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Title: APPLICATION OF OCTADECYLAMINE AS AN INTERNAL SIZING AGENT

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Octadecylamine, $CH_3(CH_2)_{17}NH_2$, was found to be an effective sizing agent when used alone, i.e. without alum as a mordant. Its use as an internal sizing agent has not been previously reported. With unbleached pulp, 0.25% (based on dry pulp) octadecylamine was enough to induce sizing, while 0.5% was required to induce sizing with bleached pulp. The role of lignin, which allows unbleached pulp to be more easily sized, was discussed. Unbleached paper sized with octadecylamine is very resistant to penetration by acidic solutions; for example, the Hercules Size Test gives higher values with 1% formic acid ink than with neutral ink. With both pulps the optimum pH range of the pulp slurry was 7 to 10. The sizing efficiency was highly dependent on the temperature, presence of metallic ions, and storage time of the stock, indicating the complex chemistry involved in this process.

The hypothesized sizing mechanism was discussed based on two interactions: the interaction between protonated octadecylamine and cellulosic fibers and the interaction between the cationic amine and the aromatic π bonding of lignin. Drying handsheets at high temperature or long periods of time increases the sizing efficiency. Paper strength decreased with the use of octadecylamine.

APPLICATION OF OCTADECYLAMINE AS AN INTERNAL SIZING AGENT

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1. Introduction

1.1 What is paper sizing? Why paper sizing?

Sizing is the property of paper products to resist wetting and penetration of aqueous liquid. It is also the name of the process to impart this property to paper products. Wood fibers naturally tend to be wetted and be penetrated by water due to the plentiful hydrophilic groups in cellulose and hemicellulose. A high degree of water adsorption is a goal for some grades of paper, such as tissue, toweling and sanitary grades of paper. These grades of paper are designed for rapid adsorption of aqueous fluid. For most of other paper grades, a high level of water-adsorption is not desired. Usually, in wrapping and packaging papers, wall paper, writing paper and printing paper, liquid penetration resistance is important[1-2]. The level and the process of sizing depend on their end use.

1.2. Internal sizing versus surface sizing:

Sizes can be applied in two ways, "internally applied"--internal sizing or "surface applied"--surface sizing. In internal sizing, sizes are added to the pulp stock prior to

the wet end of the paper machine. In surface sizing, sizes are applied to the dry or partially dried paper sheet at the size press or calender stack. In surface sizing, all the sizes are applied directly to the surface of sheet. A uniform and continuous film is formed after this process and retention of the size on the sheet is assured.

Liquid resistance can be achieved by either internal sizing or surface sizing. However, different sizing mechanisms are involved. Internal sizing agents are usually amphoteric materials with both non-polar and polar groups in their structures. Water wetting and penetration are limited by the nonpolar portions of the sizing molecules, which are oriented away from the fiber surface. Polar groups are reactive to functional groups in wood fibers and are anchored to the surface of the fibers through this bonding.

Surface sizing works at the size press or calendarstack. Water repellency may be one goal of surface sizing, but it is usually not the main one. The principal objectives of surface sizing are to improve surface strength, surface smoothness for printing and ink hold-out. Conventional surface sizing agents, such as animal glue and starch, achieve resistance to liquid penetration by filling the capillaries of paper. More recently, some synthetic polymers are being developed very fast to be applied as surface sizes. Examples are styrene-maleic anhydride

copolymer, polystyrene acrylic acid copolymer and polyurethane.

In this report, only internal sizing will be considered in detail.

1.3 Related knowledge in surface and colloid chemistry

Since the purpose of internal sizing is to impart to wood fiber the ability to resist the wetting and penetration of liquid, it is important to understand first how aqueous fluids wet and penetrate into wood fibers.

When a nonvolatile pure liquid drop is placed on a clean, smooth, insoluble, plain solid surface, a balance of forces will be established between vapor, liquid and solid. This balance is expressed by Young's equation:

$$\cos\theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV}$$

θ: Contact angle between the liquid drop and liquid surface.

σ_{SV}: Surface tension at the solid and vapor interface

σ_{SL}: Surface tension at the solid and liquid interface

σ_{LV}: Surface tension at the liquid and vapor interface

If the adhesional forces between liquid and solid are greater than the cohesional forces of the liquid then the

liquid spontaneously spreads on the solid surface. It perfectly wets the solid surface. Otherwise, it partially wets the surface and it will establish a contact angle with the solid surface as shown in Fig. 1.1.

$$\theta < 90^0 \qquad \theta > 90^0$$

$$\theta = 90^0 \qquad \theta = 0^0$$

Instant and
Complete wetting
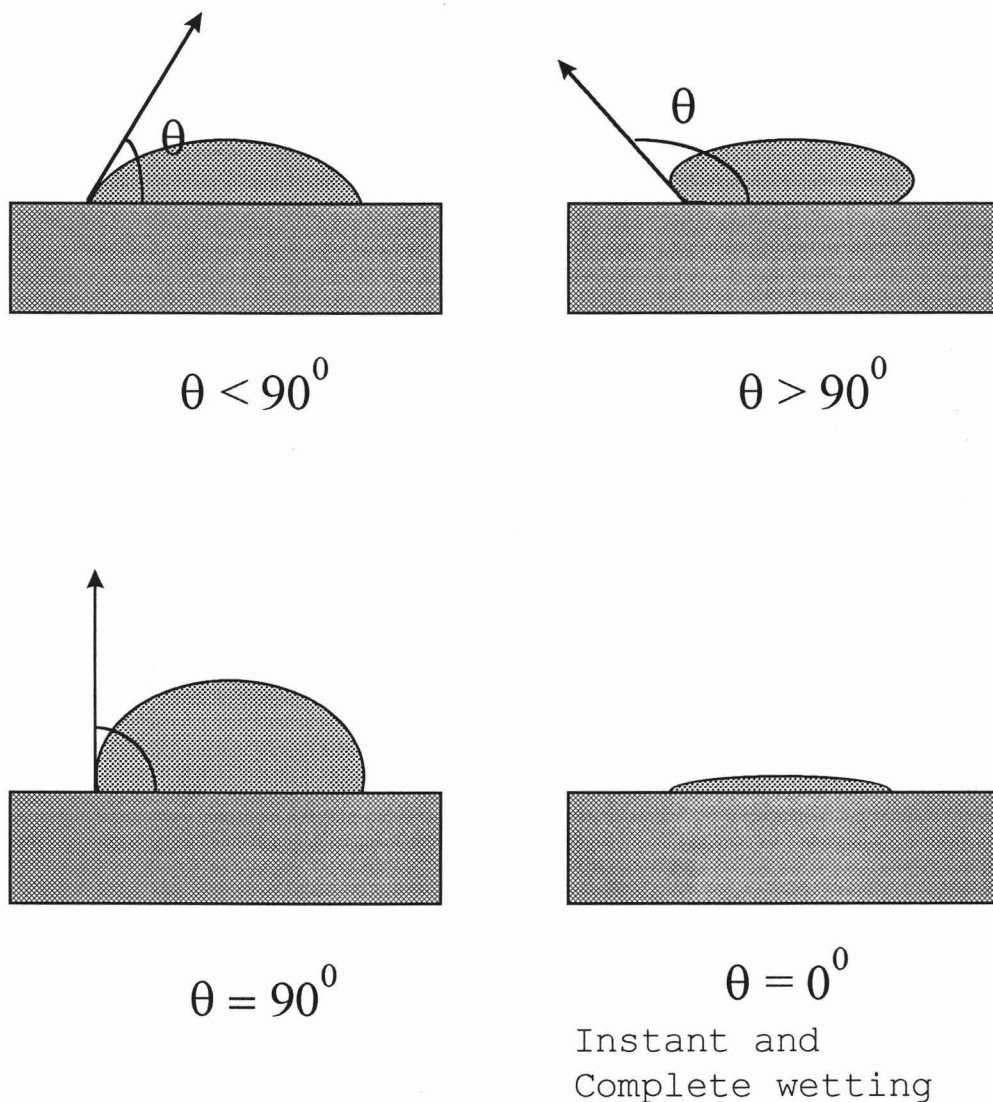
Fig. 1.1   Contact angle between liquid drop and
solid surface

Without any sizing treatment, water penetrates into fibers through three mechanisms:

(1) Capillary action through the pores formed between fibers of the fiber network.

(2) Liquid water diffusion through pores and fiber solid, the latter one could be very difficult due to the small mass transfer coefficient in solid fiber material.

(3) Water vapor diffusion followed by condensation.

Among all of above movement mechanisms of water, capillary flow thorough extensive pores of fibre network is the predominant one. The Washburn equation is used to describe the capillary penetration rate[3] in this process.

$$\text{penetration rate} = \frac{dl}{dt} = \frac{1}{4}\frac{r}{l}\frac{\sigma}{\chi} * \cos\theta$$

Where,

l=capillary depth penetrated by liquid at time t,

t=penetration time, s

r=capillary radius, cm

σ=surface tension of liquid, dyn/cm

χ=liquid viscosity coefficient, poise

θ=contact angle

One is especially interested in penetration rate control. In order to get a small value of capillary penetration rate, one could either improve the contact angle θ or reduce the capillary radius, r.

In the surface sizing approach, water resistance is mainly achieved by reducing pore radii or filling pores by applying a filming substance at the size press. In contrast, in the internal sizing approach, the internal sizing agent converts the hydrophilic fiber surface into a hydrophobic surface, thus changing the surface tension at the solid/vapor interface, which results in a larger contact angle due to Young's equation described above.

Young's equation and the Washburn equation are very helpful for us to understand the theories of sizing. They, however, have limited value for our extremely complex practical sizing process. Instead, the hydrophobicity of the chemical and the stability of bonding between sizing agent and fiber surface are becoming two big concerns in our practical approach of developing new chemicals for the internal sizing process.

1.4 Rosin-based sizing system

Rosin sizing of paper dates back from the very early 1800's. "Papermaker"s alum (aluminum sulfate solution) was

used with rosin to achieve sizing. It is very interesting to note that rosin comes from the tree itself. There are three kinds of rosins which are categorized by the production procedure: gum rosin, wood rosin and tall oil rosin. Gum rosin is obtained by distilling the gum(an extractive of softwood) and removing turpentine, low boiling point component. Wood rosin is extracted from aged softwood stumps with organic solvents. Tall oil rosin is obtained by distillation of acidified black liquor skimmings from the kraft pulping of softwood. Tall oil is the main source of rosin size in America's paper industry.

Rosin is a complex mixture of organic acids[4]. Two principle components of rosin are abietic acid and pimaric acid(Fig. 1.2.)

Abietic Acid   Pimaric Acid
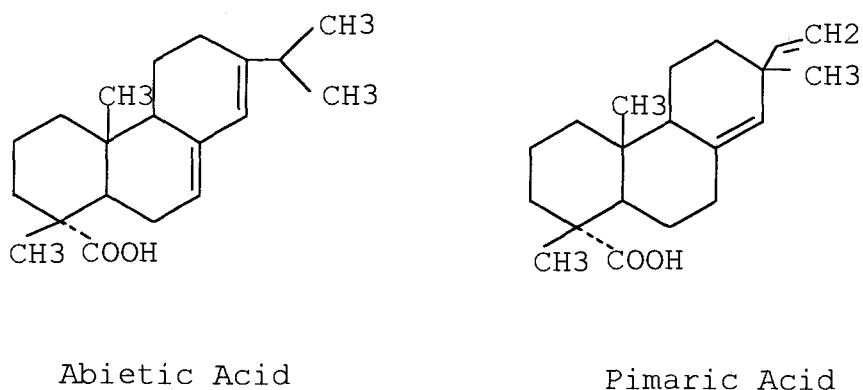
Fig. 1.2 Two main components of rosin

The rosin-alum sizing system has been used for about 200 years and is still widely used in the paper industry.

But it has gone through several modifications since its initial use.

Rosin, itself, is not water soluble, so the earliest rosin size is actually saponified soap[5].

In the late 1950s, the fortified rosin was invented[6]. It is the reaction product of rosin with maleic-anhydride(see Fig. 1.3). Fortified rosin size is a much more effective size than saponified rosin soap. The improved effectiness comes from the added carboxyl groups which can chelate to metal ions [7-8]. This leads to better reaction with alum.
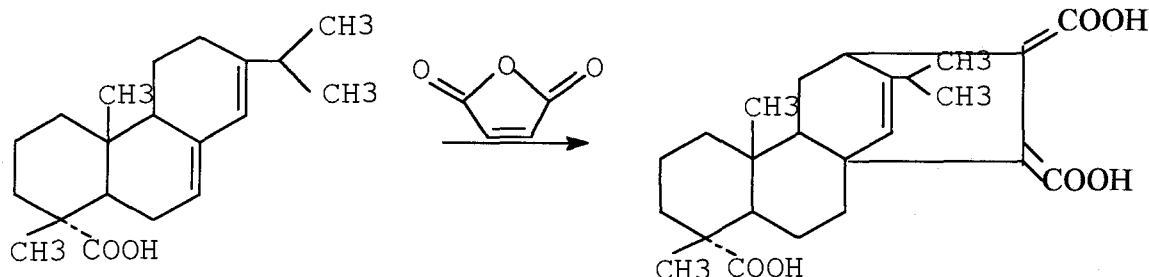
Figure 1.3 Formation of fortified rosin
from abietic acid

In 1970, the microparticulate dispersed sizes appeared. The free rosin acid content is in the range of 75 to 100 percent. The free-rosin acid is emulsified and stabilized with a very small content of protective colloid, such as surfactants or proteins. The advantages of dispersed rosin

size over rosin soap are higher operating pH at the wet end, better paper strength and better efficiency.

It is possible to extend the use of dispersed rosin to pH 6.5-7.5 by using polyaluminum chloride (PAC) as the mordant[9-10].

1.5 "Mordant" and alum chemistry in rosin size:

"Mordant" is a term used to describe the chemical that fixes dyes to fiberous materials in the textile industry. In paperchemistry, it refers to the bridge between rosin soap size and fibers. Alum plays the role of mordant in the rosin sizing system. However, alum can only function as an effective mordant at pH in the range of 4.0 to 5.5. Research has been undertaken to understand the mechanism of rosin-alum sizing. Many hypotheses have been brought forth but they all explain only part of the interaction. Among these, the electrostatistic force theory is the most popular one[11].

It was believed that the aluminum has little retention at pH below than 4.0. And at pH higher than 5.5, the ineffectiveness of sizing resulted from the low cationic charged of $Al(OH)_3$, which becomes the predominant complex at this pH. Electrostatistics theory could not explain why

Al^{3+} is not retained by fibers at pH below 4. Coordination chemistry offered a better explanation.

Aluminum sulfate undergoes several stages of hydrolysis in water(Fig. 1.4). The dominant complex depends on the pH value of the solution.

$$\begin{bmatrix} H_2O\diagdown \quad \diagup H_2O \\ H_2O-Al-H_2O \\ H_2O\diagup \quad \diagdown H_2O \end{bmatrix}^{3+} \xrightleftharpoons{OH^-} \begin{bmatrix} H_2O\diagdown \quad \diagup OH \\ H_2O-Al-H_2O \\ H_2O\diagup \quad \diagdown H_2O \end{bmatrix}^{2+} \xrightleftharpoons{OH^-}$$

$$\begin{bmatrix} H_2O\diagdown \quad \diagup OH \\ H_2O-Al-OH \\ H_2O\diagup \quad \diagdown H_2O \end{bmatrix}^{1+} \xrightleftharpoons{OH^-} \begin{bmatrix} H_2O\diagdown \quad \diagup OH \\ H_2O-Al-OH \\ H_2O\diagup \quad \diagdown OH \end{bmatrix}$$
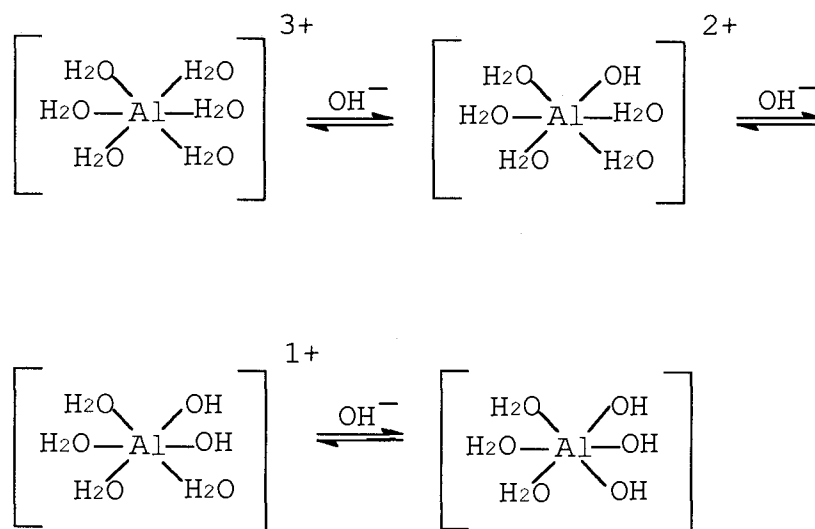
Fig. 1.4 Hydrolysis of alum in water solution

Thomas is the first one who postulated that aluminum might be effective in rosin sizing because the cation could coordinately bind both cellulose and rosin sizing agent[12]. Compared to other transition metal ions that may have better coordinating capability, the uniqueness of the aluminum ion complex is its ability to form polynuclear species through the formation of hydroxo or oxo bridging[12-14]. At pH below 4.0, the hydrated form of Al^{3+} ($Al(H_2O)_6^{3+}$) is the

dominant complex. It, however, has no ability to form polynuclear species because it lacks the OH- ligand in its structure. At pH > 5.5, $Al(H_2O)_3(OH)_3$ will begin to precipitate in solution instead of forming oxo bridge with another unit. The polynuclear complex formation is dominant in the pH range of 4.0 to 5.5. The large complex formed by oxo-linkage or hydroxo-linkage of several units makes it of low solubility in aqueous solution, but not a precipitate. Further, it still has good ability to coordinate with other ligands, such as carboxylate groups of cellulose, sulfate anions, and carboxylic acids of rosin. In other word, this polynuclear species could function as a mordant, the bridge to connect rosin and wood fiber. The hypothesized large complex[15] of this complicated structure is depicted in Fig. 1.5. Alum is not the only chemical that could coordinate and form polynuclear complex with rosin and fiber. Gallium, cerium, lanthanum, ferric ions and highly protonated polyamines are also very effective mordants in rosin sizing[16-17].

OOC-Cellulose
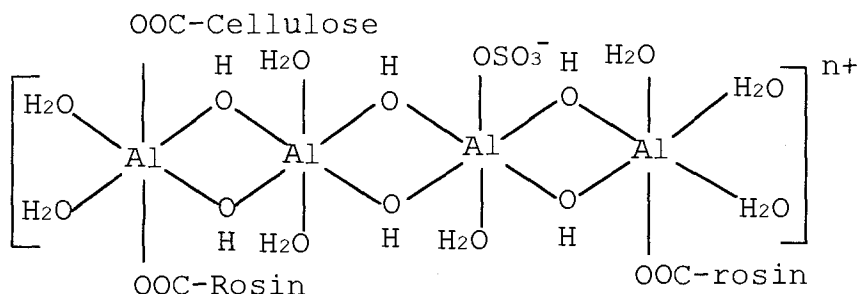
Fig. 1.5 Hypothetical structure of aluminum complex
with rosin and fiber

1.6 AKD and ASA sizng system:

AKD(alkyl ketene dimer) is the first synthetic sizing
agent in the world. It was invented in 1953 and was used as
a sizing agent three years later[18]. However, it was not
widely adopted until thirty years later with the transition
of the paper industry from acid to alkaline papermaking.
The driving force of this transition is the availability of
precipitated calcium carbon(PCC) as fillers. PCC offers
high opacity, high brightness and low cost. Calcium
carbonate can only be used as a filler in alkaline
papermaking systems since it will react with acid.

AKD is a ketene dimer with two hydrocarbon chains. It
is synthesized by dimerizing the acyl chlorides of fatty
acid hydrocarbon chloride. AKD reacts with the hydroxyl
groups of wood fibre through its four-membered lactone
ring(Fig. 1.6). The β-keto ester linkage is formed after

this reaction. The existence of the β-keto ester linkage has been proved by Botorff through ^{13}C NMR study[19]. This linkage is stable and is the reason why AKD and ASA are more effective sizing agents than rosin on the same weight basis and why AKD and ASA sized papers tend to have better resistance to liquid attack. The reaction rate of AKD with cellulose is moderate however, indicating the high activation energy, Ea. of this reaction.

$$
\begin{array}{c}
\quad\quad\quad\ \ O \\
\quad\quad\quad\ \ \| \\
\text{Cellulose-O-C} \quad O \\
\quad\quad\quad\ \ | \quad\ \ \| \\
\quad\quad\text{R-CH-C-CH}_2\text{-R}
\end{array}
$$

↑ Cellulose-OH

$$
\begin{array}{c}
\text{R-CH=C-O} \\
\quad\ \ | \quad | \\
\text{R-HC-C=O}
\end{array}
$$

↓ H_2O

$$
\begin{array}{c}
\text{R-CH}_2\text{-C=O} \\
\quad\quad | \\
\text{R-HC-C=O} \\
\quad\quad\ | \\
\quad\quad\ \text{OH}
\end{array}
$$

↓

$$
\begin{array}{c}
\text{R-CH}_2\text{-C=O} \\
\quad\quad\ | \\
\quad\quad\ \text{R-CH}_2 \quad + \quad CO_2
\end{array}
$$
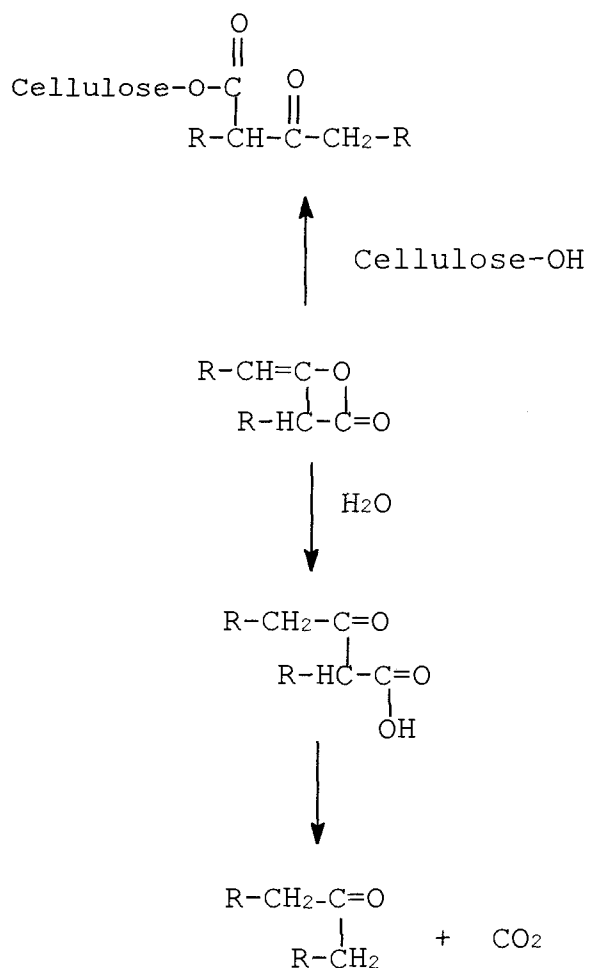
Fig. 1.6 AKD sizing and hydrolysis process

Therefore, sizing occurs only after sheet-drying. It might take days or months to develop full sizing. The reaction rate with cellulose can be increased by using a catalyst or by heating. Bicarbonate ions and polymers[20] containing basic amine groups are very effective catalysts for this reaction. Heating treatment, in addition increasing the reaction rate, would increase the diffusion of size and benefit the size distribution[20].

ASA(Alkenyl succinic anhydride) is another widely used synthetic size in alkaline papermaking. It is synthesized from isomerized alpha-olefin(Fig. 1.7). Alpha-olefin usually contains 16-20 carbon atoms. ASA also reacts directly with cellulose(Fig. 1.7) by forming covalent ester bond.

The reaction rate of ASA with cellulose is faster than that of AKD. About 80% of sizing is achieved on paper machine[21-22].

Both AKD and ASA are nonionic molecules that have no innate attraction for anionic fibers. Thus, cationic starch or synthetic cationic polymers must be used as size retention aids.

Hydrolysis of AKD and ASA is one of problems associated with their application in sizing. This process would compete with the ester formation[20](See Fig. 1.6 and Fig. 1.7). The hydrolyzed portions of AKD and ASA are not

effective sizing agents. Low temperature, shorter storage times and lower pH emulsifying formulations will limit the rate of hydrolysis.
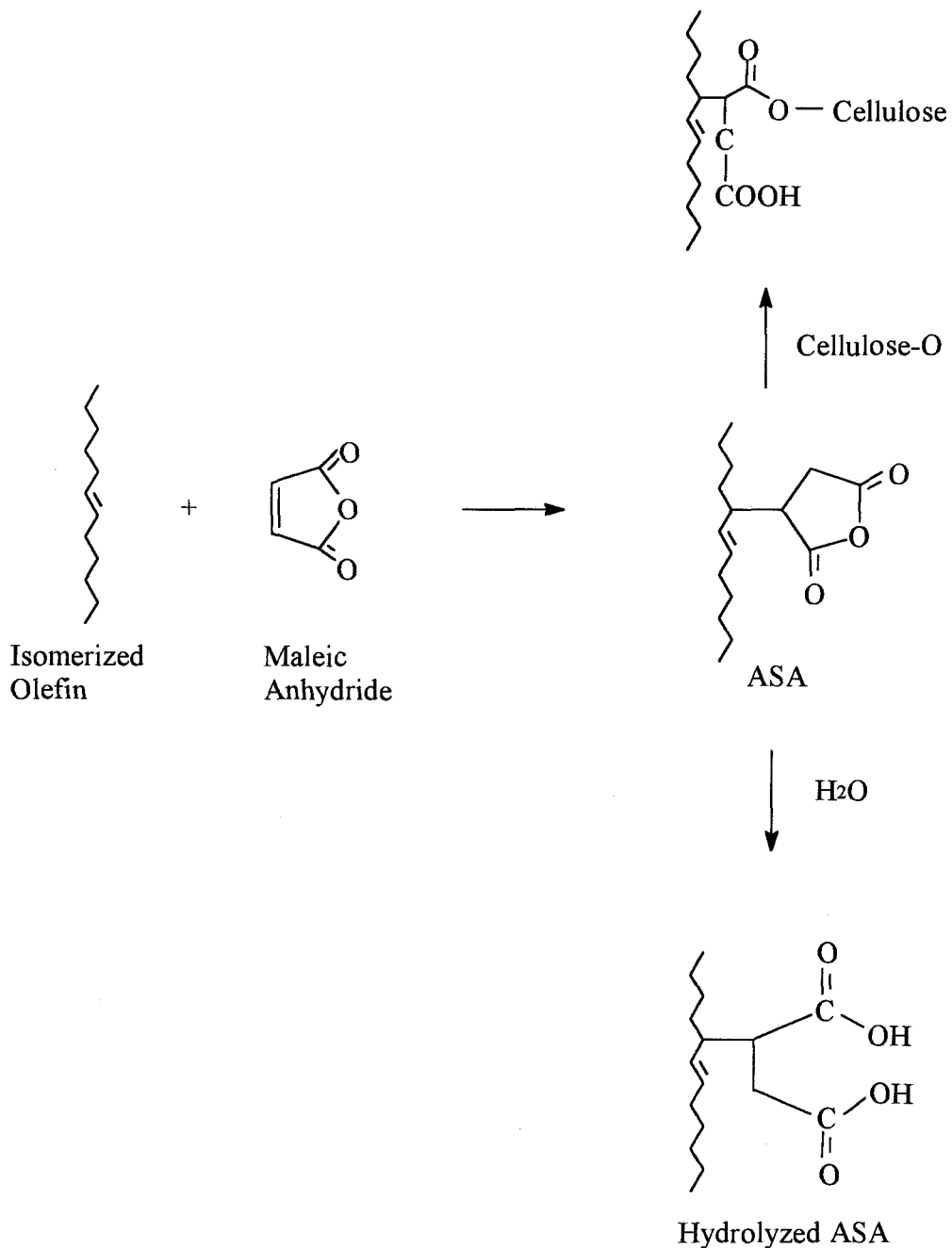
Fig. 1.7 Preparation, sizing and hydrolysis reactions of ASA

Problems with the application of ASA and AKD also include: slipperiness, difficulty of retention and instability of size emulsion.

1.7 Paper sizing measurement

The two purposes of measuring sizing in the laboratory are to predict whether the product will meet the customers' specification and to control the sizing process. There are a wide variety of methods employed by papermakers. However, there is no universal one that applies to all paper products. Suitable methods are selected for various paper products.

Generally, the most common classifications of testing methods are 1)absorption tests, 2)penetration tests and 3) surface tests[1-2]. In adsorption tests, the amount of liquid absorbed by the paper specimen is measured. Cobb test is an example of this group. In penetration tests, the required to achieve a given degree of liquid penetration is measured. Water drop adsorption, Hercules size test, ink flotation, and edge penetration test, are some examples of this group. In the surface tests, surface properties of the paper specimen are measured. An example of this group is contact angle measurement.

In all of these methods, the size test procedure, penetrant and test conditions, such as pH and temperature, must be carefully selected. It is a challenge to select the test method conditions that accurately reflect the desired end-use performance.

The following are descriptions of some methods that are commonly used in the paper industry.

1.7.1 Cobb test[23]

This test was first described by Cobb. The basic idea is to measure the amount of water adsorbed by a paper sample at a given time, usually 2 minutes. Water is confined to a fixed area of the sample (usually $100cm^2$) by means of a metal ring clamped to the sheet. The amount of absorbed water is indicated by the gain in the weight. Details of the apparatus and method are given in TAPPI Method T441. The method is very easy and convenient to use. However, it is not applicable to distinguish the differences of sizing efficiency for hard-sized paper.

1.7.2 Contact angle test[24], also TAPPI Method T458.

In this test, a drop of liquid is rested on a sheet of paper or board surface. After five seconds, the angle is

measured from the drop side of a tangent drawn to the surface of the drop at the point of contact with the paper. A larger contact angle means poor wetting of the surface, which usually represents increased sizing.

1.7.3 HST(Hercules Sizing Test)[25]

The Hercules sizing test measures the penetration rate of a darkly colored ink. As the liquid penetrates through the paper sample, the reflectance of the other side of the paper will decrease. Photocells within the equipment register the reflectance during the penetration process. The timer starts when the ink is poured onto the paper sample, which is also the beginning point of the liquid penetration. The timer stops automatically at the point where the reflectance at the back side of sample reaches a predetermined value, usually 80%. A long penetration time indicates a high level of sizing of the sheet.

1.7.4 Other commonly used methods[1-2]:

Water drop test:

A water drop is applied to the surface of the sample from a fixed height and drop size. The test measures the time for one or more drops to completely soak in.

Ink Jet printability:

The suitability of paper for ink jet printing is determined by printing a standard pattern and measuring the print density and feathering by eye or instrument.

Ink flotation tests:

A sample of paper is floated on an aqueous ink solution at a controlled temperature. The time is noted for a specified degree of color to appear on the upper surface. The indefiniteness of the end point makes it difficult to secure close agreement between different operators. Also, the water diffuses faster than the dye in the ink solution for hard sized paper, so it is doubtful if the results by observing the change of color could reflect the water-resistance of paper correctly.

1.8 Research interests in internal sizing

Scientist and papermakers who are working on internal sizing have put most of their energy on the following:

(1) Searching for new chemicals and strategies that could introduce more effective sizing while maintaining other favorable properties of paper.

(2) Understanding the sizing mechanism of existing sizing systems so that they might be used more effectively.

(3) Modifying existing sizing system to improve their performance.

(4) Developing new methods to measure sizing on-line so that better control of the sizing process might be achieved.

This thesis concentrates on the development of a new internal sizing chemical.

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2. Application of octadecylamine as an internal sizing agent

2.1 Introduction

Sizing is paper's ability to resist the wetting and penetration of aqueous solutions such as water, ink, or milk. Wood fibers naturally attract water molecules through extensive hydrogen bonding due to the hydroxyl groups of cellulose and hemicellulose. Internal sizing treatments convert the hydrophilic fiber surfaces into hydrophobic surfaces. Effective internal sizing systems must meet all of the following requirements [1,2]:

1. the sizing agent must be highly hydrophobic.

2. the sizing agent (and anchoring system) must be retained during papermaking.

3. the sizing agent must have good coverage on the fiber surface.

4. the sizing agent must be anchored to the fiber surface of paper.

5. the sizing agent and its anchor must be chemically inert to the liquid.

Rosin soap with alum as a mordant was the principal internal sizing system used in the paper industry for many years. The optimum pH of the pulp slurry for this sizing system in the range of 4.5 to 5.5. Even with some

modifications, its use was not practical for neutral to alkaline papermaking processes using calcium carbonate as a filler. Other sizing agents are usually used for these grades of paper, including alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). However, these materials have several disadvantages: high cost, formation of static electricity on the sized paper, paper surface slipperiness, and fugitive sizing [3].

It would be advantageous to develop new internal sizing agents that could induce sizing under alkaline conditions. In our laboratory, efforts have focussed on determining the mechanism of action for mordants based on coordination chemistry and developing new mordants for rosin sizing soap sizing that would be effective under alkaline conditions [4-7]. When polyamine was applied as a substitute for alum as a mordant in rosin sizing, highly effective sizing was achieved at high pH. Although neither polyethylenimine (PEI) nor polyallylamine (PAA) alone could induce sizing, their function as mordants inspired us to try aliphatic amines as internal sizing agents. The hypothesis is that these materials would be self-substantive since they have high hydrophobicity from a long aliphatic chain and an amine group to provide direct anchoring to the fiber; therefore, octadecylamine, $CH_3(CH_2)_{17}NH_2$, was selected as a candidate internal sizing agent.

2.2 Results and discussion

Unbleached kraft (Canadian Standard freeness, CSF, of 600 mL) and bleached kraft (CSF of 400 ml). Softwood pulps were used to make laboratory handsheets using 0.1% to 1.0% octadecylamine (based on the mass of oven-dry pulp) as an internal sizing agent. The sizing levels in these handsheets were compared to control sheets using 1% rosin and 2% alum sizing at pH 4.5. Some handsheets were air dried, while others were dryer-dried at 250°F for 4 minutes. The level of sizing was determined by the Hercules Size Test (HST, using neutral and 1% formic acid inks) and Cobb size values; these results are shown in Table 2.1. In general, the Cobb size test does not show changes in well sized papers and their values are not discussed. Size tests were repeated after various lengths of time up to one month with very little change in values. In other words, no apparent aging or curing time is observed.

2.2.1 Sizing with bleached pulp and unbleached pulp

For handsheets made from unbleached softwood pulp and dryer-dried, it was found that 0.25% octadecylamine imparts paper well sizing efficiency (HST values are 1312 s with 1% formic acid ink and 534 s with neutral ink). It is interesting to note that for handsheets made with unbleached

Table 2.1. The effect of the amount of amine size and drying method on sizing efficiency and paper strength[a]

A. Unbleached kraft softwood pulp, air-dried handsheets

Sizing Method	HST, s 1% FA[b]	HST, s Neutral ink	Cobb (g/m^{2}s)	Brk.Length (km)
1% ODA[c]	3072.9	1567.1	24.5	3.25
0.5%ODA	865.1	729.4	31.5	4.06
0.25%ODA	368.9	293.5	40.25	4.35
0.1% ODA	5.1	3.0	soaked	4.56
rosin-alum[d]	258.5	1696.1	24.5	4.19
Blank Control	–	–	–	5.15

B. Unbleached kraft sofwood paper, dryer dried[e]

Sizing Method	HST, s 1% FA[b]	HST, s Neutral ink	Cobb (g/m^{2}s)	Brk.Length (km)
1%ODA	4445.6	2930.6	22.75	3.06
0.5%ODA	3546.2	1310.1	26.25	3.63
0.25%ODA	1312.3	533.7	28.88	4.21
0.1%ODA	4.6	4.2	soaked	4.64
rosin-alum[d]	694.5	3175.0	22.75	4.24
Blank control	–	–	–	5.14

Table 2.1 (Continued)

C. Bleached kraft softwood paper, air dried over-night

Sizing Method	HST, s 1% FA[b]	HST, s Neutral ink	Cobb (g/m^{2}s)	Brk.Length (km)
1% ODA	103.6	174.7	29.75	3.06
0.5% ODA	6.5	23.0	36.75	3.67
0.25% ODA	0.5	0.1	soaked	3.71
0.1% ODA	0.2	0.1	soaked	4.03
rosin-alum[d]	63.8	174.2	27.13	4.20
Blank control	-	-	-	4.35

D. Bleached kraft softwood paper, dryer dried:

Sizing Method	HST, s 1% Fa[b]	HST, s Neutral ink	Cobb (g/m^{2}s)	Brk.Length (km)
1% ODA	941.1	805.2	23.63	3.78
0.5% ODA	130.2	161.6	24.5	3.18
0.25% ODA	5.1	3	soaked	3.64
0.1%	0.9	1.5	soaked	4.09
rosin-alum[d]	200.7	426.3	20.125	3.78
Blank control	-	-	-	4.18

[a]Stock adjusted to around 7.3 for amine sized pulp; cold tap water in sheet mold

[b]1% Formic acid ink

[c]Octadecylamine

[d]1% rosin and 2% alum used at pH 4.5

[e]Handsheets in sheet dryer at 250°F for 4 minutes after press cycle.

kraft pulp and ODA, the HST values with 1% formic acid ink are always much higher than those values with neutral ink. In the rosin-alum sizing system, the opposite is observed, while in the case of AKD sizing, HST values with 1% formic acid ink are approximately the same as HST with neutral ink [8-9].

In the case of handsheets made with bleached pulp and ODA, however, the HST values with 1% formic acid ink was not consistently lower or higher than HST values determined with neutral ink. Furthermore, bleached paper is not easily sized by ODA compared with unbleached paper; a higher level of ODA was needed to keep the sizing efficiency comparable to that of the rosin-alum system. These results could indicate that several mechanisms are involved in the sizing process with ODA.

2.2.2 Effect of heating treatment on sizing

The drying conditions of the handsheets affected the level of sizing. Higher levels of sizing was found in handsheets oven-dried at 250°F for 4 min than in those that were air-dried for sheets made of both bleached and unbleached pulp. For example, air-dried handsheet made with bleached softwood pulp and 0.5% ODA had HST values of 7 s with 1% formic acid ink and 23 s with neutral ink. In contrast, the corresponding dryer-dried handsheet had HST values of 130 s with 1% formic acid ink and 162 s with neutral ink. Drying sheet for longer period would also increase the sizing

efficiency. For example, dryer-dried handsheet made with unbleached softwood pulp and 0.25% ODA had HST value of 1327.5 with 1% FA if the sheet was dried for 4 minutes. In contrast, the handsheet had HST value of 1802.1 s with 1% FA if the sheets was dryer-dried for 30 min instead.

2.2.3 Strength property after sizing

The tensile strength of paper decreases with the use of rosin-alum sizing systems. Therefore, it is important to determine how ODA affects paper strength. Table 2.1 shows that the higher the level of sizing achieved with ODA, which also corresponds with the amount of ODA added, the lower the level of tensile strength, reported as the breaking length. Octadecylamine could be retained onto fiber by itself. This self-retention, however, will promote the flocculation of the fiber in pulp stock. The flocs brought by some low-molecular retention aid, such as alum, are usually small, weak and easily dispersed, so called "soft flocs" [10-11]. These soft flocs will not affect the final paper strength too much. In contrast, flocs brought by high-molecular polyelectrolyte retention aid are called "hard flocs". They cause many problems with sheet properties, such as large differences in mass distribution. The weak spots developed between the flocs in the sheet will affect overall strength of the final sheet. The performance of octadecylamine in decreasing breaking length is very similar to that of polyelectrolyte as

Table 2.2. Effect of cationic starch on sizing and strength[a]

A. Unbleached kraft pulp with 0.5% ODA

Starch Addition	HST, s 1% Fa[b]	HST, s Neutral ink	Cobb (g/m^2s)	Brk.Length (km)
0%	3546.2	1310.1	26.25	3.63
0.5%	3539.6	1572.7	29.75	4.42
1%	2138.1	1218.0	29.75	4.66
2%	2200.4	1400.0	32.375	5.21

B. Bleached kraft pulp with 0.5% ODA

Starch Addition	HST, s 1% FA[b]	HST, s Neutral ink	Cobb (g/m^2s)	Brk.Length (km)
0%	130.2	161.6	24.50	3.18
0.5%	59.80	85.70	26.25	3.53
1%	83.70	80.90	26.25	3.88
2%	91.80	106.3	29.75	3.93

[a]Sheets were formed at pH 7.3 in cold tap water and dryer dried at 250°F for 4 min

[b]1% Formic acid ink

retention aid in paper industry. This, however, could be overcome by the use of mechanical (hydrodynamic) action in the headbox.

Table 2.2 shows that the application of cationic starch overcomes the decrease in strength, but it also resulted in a decrease in the level of sizing.

2.2.4 Effect of pH value on sizing

The effect of pH value of the pulp stock on sizing with ODA is shown in Table 2.3. The optimum pH range for effective sizing with rosin-alum sizing system is 4.5 to 5.5. In this range the aluminum rosin complex that is formed can be retained onto fibers from aqueous solutions [3]. The optimum pH range for sizing with ODA is relatively broad, and effective sizing was achieved for handsheets in a pH range from 7 to 10. It was found that the upper limit of this range is near that pKa of the conjugate acid of octadecylamine (approximately 10.65 using the pKa of octadecylamine for comparison). The equilibrium equation of octadecylamine in aqueous solution is as follows:

$$C_{18}H_{37}NH_3^+ \iff C_{18}H_{37}NH_2 + H^+ \qquad pK_a = 10.65$$
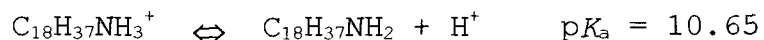
Table 2.3. Effect of pH on sizing and paper strength property[a].

A. Unbleached pulp with 0.25% ODA

pH value of stock	HST with 1% FA[b], s	HST with Neutral ink,s	Cobb (g/m²s)	Brk.Length (km)
6	12.1	9.0	soaked	–
7	780.2	426.9	28.88	4.31
8	1358.1	613.1	28.88	4.34
9	1359.8	580.4	30.63	4.36
10	1265.3	393.2	30.63	4.16
11	528.1	185.9	31.50	4.45

B. Bleached pulp with 0.5% ODA

Sizing Method	HST with 1% FA[b], s	HST with Neutral ink,s	Cobb (g/m²s)	Brk.Length (km)
5	0.1	0.1	soaked	4.79
6	8.4	28.5	soaked	4.54
7	43.9	62.8	27.13	3.78
8	157.5	146.4	24.50	3.83
9	194.6	196.3	25.38	3.51
10	195.3	207.9	24.50	3.48
11	100.1	142.1	27.13	4.54

[a]Sheets were formed in cold water with adjusted pH value and dryer dried at 250F for 4 min

[b]1% Formic acid ink

Therefore, at pH above 10.65, the concentration of octadecylamine is higher than that of protonated octadecylamine and the former form may not be an active sizing agent. The lower limit of the optimum pH range, on the other hand, might be related to the fiber performance. At pH below 7 carboxylate groups on the surface of fibers may become less anionic as they become protonated.

2.2.5 Other factors that affect sizing result

The addition of metal ions has been shown to increase the level of sizing when using polyamine as a mordant for rosin sizing [5]. Addition of selected metallic ions with ODA, however, decreased the sizing efficiency of handsheets as shown in Table 2.4. Decoloration in the handsheets treated with Fe^{2+} and Cu^{2+} salts indicates the retention of these salts.

An increase in temperature of the pulp stock while making handsheets decreased the level of sizing with ODA, especially at temperatures above 30°C as shown in Table 2.5. It was also found that a long storage time of pulp stock with the ODA already added would lower the level of sizing in the handsheets. For example, if the bleached softwood pulp with 0.5% ODA added was stored for 1 hr before making handsheets, the sheet made only had an value of HST of 33.1 s with neutral ink. Therefore, in our tests, the stock wasn't kept longer than 1/2 hr before making handsheets.

Table 2.4. Effect of metallic ions (1%) on sizing[a]

A. Unbleached pulp with 0.25% ODA

Type of ions	HST with 1% FA, s	HST with neutral ink (s)
Fe^{2+}	5.8	6.3
Cu^{2+}	23.4	190.8
Zn^{2+}	636.5	455.7
Al^{3+}	19.1	10.3

B. Bleached pulp with 0.5% ODA

Type of ions	HST with 1% FA, s	HST with neutral ink, s
Fe^{2+}	42.1	5.5
Cu^{2+}	20.0	91.2
Zn^{2+}	29.8	10.4
Al^{3+}	1.2	2.0

[a] Sheets were made from stock at pH around 7.3 and dryer dried at 250°F for 4 minutes.

[B] Formic acid ink

Table 2.5. The effect of stock temperature on sizing

A. Unbleached kraft pulp with 0.5% ODA

Temperature of stock, °C	HST with 1% FA, s	HST with neutral ink, s
20	3596.4	1698
30	3389.8	1424.1
35	1851.4	956.8
40	210.9	141.6
50	15.9	29.4
60	4.6	14

B. Bleached kraft pulp with 0.5% ODA

Temperature of Stock, °C	HST with 1% FA, s	HST with Neutral Ink, s
20	130.2	161.6
30	60.3	94
35	60.6	76.3
40	2.4	6.1
50	2.3	2.4
60	2.2	1.8

[a] Sheets were made from stock at pH 7.3 and dryer-dried at 250°F for 4 minutes

Table 2.6. Sizing result for bleached hardwood and TMP pulps[a]

Pulp Type	ODA (%)	CSF(ml)	HST with 1%FA, s	HST with neutral ink, s
Bleached hardwood	0.5	590	243.0	240.5
TMP[b]	1	200	>8,000	>8,000
TMP[b]	0.5	200	493.2	995.5
TMP[c]	2	103	1303.2	642.8
TMP[c]	1	103	4.7	3.5

[a] Sheets were made from stock at pH 7.3 and dryer-dried at 250°F

[b] "Old" TMP pulp, which has been kept in refrigeration for two and half years.

[c] Fresh TMP pulp

Table 2.6 shows that sizing results of ODA on bleached hardwood pulp, and TMP pulps. There are two kinds of TMP pulps applied in our test: fresh pulp and "old" pulp, the latter one has been kept in refrigerator for two and half years and has a dark color. The sheets made from the "old" pulp didn't look very uniform. It is very interesting that the sizing results are remarkably different from each other. The "old" pulp is easily sized by ODA. In contrast, the fresh pulp is hard to size. The very small value of CSF of fresh TMP pulp indicates it has a large specific surface area. That might explain why it is difficult to size.

2.2.6 The mechanism(s) of sizing

As mentioned, there may be several mechanisms involved in the sizing process with ODA. Differences probably center among anchoring mechanisms. Octadecylamine has a very long carbon chain as its tail. This long carbon chain provides the hydrophobic group to resist wetting by aqueous solutions. The amine group must provide the anchoring mechanism. The amine is largely unprotonated above pH 10.64 and largely protonated below pH 10.64.

Recent work summarizes cationic-π interactions [12] that exist widely between cations and aromatic structures. In this case of sizing with ODA, lignin contains aromatic groups while protonated octadecylamine acts as a cation. This mechanism supports the observations that unbleached pulp is more easily

sized than bleached pulp and that formic acid ink has a lower penetration rate than neutral ink in the HST test.

The cationic-π interaction is a non-covalent interaction involving a quadrupole moment of the aromatic group. While a relatively weak interaction, it can be much stronger than hydrogen bonding. For example, NH_4^+ and $N(CH_3)_4^+$ have binding energies to benzene of 19 kcal/mol and 9 kcal/mol, respectively. (For comparison, the interaction of NH_3 with benzene is 1.4 kcal/mol). Therefore, protonated primary amines should be more effective sizing agents than secondary, tertiary, and quaternary ammonium amines in unbleached pulp. It was found that 1% didecylamine (on pulp) gave no sizing with unbleached kraft pulp. For that matter, 1% diphenylmethaneamine, 1% adamantanamine, and 1% aminoanthracene did not give sizing, either.

It is also possible that lignin, being less hydrophilic than cellulose and hemicellulose, makes unbleached pulp easier to size. The fact that bleached pulp can be sized indicates that other interactions beside cation-π interactions must be possible. The highly effective sizing system using polyallylamine as a mordant for rosin sizing of bleached kraft hardwood pulp [4] must be due to other types of interactions involving carboxylate groups of rosin and fibers. Interactions between cationic surfactants (ODA) and polyanionic solid polymers (cellulose and hemicellulose) in aqueous solutions are described as cooperative binding [13].

This interaction provides the possibility of retention of amine onto cellulose. Some characteristics of this cooperative binding model between polyanionic solid polymer and cationic surfactants are that binding highly depends on temperature, pH of aqueous solution and ionic strength [13-14]. It is believed that higher temperature and the existence of some electrolytes decreases the binding, as was observed in our work.

It seems obvious that a preferable sizing agent to ODA would be rosin amine. However, commercial rosin amine (Rosin Amine D, Hercules) on unbleached kraft pulp gave an HST value of only 14.7 s with neutral ink(Table 2.7). The steric hindance of the amine in this structure may prevent adequate anchoring. Also, 1% dehydroabietylamine (Aldrich, Milwaukee, Wisconsin) on unbleached kraft pulp gave an HST value of 15 s with neutral ink. In contrast, tetradecylamine(Aldrich, Milwaukee, Wisconsin) on unbleached kraft pulp gave better sizing: HST value was 23.3 s with neutral ink.

2.3 Conclusions

Octadecylamine was shown to be a highly effective sizing agent for unbleached kraft Douglas-fir pulp at a level of 0.25% addition on pulp. It did not require the use of a

Table 2.7. Sizing results with ODA-substitute amine chemicals

Type and amount of chemical	HST with 1%FA, s	HST with neutral ink, s
1% Rosin amine	21.7	14.7
1% adamantana	0.5	0.3
1% diphenyl amino	0.6	-
1% dehydroabietylamine	20	15
1% tetradecylamine	28	23.3
1% didecylamine	0.8	-
1% dodecylamine	1.2	1.2

mordant, such as alum. It was less effective on bleached kraft Douglas-fir pulp at 0.5% level of addition. The pH range of the pulp slurry that gave the highest level of sizing was 7 to 10. Notably, the sized handsheets made from unbleached kraft pulp were more resistant to formic acid ink than to neutral ink by the HST test.

2.4 Experimental procedures

The unbleached Douglas-fir kraft pulp had a Canadian Standard freeness (CSF) of 600 mL and a 40 mL permanganate (K) number of 62. The bleached Douglas-fir Kraft pulp had a CSF of 400 mL. Six grams of air dried pulp was added to 450 mL of water and the slurry was blended in food blender for 3 minutes until the stock was well dispersed. The desired amount of octadecylamine (ODA) solution (1% wt/vol in ethanol since ODA is not water soluble) was added and the mixture was stirred for another 2 minutes. Cationic starch or metal ions were added at this point in those samples identified as such. The pH was adjusted to the desired value. The slurry was then diluted to a consistency of 0.15% and the pH value was readjusted. In some experiments, hot water was heated in advance and the temperature was adjusted and kept consistent as necessary.

Handsheets of 60 g/m^2 basis weight were made according to TAPPI Test Method 205 on-88 in the British Sheet Mold. The

standard press cycle was used, and then the sheets were either dried in a sheet dryer at 250°F for 4 min or air-dried according to the test method. Dryer-dried sheets were conditioned at 72°F and 50% relative humidity for at least 4 hr prior to testing. Cobb size values were determined by TAPPI T441 on-90. Ink penetration resistance was determined on a Hercules Sizing Tester according to T530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution. Paper tensile strength was tested according to TAPPI T494 on-88.

Cationic Starch was obtained from Grain Processing Corporation with a brand name "Chargermaster R430 Cationic Starch". Octadecylamine was obtained by Aldrich Chemical Company, Inc. with the purity at 98%. All metal ions were in the form of reagent grade chemicals. The percentages are the masses of chemical relative to that of oven-dry pulp. Al^{3+} is as $Al_2(SO_4)_3 \cdot 16H_2O$, Cu^{2+} is as $CuSO_4$, Fe^{2+} is as $FeSO_4 \cdot 7H_2O$, and Zn^{2+} is as $ZnCl_2$. For example, 1.0% Al^{3+} is 1.0% alum based on the mass of dry pulp.

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