

Rosin soap sizing with ferric and ferrous ions as mordants

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ABSTRACT: Ferric and ferrous ions were investigated as mordants for rosin soap size. While ferric ion at pH 3.0–4.0 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 formation of highly stable five-member chelate rings between lignin units and iron ions and the high bond dissociation energy of η^6 arene polyhapto ligand-metal ion bonds are thought to be the reasons why their Hercules size test values with 1% formic acid ink or neutral ink are extraordinarily high compared to the optimal condition when alum is used as the mordant. The excellent sizing results achieved by iron ions in mechanical pulp strongly support this hypothesis. Although the paper is darkened to some extent when iron ions are used, it is recommended that ferrous or ferric ions be used in rosin soap sizing instead of alum in unbleached chemical pulp and mechanical pulp in cases where the color of paper or paperboard products is not a concern. Iron mordants would also act as effective mordants for some dyes to deeply color mechanical pulp, such as in black or darkly colored construction paper.

KEYWORDS: Chemistry, ions, iron compounds, mordants, Pseudotsuga, rosin size, rosin soap, sizing, wet ends.

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 of 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 (1). Obviously, the understanding of the chemistry involved in rosin soap sizing is crucial if we want to make rosin soap sizing under neutral and alkaline papermaking conditions commercially applicable.

A recent study (2) from our laboratory has looked at the issue closely and the importance of coordination chemistry in rosin sizing was demonstrated. A series of coordinating metal ions 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.

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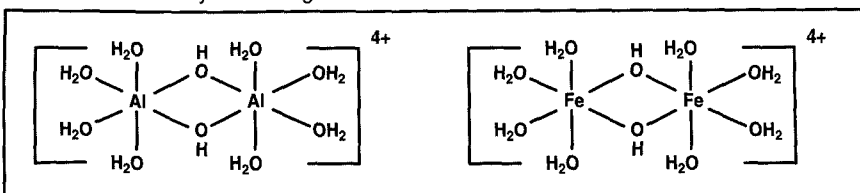
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If the coordination chemistry mechanism is true in rosin soap sizing, why is alum the most effective mordant among all the coordinating metal ions? We know from coordination chemistry that Al^{3+} is far from the best metal ion as for its coordinating 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+} .

Based on experiment results and an extensive discussion, two important criteria for an effective mordant of rosin soap size have been pointed out (1, 2). 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 (Fig. 1) and oxo bridges, but few other metal ions can do so. This may be an important reason.

If a metal ion has a better coordinating capability than 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 candidates from this point of view. They are both transition metal ions and have very good coordinating capability. In addition, the aqueous chemistry (3) of ferric ion is similar to that of Al^{3+} in that they are both trivalent cations and ferric ion is also able to form a binuclear species (Fig. 1) by the formation of a hydroxo bridge, even at

1. Formation of the hydroxo bridge with aluminum and ferric ions



I. Sizing results of unbleached Douglas-fir kraft pulp

Mordant	Amount ^a added, %	pH of sizing	Cobb size, g/m ² /2 min	HST ^b (S), neutral	HST (S), 1% FA ^c	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	—
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	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
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	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 ^d	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

^aBased on oven-dry pulp.

^bHercules size test.

^cFormic acid ink.

^dTest terminated at this point.

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 π -complexes with benzenoid aromatics (4), 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 (5) and Duston (6) 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 the use of ferrous ion as a mordant of rosin sizing was reported in the literature either.

Results and discussion

Ferric chloride was used as a mordant in the 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 I**, ferric ion induces better sizing at pH around 3.5 than alum does at its optimum conditions which are pH 4.5–5.0 and 1.0–2.0% dosage. (Remember that high HST (Hercules Size Test) values and low Cobb size values indicate good sizing.) Noteworthy is the fact that the HST values with 1% formic acid (FA) ink are much higher (about 10 times) than in the case of alum. The HST values with neutral ink are so high that only a few samples were measured.

There is still no agreement on why formic acid can accelerate the penetration of ink into paper. Two different mechanisms (7) have been postulated. One attributed the function of formic acid to its lower surface tension. A test liquid of lower surface tension will be able to penetrate faster via the pores of the paper; however, the surface tension of 1% formic acid aqueous solution is 70.1 dyne/cm at 30°C and that of pure water is 71.3 dyne/cm at 30°C (8), a small difference. It is likely that the ink decreases the surface tension as much as 1% formic acid since it has polar and nonpolar portions like a surfactant. In some of our results, the ratio of the HST values time with neutral ink to that with 1% formic acid ink varies from as low as 2.2 to as large as 70; if the surface tension change were the only factor, one would expect this ratio to be small and reasonably constant. Another mechanism stated is that the size-fiber bond strength may be a factor in determining the HST values with formic acid ink. Other work also supports the latter hypothesis (2).

We believe the essence of the HST test with 1% formic acid ink is a ligand substitution reaction. Formic acid substitutes for carboxylic acids groups of rosin or fiber components (and perhaps other ligands as well) to complex

with mordant metal ions. Thermodynamically, the much higher HST values mean the bonding in 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, formic acid. Of course, reaction kinetics may also play a role.

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 (9), 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 I**. 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.

The effects of pH and the amount of mordant on rosin sizing results were investigated with the same unbleached pulp with rosin soap size kept at 0.5% on pulp. **Table I** shows that ferric ion induces optimum sizing at pH around 3–4, while sizing results decrease steadily when the pH is increased above 4.5. Ferrous ion induces optimum sizing at pH around 5.5. The sizing efficiency is decreased slowly at lower or higher pH but is quite high in the wide pH range of 3–6. Like alum, both ferric and ferrous ions work best at an optimum level of addition. Under these experimental conditions, ferric ion induces its best sizing at 2.0% (on pulp) as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and ferrous ion induces its best sizing at 2.5% (on pulp) as $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. Ferrous sulfate has also been used to compare its performance with ferrous chloride, but the difference is not notable when their molar amounts are the same. The brightness of the handsheets has also been measured, as indicated in **Table I**. It is

usually lowered by about 2.5 points either when ferric or ferrous ion is used as 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 Fe^{3+} - Fe^{2+} electrode is 0.771 V, which means that molecular oxygen in water solution can convert ferrous into ferric ion in aqueous solution (3):



$$E = 0.46 \text{ V}$$

Even though this is a thermodynamically favorable reaction, one kinetics study (10) showed that the oxidation rate is extremely slow and practically negligible (half-life of many years) at pH below 5.5. **Table I** also shows 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 a 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 $\text{p}K_1$ of metal ions has been pointed out to be a good indication of the pH of their maximum sizing efficacy (2). The $\text{p}K_1$ of ferrous ion is 6.74 and that of ferric ion is 2.83, while their pH of maximum 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 (10) also showed that the oxidation rate becomes very rapid when the pH is increased toward neutral or higher values (half-life less than 1 h) and this can be the reason why ferrous ion loses its effectiveness rapidly at pH above 6.5 even though its $\text{p}K_1$ is 6.74.

While ferric and ferrous ions are both very good competitors of alum in sizing in unbleached pulps with lignin, when they are used as mordants of

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rosin soap sizing in bleached Douglas-fir kraft pulp and bleached hardwood chemical pulp, as shown in **Table II**, they both induce practically no sizing at their optimum sizing conditions for unbleached pulp. Nevertheless, alum still induces good sizing.

It is well known (11) that unbleached pulps are easier to size than bleached pulps. The reason is generally attributed to the higher carboxylic acid content (12) and higher levels of "desirable" colloid content such as saccharinic acids or anionic hemicellulose in unbleached pulps (11). Even though this may partly explain the different behavior of the two pulps, it cannot be the whole story here since alum is able to induce good sizing in both unbleached and bleached pulps. We are now forced to believe 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 Fig. 1, is not significant, if it occurs at all, 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 $[Al_3O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (3). But for ferric ion, the most important polynuclear species is the dimer $[Fe_2(OH)_2(H_2O)_8]^{4+}$ and the dinuclear complexes are only important in relatively concentrated solution (13). That is, even the dimer may have a negligible concentration in dilute solutions as in the case of the rosin sizing process.

It is documented (14) that to achieve good sizing, the size precipitate must have: (a) high retention and uniform distribution on fibers; (b) high hydrophobicity; and (c) strong bonding to fibers. No sizing can be achieved if any of the above requirements is not met. 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 and may improve the hydrophobicity and retention of the size

II. Sizing results of bleached chemical pulps

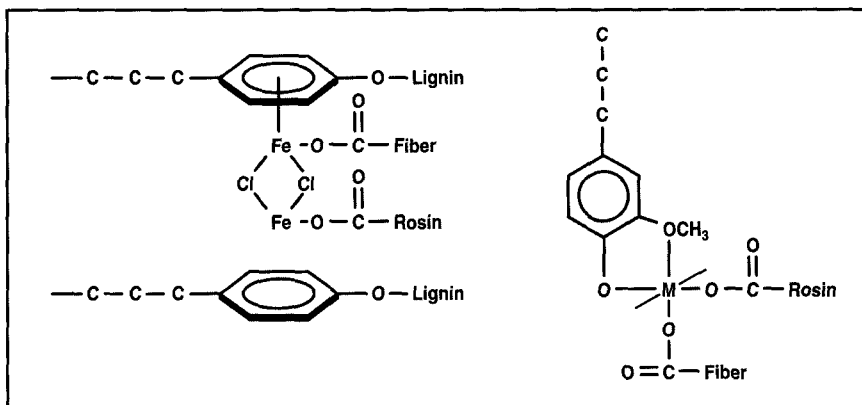
Mordant	Amount ^a added, %	pH of sizing	Cobb size, g/m ² /2 min	HST ^b (S), neutral	HST (S), 1% FA ^c
Bleached Douglas-fir kraft pulp					
Alum	1.0	4.5	25.2	88	47
	2.0	4.5	23.5	136	34
FeCl ₃ 6H ₂ O	2.0	3.0	Soaked	1.7	1.4
	2.0	3.5	Soaked	0.6	0.7
	2.0	4.0	Soaked	0.5	0.5
FeCl ₂ 4H ₂ O	2.5	5.0	Soaked	2.3	1.2
	2.5	5.5	Soaked	0.8	0.8
	3.5	5.5	Soaked	0.9	0.7
Bleached hardwood chemical pulp					
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 ₃ 6H ₂ 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 ₂ 4H ₂ 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

^aBased on oven-dry pulp.

^bHercules size test.

^cFormic acid ink.

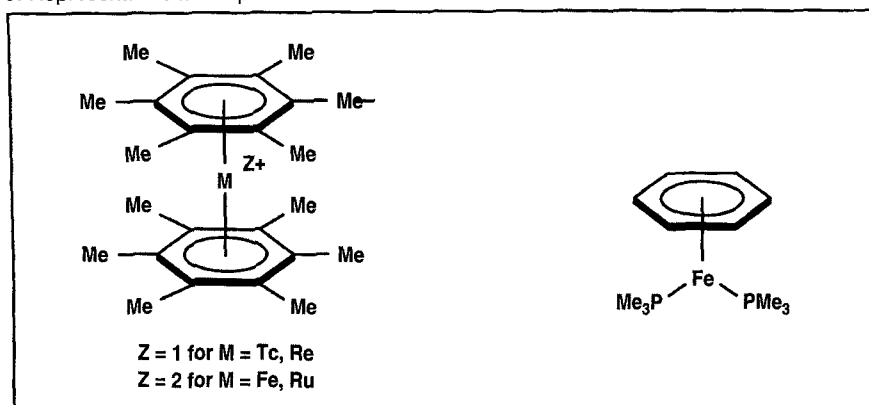
2. Postulated π -complex (left) and chelating ring formed between lignin and coordinating metal ions



precipitate as well. The very different behaviors of iron ions in unbleached and bleached pulps leads us to a conclusion 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. More specifically, rosin size is able to strongly bond to unbleached fibers via iron ions but is not able to bond to bleached fibers strongly enough to give sizing in the same sizing conditions.

3. Representative π -complexes between arenes and transition metals



III. Sizing results of mechanical pulp

Mordant	Amount ^a , %	pH of sizing	Cobb size, g/m ² /2 min	HST ^b (S), neutral	HST (S), 1% FA ^c	Brightness, %
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 ₃ · 6H ₂ O	2.0	3.5	21.0	>12,000 ^d	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 ₂ · 4H ₂ 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	—

^aBased on oven-dry pulp.
^bHercules size test.
^cFormic acid ink.
^dTest terminated at this point.

The most obvious difference between the unbleached and bleached chemical pulps is their lignin contents, and we believe this is the reason why iron ions have very different behaviors in them. Reasoning from the basic

principles of coordination chemistry, one can postulate that transition metal ions can form complexes with lignin in the two bonding patterns shown in Fig. 2, especially in the papermaking stages of pressing and drying. The

brightness data in Table I shows that the handsheets are darkened when ferric or ferrous ion is used as mordant 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 (15). Wood extractive tannin can also react with iron and produce blue-black color (16). But we cannot 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 Fig. 2 (right) should be possible for all coordinating metal ions, including Al³⁺. The one set of lone electron pairs in each of the two oxygen atoms on the benzenoid lignin unit are donated to empty metal orbitals. The five-member chelate rings should greatly enhance the stability of the complexes. Since bleached chemical pulp has much lower lignin content than unbleached chemical pulp, it is postulated 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 phenyl propane, a benzenoid aromatic. We know from organo-transition metal chemistry (4) that benzenoid aromatics can form π -complex (as indicated in Fig. 3) with virtually all transition metals. There are two kinds of bonding interactions involved in the formation of π -complexes. One is the overlap between empty metal *d*-orbitals and filled π 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 is through all six carbon atoms in the benzenoid ring so the arene group is called a η^6 ligand.

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Another interaction is the overlap between the filled metal *d*-orbitals and the empty benzene ring π^* 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 polyhapto ligands such as η^6 arene have significantly higher BDE values (4) than η^1 ligands (bonding through one atom in the ligand). Iron ion is well known for being able to form π -complexes (Fig. 3) with arene groups so it is postulated that they can form π -complexes with lignin as shown in Fig. 2 (left). The higher BDE of this kind of bonding and the excellent stability of five-member chelate rings probably explain why the HST values with 1% formic acid are extraordinarily high when iron ions are used as mordants in the sizing of unbleached softwood pulp.

It is known that mechanical pulp has the highest lignin content 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 and the absence of "desirable" colloid content such as hemicellulosic material on the fiber surface (11). If our hypothesis about the importance of lignin in the sizing mechanism with iron ions is true, we should expect iron ions to be able to induce better sizing than alum in mechanical pulp. Our results show that this is the case. As shown in Table III, ferric ion induces extraordinarily good sizing in the pH range from 3.5 to 5.0 when it is used as the mordant for rosin soap size in mechanical pulp. So does ferrous ion at pH 5.5 when an appropriate amount (3.5–5.0%

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ on pulp) is added. The Cobb Size values are as low as 21 g/m²/2 min and the HST values with neutral ink are above 10,000 s, which alum could never be expected to 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.

The handsheet brightness was also measured (Table III). 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. Nevertheless, iron ions might be used as mordants for rosin soap sizing of paper or paperboard where color is not critical, 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 paper. Ferrous ion with its applicability in a higher pH range than alum and ferric ion can show even more advantages. Also, the use of higher pH and divalent cations in place of alum during papermaking are both expected to lead to increased paper strength (17).

Conclusion

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 signifi-

cant 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 is 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.

Experimental

The unbleached Douglas-fir kraft pulp had a Canadian Standard freeness (CSF) of 450 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 min. The appropriate amount of mordant was added and the pH was adjusted with dilute HCl and NaOH solutions with stirring for 5 more min. After one or more hours, the stock was then diluted to 5.0 L with tap water and the pH was readjusted to the appropriate value. Handsheets of 60 g/m² 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 L instead of 7.0 L 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 h 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 the 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. **□**

Literature cited

1. Biermann, C. J., *Tappi J.* 75(5): 166(1992).
2. Subrahmanyam, S. and Biermann, C. J., *Tappi J.* 75(3): 223(1992).
3. Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, 4th edn., Interscience, New York, 1980.
4. Collman, J. P., Hegedus, L. S., Norton, J. R., and Finke, R. G., *Principles and Application of Organo Transition Metal Chemistry*, 2nd edn., University Science Books, Mill Valley, CA, 1987, p. 158–168, 239, 149.
5. Strazdins, E., *Tappi* 46(7): 432(1963).
6. Duston, H. E., *Tech. Assoc. Papers* 25: 475(1942).
7. Gess, J. M., *Tappi J.* 64(1): 35(1981).
8. Weast, R. C., *CRC Handbook of Chemistry and Physics*, 67th edn., CRC Press, Inc., Florida, 1986, p. F-31.
9. Huheey, J. E., *Inorganic Chemistry, Principles of Structure and Reactivity*, 3rd edn., Harper & Row, New York, 1983, p. 381.
10. Snoeyink, V. L. and Jenkins, D., *Water Chemistry*, John Wiley and Sons, New York, 1980, p. 384.
11. Reynolds, W. F., *The Sizing of Paper*, 2nd edn., TAPPI PRESS, Atlanta, 1989, p. 16.
12. Lindstrom, T., *Svensk Papperstid.* 85(3): R14(1982).
13. Pankow, J. F., *Aquatic Chemistry Concepts*, Lewis Publishers, Chelsea, MI, 1991, p. 369.
14. Strazdins, E., *Tappi* 64(1): 31(1981).
15. Singh, R. P., *The Bleaching of Pulp*, 3rd edn., TAPPI PRESS, Atlanta, 1979, p. 263.
16. Zabel, R. A. and Morrell, J. J., *Wood Microbiology, Decay and Its Prevention*, Academic Press, San Diego, 1992, p. 331.
17. Biermann, C. J., *Essentials of Pulping and Papermaking*, Academic Press, San Diego, 1993, p. 156.

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