Neutral to alkaline rosin soap sizing with metal ions and polyethylenimine as mordants

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ABSTRACT: With the understanding of coordination chemistry, metal ions Mg^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} are used with polyethylenimine (PEI) as mordants of rosin soap size. While Mg^{2+}/PEI and Mn^{2+}/PEI show no effect and Fe^{3+}/PEI is very effective in acidic pH range, Zn^{2+}/PEI can induce moderate sizing and Fe^{2+}/PEI and Cu^{2+}/PEI can induce very high levels of sizing under neutral to alkaline conditions (up to pH 10) in various pulps. The tensile and bursting strength of the handsheets can also be improved by 20–30% with the new mordants. It is observed that the pH of maximum sizing efficacy of these metal ions is in the vicinity of their pK_1 values. In addition, their performances as mordants or rosin soap sizing coincide with the Irving-Williams Effect which describes the general trends in the stability of metal complexes. Discussions on the mechanism of the HST sizing test with formic acid ink are also given based on some unusual observations.

KEYWORDS: Alkalinity, chemistry, ions, metal compounds, mordants, polyamines, polyethylenimine, rosin size, rosin soap, sizing, wet ends.

Cellulosic paper is very vulnerable to water since it contains many hydroxyl groups; therefore, sizing becomes a necessary process for many paper grades. Rosin soap size has been the most widely used sizing agent since the sizing technique was developed in 1807, because the material is fairly inexpensive and abundant and the sizing process is easy to operate. However, this sizing agent can now be applied only in an acidic pH range since alum has always been the predominant mordant of choice in industry and it is not effective at elevated pH due to its chemical characteristics.

Neutral to alkaline papermaking is becoming more and more popular because of its advantages *(1)* of lower paper cost, higher paper strength, reduced corrosion, improved paper stability on aging, and increased paper machine productivity. For example, in wood-free printing and writing papers *(1)*, the grades where the shifting from acidic to neutral or alkaline conditions has been the most successful and profitable, about 80% of the European production and 60% of the North American production was alkaline in 1993, while the corresponding figures in the two regions are expected to be about 100% and 85% by the turn of this century. However, neutral to alkaline papermaking can now be achieved only with emulsified rosin or synthetic sizing agents which are more expensive and more complicated to use than rosin soap size. Rate of cure, surface slip and fugitive sizing problems *(2)* can also discourage mills from using the synthetic sizing agents.

It would be a great advance to papermaking if neutral to alkaline

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I. Sizing results of bleached hardwood chemical pulp

Mordants	Amount[a] added, %	pK_1 of the metal ion	pH of sizing	Cobb size, $g/m^2/2$ min	HST[b] (S) (neutral)	HST (S) (1% FA[c])
Alum	1.0	5.01	4.5	24.5	650	209
	1.0		5.0	25.1	585	133
	1.0		7.0	Soaked	13	4.6
PEI	0.5		7.0	Soaked	87	34
Mg^{2+}/PEI	1.5/0.5	11.4	7.0	Soaked	53	42
	1.5/0.5		10.0	Soaked	0.1	0
Mn^{2+}/PEI	1.5/0.5	10.6	8.0	Soaked	1.0	0.5
	1.5/0.5		10.0	Soaked	0.3	0.1
Fe^{3+}	2.0	2.83	3.5	Soaked	0.6	0.7
Fe^{3+}/PEI	1.0/0.5	2.83	3.5	27.2	1177	709
	1.0/0.5		4.0	27.6	1463	1102
	1.0/0.5		7.0	Soaked	341	97
Fe^{2+}	2.5	6.74	5.5	Soaked	0.8	0.8
	2.5		7.0	Soaked	0.5	0.3
Fe^{2+}/PEI	1.5/0.5	6.74	5.5	23.5	2250	2077
	1.5/0.5		6.0	27.0	2065	1855
	1.5/0.5		7.0	24.3	4084	3017
	1.5/0.5		8.0	Soaked	943	47
Cu^{2+}	2.5	8.0	5.0	Soaked	2.0	1.0
	2.0		7.0	25.8	405	0.6
	2.5		8.0	26.4	372	0.6
	2.5		9.0	Soaked	1.9	0.2
Cu^{2+}/PEI	0.5/0.5	8.0	7.0	Soaked	835	2.0
	2.5/2.5		7.0	23.5	5110	57
	4.0/0.5		7.0	23.2	6050	144
	2.5/0.5		4.0	50.5	1430	11
	2.5/0.5		6.0	25.2	2780	29
	2.5/0.5		8.0	23.1	4770	59
	2.5/0.5		10.0	28.4	3420	21
	2.5/0.5		10.5	39.0	3390	7.3
Zn^{2+}	1.0	9.00	7.0	Soaked	0.6	0.4
Zn^{2+}/PEI	1.0/0.5	9.0	7.0	35.1	987	50
	1.5/0.5		8.0	69.4	320	3.2

[a] Based on oven=dry pulp.
[b] Hercules Sizing Tester.
[c] Formic acid ink.

sizing could be achieved with rosin soap size. However, this was believed to be theoretically impossible, so little research was done in the field. Although many polymers including protein have long been known to be able to improve rosin sizing *(3)*, no reasonable explanations have been given. Polyamines such as polyvinylcycloamidine *(4)* and polyethyleneimine (PEI) *(5)* were used with rosin soap size and alum to size paper, and acceptable levels of sizing could be achieved at a pH as high as 8 or 8.5; but again the mechanism of the sizing improvement was not clear.

In our laboratory, various lanthanide metal ions *(6)* were used as mordants of rosin soap sizing and showed some efficacy up to pH 7.5, even through the sizing was generally not as good as when alum is used under its optimal condition. Polyallylamine *(7)* was shown to be an effective mordant of rosin soap

1. The pK_1 of metal ions

$$[M(H_2O)_6]^{3+} \overset{k_1}{\rightleftharpoons} [M(H_2O)_5OH]^{2+} + H^+$$

K_1 is the equillibrium constant

$pK_1 = -\log K_1$

M is a trivalent metal ion

II. The crystal field stabilization energy (CFSE) in a weak field[a]

Metal ions	*No. of d electrons*	*CFSE, kJ/mol Oct.*	*Tetr.*
Mg^{2+}	0	0	0
Mn^{2+}	5	0	0
Fe^{2+}	6	47.6	31.4
Co^{2+}	7	71.5	62.7
Ni^{2+}	8	122.4	27.2
Cu^{2+}	9	92.8	27.6
Zn^{2+}	10	0	0

[a]Data is from Ref. *(10)*.

2. Bonding between rosin and fibers

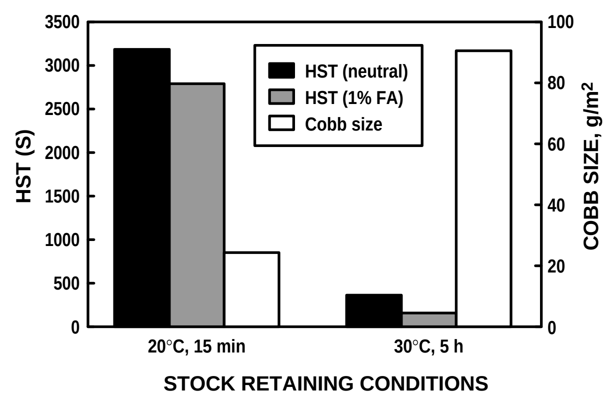
Without PEI:

Rosin-M-Fiber
(M = a metal ion)

With PEI:

|
N-M-Fiber
|
N-M-Fiber
|
Rosin-M-N-M-Fiber
|
N-M-Fiber
|
N-M-Fiber
|

3. The effect of the oxidation of ferrous ions on sizing



Bleached hardwood KP. rosin soap 0.5%
Fe^{2+} 1.5%, PEI 0.5%, and pH7

sizing from pH 3 to pH 10 in bleached hardwood chemical pulp, although its effectiveness in bleached softwood pulp was much lower and it was practically ineffective in thermomechanical pulp. These studies *(6–8)* give more detail on the subject of metal ion and polyamine mordants.

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

III. Sizing results of unbleached kraft pulp and TMP

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

[a] Based on oven-dry pulp
[b] Hercules Sizing Tester
[c] Formic acid ink
[d] Test terminated at this point

derstanding the sizing mechanism and providing guidance to the future efforts in the field.

Principles and hypothesis

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

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

While the hydrophobicity and the distribution of size on fibers are more related to the inherent properties of the sizing agent, mordants are usually required to retain and anchor the size molecules onto fiber surfaces. Energetic analysis *(9)* of the rosin sizing process leads one to believe that rosin soap size must be anchored to the fiber surfaces through primary chemical forces such as covalent bonds (dative bonds, which are also called coordinate covalent bonds, are a specific type of covalent bonds) to effect sizing; the stronger the bonding between rosin size and fibers, the better the sizing can be. Secondary chemical forces such as hydrogen bonding or van der Waals forces are not strong enough to resist the attack of polar water molecules, so are not effective bonding types. The fact *(8)* that ferrous and ferric ions cannot induce any sizing in bleached pulps but are very effective mordants of rosin soap size in lignin-rich pulps (unbleached kraft pulp and TMP) shows that even a single dative bond might not be strong enough. Effective bonding between rosin size and fibers should involve multiple dative bonds (via coordinating metal ions) or other types of covalent bonds.

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

Our previous studies *(6–8)* lead us to believe that the most important aspects of Al^{3+} chemistry in regard to rosin sizing are: (a) Its coordinating capability, which enables Al^{3+} to anchor rosin size onto fibers through dative bonds and is the basic requirement for a metal ion mordant. (b) Its ability to form polynuclear species via hydroxo or oxo bridging; this can enhance the bonding strength between rosin size and fibers because of the possibility of multiple bonding and is one of the reasons why alum has been used predominantly as the mordant of rosin sizing. Many metal ions have stronger coordinating capability than alum but cannot form polynuclear species. This is why they are usually not as effective mordants as alum since a single dative bond is often not strong enough. (c) Its high affinity to hydroxide anions, which is indicated by its low pK_1 (**Fig. 1**) value of 5.01. This is the reason why alum is only effective at acidic pH because at high pH, the concentration of OH^- is high. With its high affinity to Al^{3+}, the OH^- ligand will dominantly occupy the coordinating sites on Al^{3+} so that Al^{3+} can no longer react with rosin size and fiber components to accomplish its function as a mordant. Alum's function as a retention aid of rosin soap size is also poor at high pH, but this is not the main reason why sizing can not be achieved at high pH.

If there is a species which has very strong coordinating potential and is able to form large complexes with rosin size and fiber components in some way, but has lower affinity to hydroxide anions, it might be an effective mordant of rosin soap sizing even at elevated pH. Transition metal ions *(10)* show greater potential than alum to coordinate with species having a lone pair of electrons to donate because of the poor shielding of d-electrons to the nuclei and the existence of empty d-orbitals. With their higher pK_1 values (**Table I**) than Al^{3+}, they have much lower affinity to OH^-. However, they usually cannot form polynuclear species.

Polyamines such as PEI contain many nitrogen atoms on their chain. Having a lone pair of electrons around the nucleus, nitrogen atoms in many molecules are excellent ligating atoms *(10)*. The formation of a large complex (**Fig. 2** gives a postulated bonding structure) among rosin, coordinating metal ion, polyamine, and fiber components is very possible. The incorporation of polyamine with coordinating metal ions could greatly enhance the bonding strength between rosin molecules and fibers (via metal ions and the polyamine) by increasing the number of bonds if the type of postulated complex can be formed.

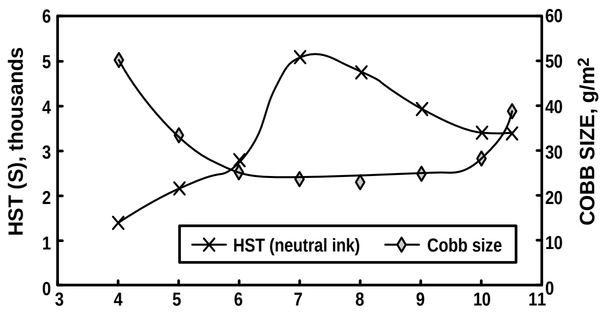
In summary, the combination of transition metal ions and polyamines may possess the same chemistry in regard to rosin sizing at neutral to alkaline pH as alum does at acidic pH; therefore, it may be an effective mordant of rosin soap sizing even at elevated pH.

Results and discussions

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

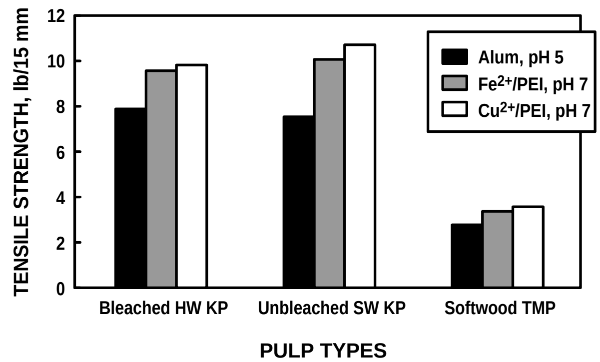
As shown in Table I, PEI alone or with Mg^{2+} or Mn^{2+} cannot induce any sizing in the reported pH ranges. Zn^{2+}/PEI can induce moderate sizing at pH 7–8, although the sizing is generally not as good as when alum is used at pH 4–5. Fe^{3+} and Fe^{2+} alone were shown to be very effective mordants of rosin soap sizing in lignin-rich unbleached softwood kraft pulp and softwood thermomechanical pulp, but they are not effective at all in bleached softwood and hardwood kraft pulps *(8)*. Table I shows that with the addition of PEI, Fe^{3+} can induce very good sizing at pH 3.5–4.0 and Fe^{2+} is very effective from pH 5.5 to 7.0 in the bleached hardwood pulp. Fe^{3+}/PEI and Fe^{2+}/PEI are also very effective mordants in the bleached softwood kraft pulp, but the results are not reported here. These results support our hypotheses that the bonding strength between size molecules and fibers is a crucial factor in determining the effectiveness of sizing. A high level of sizing can be achieved only when the

4. Effect of pH on sizing



Bleached hardwood KP, rosin soap 0.5%, Cu^{2+} 2.5%, and PEI 0.5%

5. Tensile strength of handsheets



bonding is through multiple dative bonds or other types of covalent bonds.

The oxidation of Fe^{2+} into Fe^{3+} by oxygen molecules in water was discussed extensively in our previous work *(8)*. While the oxidation rate is negligible at pH below 5.5, it is rapid (half-life less than 1 h) at pH above 6.5. **Figure 3** shows the effect of this oxidation reaction on the sizing when Fe^{2+}/PEI is used as the mordant at pH 7. When the handsheets were made soon after rosin size and the mordant were added, they possessed a high level of sizing. If, however, the stock was kept at 30°C for 5 h after the rosin size and the mordant were added and before the handsheet were made, the handsheets had practically no sizing. The reason is that most Fe^{2+} ions have been oxidized into Fe^{3+} ions under the latter condition. Fe^{2+} with its pK_1 of 6.74 can induce good sizing at pH 7 when used with PEI but Fe^{3+} with its pK_1 of 2.83 has no way to be an effective mordant at the same pH.

Table I shows that Cu^{2+} alone can induce some sizing at pH 7–8. With the addition of 0.5% PEI, it is very effective throughout a wide pH range from 4.0 to 10.5 (Table I and **Fig. 4**). The HST values with neutral ink are much higher than those when alum is used at its optimal pH. Figure 4 also shows that Cu^{2+}/PEI induces optimal sizing at pH 7–9. During the experiments, it was observed that the stock became bluer when PEI was added after Cu^{2+} had been applied. This phenomenon is a strong evidence *(10)* that PEI reacts with Cu^{2+} and forms some coordination complexes during the sizing process.

Formic acid was introduced into the HST test as an accelerator *(3)* because the HST test with neutral ink takes too long in some well-sized paper grades. An ideal accelerator should speed up the test at the same rate in all circumstances. Unfortunately, this is not true for formic acid. Table I shows that in the bleached hardwood pulp, while 1% formic acid can do little (usually less than a 50% decrease) in accelerating the HST test when Fe^{2+}/PEI is the mordant, it can accelerate the test by more than 100 times (and more than 1000 times in TMP pulp, as shown in Table III) when Cu^{2+}/PEI is the mordant. The reason is believed to be due to the existence of a chemical reaction when formic acid ink is in contact with sized paper. While the bonding among rosin size, Fe^{2+}, PEI and fiber components is fairly resistant to the attack of formic acid, the same type of bonding when Cu^{2+}/PEI is the mordant can be broken down (so the sizing is destroyed) very easily by formic acid. Actually, formic acid is not a suitable accelerant when Cu^{2+}/PEI is the mordant because it indicates the paper is poorly sized despite the fact that Cobb size and HST values with neutral ink have shown that the paper is very well sized against water. This result indicates that it is meaningless to discuss sizing without specifying the properties of the solution against which sizing is tested. The fact that two inks give such wide differences in sizing also indicates that the anchoring mechanism of the size molecule to the fiber is more important than the orientation and distribution of the size molecules on the fiber (since the orientation and distribution are equal with both inks).

The acidity of formic acid also makes it inapplicable in paper grades containing calcium carbonate filler. As a convenient sizing tester, HST has been more and more widely accepted by the industry. Further investigations into the accelerating mechanism to develop some new types of accelerators are obviously necessary to accommodate a wide variety of new sizing systems.

Table I shows that the pK_1 (the first hydrogen ion transfer in water) of a metal ion is a good indication of its pH of maximum sizing efficacy. In all the effective metal ion mordants, such as Fe^{3+}, Al^{3+}, Fe^{2+}, Cu^{2+} and Zn^{2+}, the pH values of their optimal sizing are in the vicinity of their pK_1 values. This phenomenon is easy to explain since the pK_1 of a metal ion is a measurement of its affinity to hydroxide anions. If a metal ion has a low pK_1 value, its affinity to OH^- is high. At a certain pH, it will have a strong potential to react with OH^- so it is less likely to coordinate with rosin size and fiber components. As a result, it can be an effective mordant of rosin sizing only in a relatively low pH range. If a metal ion has a high pK_1 value, the opposite will be true.

Another important phenomenon observed from Table I is that the metal ion's performances as the mordants coincide with a classic rule in coordination chemistry. In the 1950s, Irving and Williams found that *(10)* for a given ligand, the stability of complexes with dipositive metal ions follows the order: $Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+}$, $Ni^{2+} < Cu^{2+} > Zn^{2+}$. Similarly, Table I shows that when used with PEI, the metal ion's performances as mordants for rosin sizing follows the order Mg^{2+}, $Mn^{2+} < Fe^{2+}$, $Cu^{2+} > Zn^{2+}$. These two orders are the same. If a metal ion can form a more stable complex with a ligand, that is if it has a stronger coordinating potential, it is also a better mordant of rosin sizing when used with PEI. This consistency is a strong indication that coordination chemistry is playing a key role in the mechanism of sizing development; it is also an indication that the bond strength (or at least integrity) is of overwhelming importance in developing sizing.

There are two reasons *(10)* for the Iriving-Williams series of stability. One is the decrease in the diameters of the dipositive metal ions across the series due to the poor shielding of d-electrons. A smaller metal ion can draw the ligands more closely so it tends to have stronger attraction to the ligands and forms more stable complexes when other factors are the same. Another reason is the ligand field effects. **Table II** shows the crystal field stabilization energy (CFSE) of various dipositive metal ions in a weak ligand field in both octahedral and tetrahedral geometry *(10)*. Fe^{2+} and Cu^{2+} have a significant amount of CFSE, while Mg^{2+}, Mn^{2+}, and Zn^{2+} do not have any. The amount of CFSE is determined by the electronic interaction between the metal ion and ligands so it is affected by the d-electron configuration of the metal ion. Mg^{2+} has no d-electron, Mn^{2+} has 5 d-electrons (half-filled d-orbitals), and Zn^{2+} has 10 d-electrons (filled d-orbitals). This is the reason they have no CFSE in a weak field. Usually the higher the CFSE, the more stable the complex would be. But this rule of thumb is not always true since CFSE is only a part of, not all of, the stabilization energy involved in the formation of coordination complexes.

More sizing experiments were carried out in an unbleached Douglas-fir kraft pulp and a softwood thermomechanical pulp using the mordants which had been proven to be very effective in the bleached hardwood pulp (**Table III**). Sizing with alum as the mordant under its optimal conditions is also given for comparison. It can be seen in Table III that very high levels of sizing can be induced by Fe^{3+}/PEI at pH up to 7 and by Cu^{2+}/PEI at pH from 7 to 9 in the two pulps. Again formic acid has much greater accelerating effect when Cu^{2+}/PEI is the mordant than when Fe^{2+}/PEI is used, and it is obvious that the HST test with 1% formic acid ink is not applicable in the Cu^{2+}/PEI system. (On the other hand, this sizing system may not be suited to certain liquids.) The effect of the amount of PEI on sizing can also be seen from Table III. Usually the more PEI added, the better the sizing when the amount of PEI is less than 1%. The amount of metal ions added has a significant effect on sizing as well. It was found that there usually existed an optimal amount of metal ions, but no systematic investigations were done on this aspect.

Table III shows some results which are contrary to common experiences. When rosin size is compared with synthetic sizing agents such as AKD and ASA (alkyl ketene dimer and alkenyl succinic anhydride), it is said *(3)* that synthetic sizing agent can give hard sizing to paper but rosin size cannot. This statement is true when alum is the mordant, but is not true here. Table III shows that rosin soap size can give very hard sizing when proper mordants are used. Another notable result is that TMP, a pulp which has been well known as being much more difficult to size than chemical pulps *(3)*, is actually easier or much easier to size than the unbleached and bleached chemical pulps when Fe^{3+}/PEI, Fe^{2+}/PEI or Cu^{2+}/PEI is the mordant.

The strength properties of the handsheets were examined, and the results are shown in **Fig. 5**. Alum is 1.0%, Fe^{2+} is 1.5%, Cu^{2+} is 2.0%, and PEI is 0.5% (all based on oven-dry pulp) in the listed conditions. Figure 5 shows that in all the three pulps—bleached hardwood kraft pulp (HW KP), unbleached softwood (SW) kraft pulp, and softwood TMP—the tensile strength of the handsheets can be increased by 20–30% if either Fe^{2+}/PEI or Cu^{2+}/PEI is used as the mordant instead of alum. The strength improvement is due to the addition of PEI and papermaking at higher pH. Fibers can swell better and become more flexible at higher pH. As a result, bonding between fibers is stronger and paper can have higher strength. The bursting strength of the handsheets exhibited a similar improvement.

Conclusions

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

1. Very high level of sizing can be achieved with rosin soap size in all three pulps under neutral to

alkaline conditions when proper mordants are used. Fe^{2+}/PEI is a very effective mordant up to pH 7, and Cu^{2+}/PEI is very effective from pH 7 to pH 9. Zn^{2+}/PEI can also induce moderate sizing at pH 7–8, but Fe^{3+}/PEI is only effective at pH around 4. Mg^{2+}/PEI and Mn^{2+}/PEI are not effective mordants.

2. The pK_1 value of a metal ion is a good indication of its pH of maximum sizing efficacy.
3. The metal ions' performances as mordants are consistent with the Irving-Williams Effect, which describes the general trends in the stability of metal complexes. This consistency is a strong indication that coordination chemistry is playing a key role in the mechanism of sizing development and that the integrity (strength under a certain set of conditions) of the rosin-mordant-fiber complex is of central importance in sizing development.
4. Chemical reactions are involved in the mechanism of the HST test with formic acid ink. To talk about sizing without specifying the properties of the solution against which sizing is tested is meaningless since this affects the stability of the size-mordant-fiber complex.
5. The tensile and bursting strength of the handsheets can be increased by 20–30% in the three pulps when either Fe^{2+}/PEI or Cu^{2+}/PEI is used as the mordant instead of alum.

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

Experiment

The unbleached Douglas-fir kraft pulp had a Canadian Standard freeness (CSF) of 650 mL and a 40 mL permanganate (K) number of 62. The bleached Douglas-fir kraft pulp and the bleached hardwood chemical pulp had a CSF of 330 mL and 260 mL, respectively. The mechanical pulp was TMP of western U.S. true firs and hemlock. The rosin soap size was Stafor (Westvaco Chemicals) and was used at a level of 0.5% solids on pulp throughout the study.

All metal ions were from reagent grade chemicals. The percentages are to the weight of oven-dry pulp. Alum is as $Al_2(SO4)_3 \cdot 16H_2O$, Mg^{2+} is as $MgCl_2 \cdot 6H_20$, Mn^{2+} is as $MnCl_2 \cdot 4H_20$, Fe^{3+} is as $FeCl_3 \cdot 6H_2O$, Fe^{2+} is as $FeCl_2 \cdot 4H_2O$, Cu^{2+} is as $Cu(NO_3)_2 \cdot 2.5H_2O$, and Zn^{2+} is as $ZnCl_2$. For example, 2.0% Fe^{2+} as referred to in this paper is actually 2.0% $FeCl_2 \cdot 4H_2O$. The PEI (Aldrich, Milwaukee, WI) is 50,000–60,000 average molecular weight, with 40–50% primary amines, 25–30% secondary amines, and 25–30% tertiary amines.

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

Handsheets of 60 g/m^2 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 is the standard. The standard press cycle was used, and then the sheets were dried in a sheet dryer at 250°F for 3 min. The sheets were conditioned at 72°F and 50% RH for at least 4 h before testing.

Cobb Size values were determined by TAPPI T 441 om-90. Ink resistance was determined on a Hercules Sizing Tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution (a solution of the same concentration of ink as the 1% formic acid ink made with distilled water instead of 2% formic acid, with an unadjusted pH of about 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 variances within a specific mordant condition are usually far smaller than the differences among different mordant conditions, the results were simply averaged and reported. Most reported experiment results, especially those around each optimal sizing pH and those from which specific inferences have been drawn, have been repeated at least once with good reproducibility. TJ

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