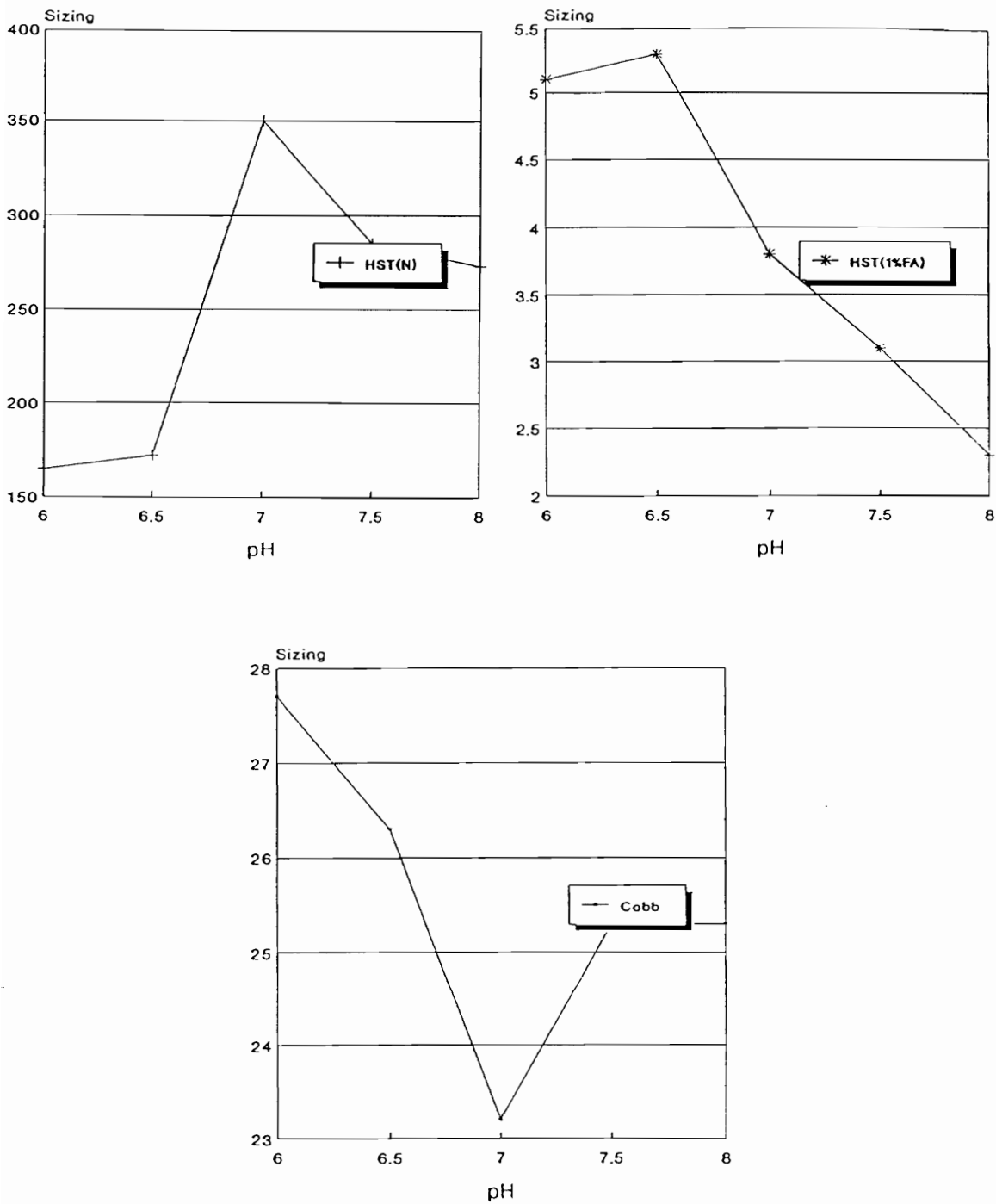


FIGURE 12: Degree of sizing at different pHs with rosin soap and erbium sulfate shown by three different tests.

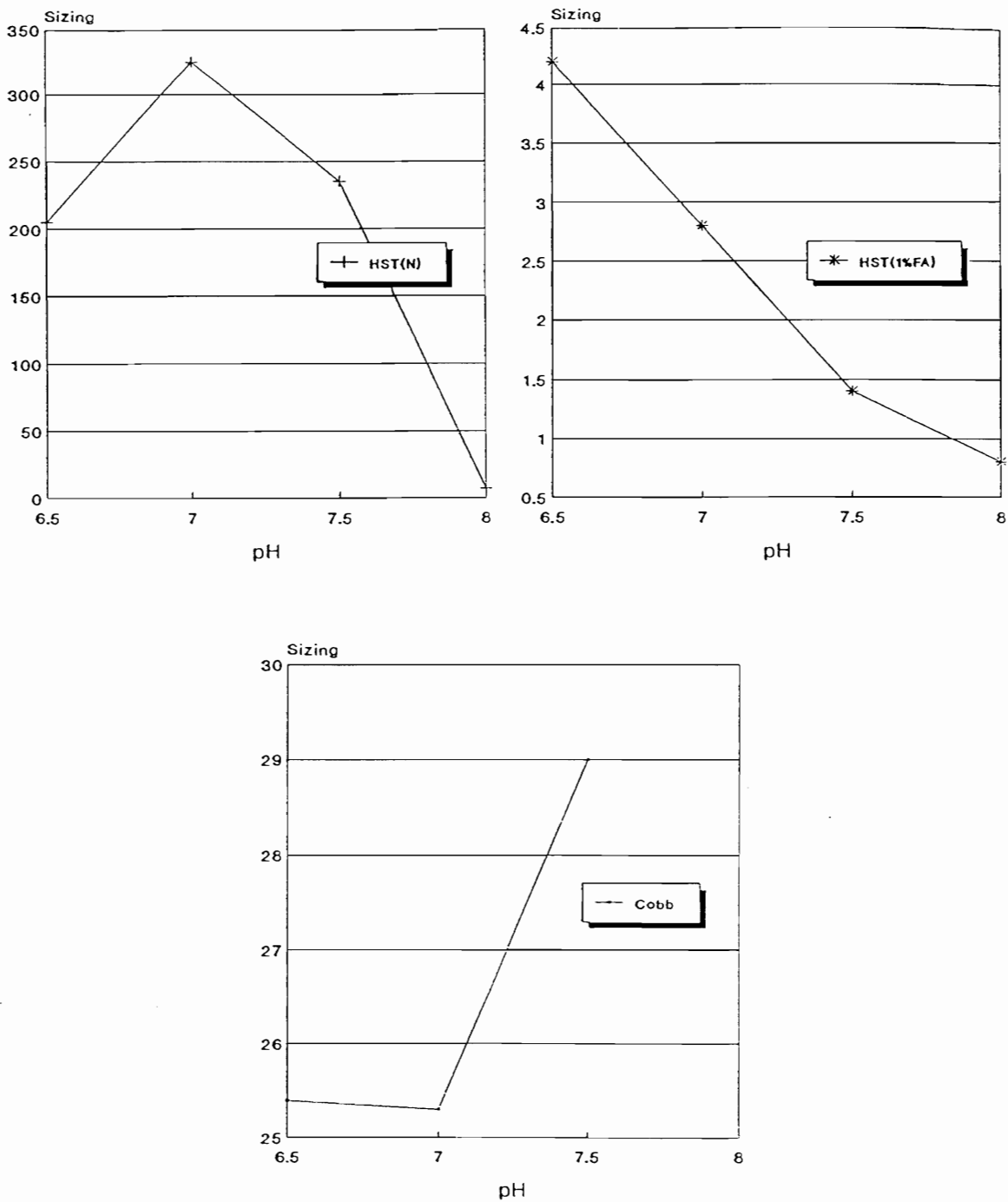


FIGURE 13: Degree of sizing at different pHs with rosin soap and europium sulfate shown by three different tests.

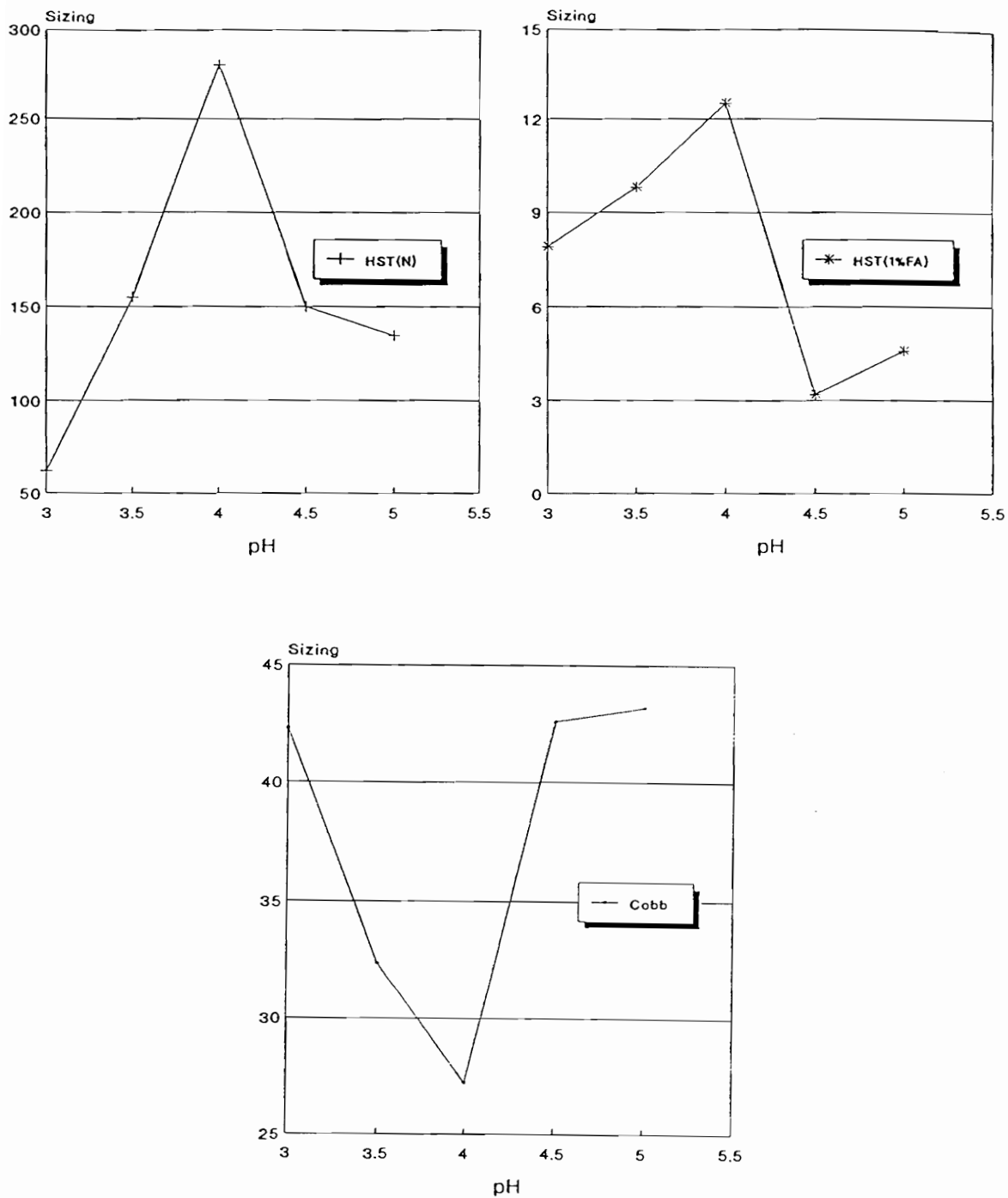


FIGURE 14: Degree of sizing at different pHs with rosin soap and gallium sulfate shown by three different tests.

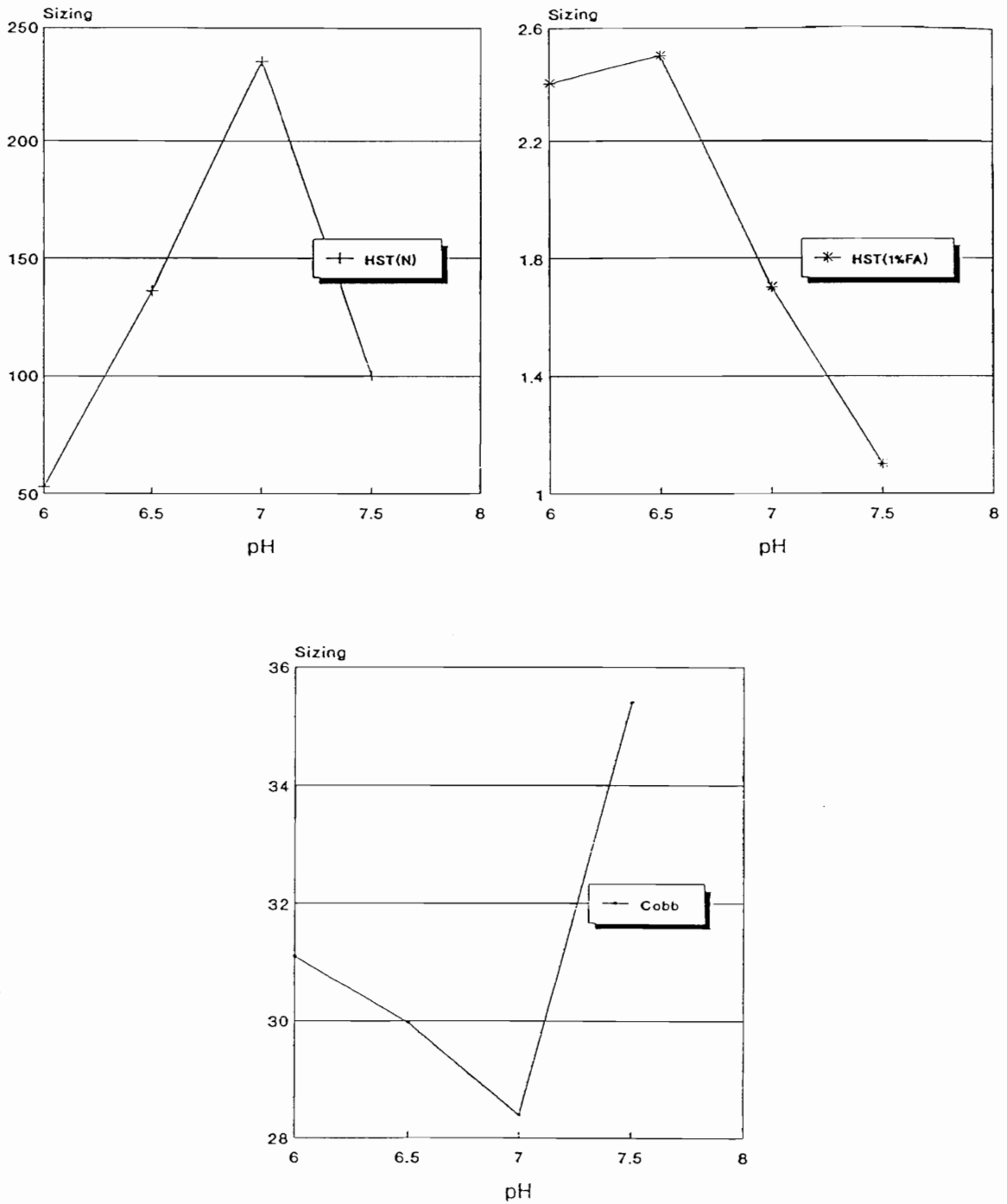


FIGURE 15: Degree of sizing at different pHs with rosin soap and lanthanum chloride shown by three different tests.

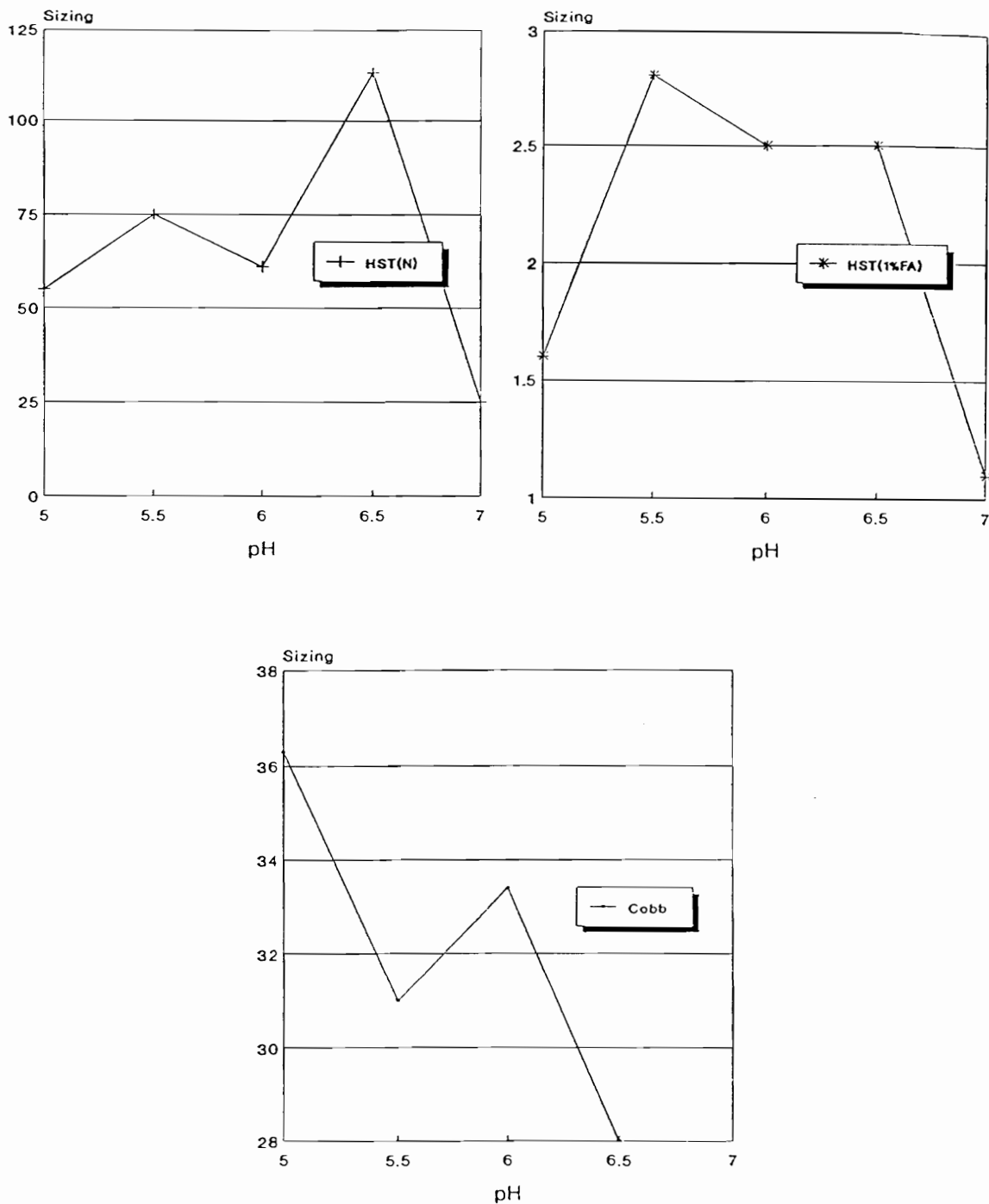


FIGURE 16: Degree of sizing at different pHs with rosin soap and lanthanum sulfate shown by three different tests.

lanthanide group elements is expected to be less when compared with alum or gallium.

Sizing with chloride salts seem to work better than the corresponding sulfate salts, for the various elements used. The results of which are shown in Table 6. This is undoubtedly due to the sulfate ligand having a greater tendency to form coordinate complex than the chloride anion, as reflected by the formation constants with the studied elements (Table 2). The sulfate ligand due to its greater tendency to form complex compounds, tends to block the active sites of the cation, which would otherwise be occupied by other ligands like rosinate groups, etc. When dilute hydrochloric acid was substituted for dilute sulfuric acid in adjusting the pH during the sizing experiments, it was noticed that sizing improved though marginally. This marginal improvement was only expected as the amount of sulfuric acid required for adjusting the pH in the neutral range was very less. Table 7 and Table 8 show the relative improvement in sizing efficiency by the above mentioned change (using dilute hydrochloric acid instead of dilute sulfuric acid for pH adjustment). As already mentioned higher values of HST and lower values of Cobb sizing tests reflect better sizing.

Unlike neutral ink, 1 % formic acid ink, when used in the Hercules sizing test, results in rapid ink penetration, as shown in Figure 7 to Figure 16. This is undoubtedly due to the formate anion acting as a good

ligand and displacing the rosinate groups from the metal complex. This ligand substitution reaction appears to be quite rapid for most elements studied except for alum and gallium. With gallium there was a noticeable improvement in sizing observed with a two hour retention at 1.5 % consistency prior to the making of handsheets. This is quite likely due to the slow coordination reactions in the formation of oxo complexes. In the case of aluminum, this reaction is known to occur much more quickly and most of the reaction is complete within five minutes of retention at 1.5 % consistency. The sizing results with gallium sulfate for 1 hr and 2 hr retention times were 12.5 and 100 respectively expressed in seconds through the Hercules sizing test with 1 % formic acid ink.

The results from the Table 2, Table 3, Table 4 and Table 5 suggest that the pK_1 of a candidate mordant in aqueous solution is a good indicator of the pH of maximum sizing efficiency. In the formation of a complex, by looking up the formation constants for different metals with various ligand, one can predict the suitability of the mordant for sizing.

Studies with divalent manganese cation reflects the earlier mentioned studies about divalent ions as sizing mordants. Divalent ions due to their lower charge are less efficient as sizing mordants in comparison to trivalent ions. The divalent cations have a lower affinity for carboxylate

groups, while having a higher affinity for hydroxyl groups. With such characteristics one might expect these ions to show lower levels of sizing. This fact is seen from the work done with various divalent cations by earlier researchers. The work done by Biermann et al with manganese also corroborates this idea (12)

V. CONCLUSIONS

1. The importance of coordination interaction in rosin soap sizing has been proven in this study and an attempt has been made to explain the coordination interactions from the results of sizing with several coordinating elements.
2. The formation of oxo complex, put forth first by Arthur Thomas, appears to be critical in the development of sizing. Thus elements which have a tendency to form oxo bonds are likely to be good mordants in sizing.
3. The nature and concentration of different coordinating ligands in the sizing system affect the sizing efficiency. The reason for different values for various sizing tests could be due to the difference in the interaction with coordinating ligands.
4. The maximum efficiency of sizing obtained with different metal salts, used as sizing mordants, were as follows and are reported in seconds for Hercules sizing test with neutral ink and as the amount of water absorbed in $\text{g/m}^2/2$ min., for Cobb sizing test respectively, at the appropriate pH: alum 585, 25.1 (pH=5.0), cerium chloride 310, 25.8 (pH=7.0), cerium sulfate 257, 28.5 (pH=7.0), dysprosium chloride 342, 24.4 (pH=7.0), dysprosium sulfate 320, 24.9 (pH=7.0), erbium chloride 436, 23.1 (pH=7.0), erbium sulfate 350, 23.2 (pH=7.0), europium sulfate 325, 25.3 (pH=7.0), gallium sulfate 280, 27.2

(pH=4.0), lanthanum chloride 235, 28.4 (pH=7.0) and lanthanum sulfate 113, 28.0 (pH=6.5).

5. The maximum sizing pH with different coordinating elements were dependent on the pK_1 value of their metal cation in aqueous solutions.
6. The retention time or the reaction time for the different reacting species in the pulp slurry is a vital parameter to get higher degree of sizing. Slow reaction is characteristic of coordination reaction of large complexes in a multi ligand systems.

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 - T205 om - 88: Forming handsheets for physical tests of pulp.
 - T227 om - 85: Freeness of Pulp.
 - T441 om - 90: Water absorptiveness of sized(non-bibulous) paper and paperboard(Cobb test).
 - T530 pm - 89: Size test for paper by ink resistance (Hercules Method).

APPENDIX

Definitions and abbreviations.

AcO-	:	Acetate ion
AKD	:	Alkyl Ketene Dimer
ASA	:	Alkenyl Succinic Anhydride
COBB	:	Cobb test is an empirical procedure to measure the extent of sizing or resistance by water.
FILLER	:	An inorganic substance added to substitute a portion of the fibers and enhance certain paper properties.
FREENESS	:	Canadian Standard Freeness is a empirical procedure which gives an arbitrary measure of the rate at which a suspension of three grams of pulp in one liter of water may be drained. The test is carried out under specified conditions.
HOAc	:	Acetic acid
HST	:	Hercules sizing test or tester. The test is for measuring the extent of sizing.
HST(N)	:	Hercules sizing test with neutral ink.
HST(FA)	:	Hercules sizing test with 1% formic acid ink (Ink #2).

- MORDANT : A substance used as a intermediary for fixing one compound on to the other.
- PAPERMAKER'S ALUM : Hydrated aluminum sulfite
- pK_a : The negative logarithm of dissociation constant of an acid.
- SIZING : A property imparted to paper to resist the penetration of aqueous liquids.
- TAPPI : TAPPI is the acronym for the Technical Association of the Pulp and Paper Industry.