

Generalized rosin soap sizing with coordinating elements

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ABSTRACT *The trend for papermaking under alkaline conditions is well known. Investigations of the mechanism of rosin sizing might allow it to be used under alkaline conditions. Viewing rosin sizing as a coordinate chemistry reaction, rosin sizing with highly coordinating species, including transition and lanthanide series elements, was predicted to occur. A variety of these elements proved efficacious as mordants for rosin sizing in the acid and alkaline regions, depending on their formation constants with hydroxide. Formation constants with rosinate, sulfate, chloride, and other ligands involved during the sizing process are also relevant to the degree of size development. These results allow prediction of the effectiveness of a variety of species with rosin sizing, add a new dimension to the current knowledge of rosin sizing, and offer promise to the use of inexpensive rosin size under alkaline papermaking conditions. Evidence is presented indicating the likelihood of oxo linkages in the alum-rosin complex.*

KEYWORDS

Alkaline sizing
Formation
Hydroxides
Rosin size
Rosin soap
Sizing

Sizing of paper, that is imparting resistance to water permeability, is important to any structural or printing grades of paper, which are all but the absorbent grades of paper. Paper is sized with molecules that have a hydrophobic portion, which resists water penetration, and a hydrophilic portion that adheres to the paper via a mordant. Since the early 1800s, rosin sizing has been used with aluminum sulfate, "papermaker's alum." More recently, rosin is used that has been "fortified" by reaction with maleic or fumaric acid, yielding tricarboxylic acids. Rosin size can be purchased as alkaline solutions of the sodium or potassium salt (soap size) or as an emulsion of the acid form (dispersion sizes). Dispersion sizes can be used at slightly higher pHs, up to pH 6.5 to 7.0 compared with pH 4 to 5 used for the soap sizes. Many studies

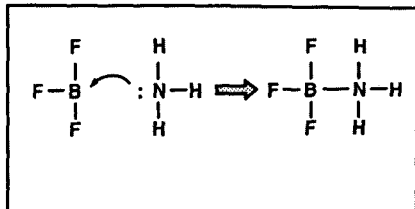
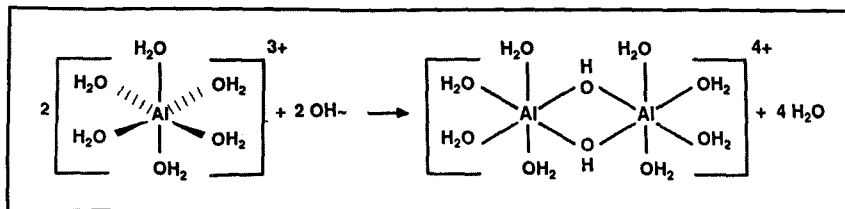
have added tangentially to the knowledge of rosin sizing, but the real importance of coordinate chemistry has not been fully exploited to extend rosin sizing to a wide variety of mordants and conditions that are now unknown.

For a variety of reasons, the pulp and paper industry is rapidly shifting toward manufacturing paper under alkaline conditions. While less than 20% of paper was made under alkaline conditions just a few years ago, the percentage is expected to be around 60–80% in just a few years. Higher strength paper, lower corrosion rates, the use of calcium carbonate fillers in printing papers, and increased longevity of archival papers prompt the industry to convert to alkaline papermaking. European mills started alkaline papermaking before U.S. mills because chalk was both cheaper and less abrasive than the clays available to them. U.S. mills started using chalk

when it became less expensive to use 96 brightness calcium carbonate than combinations of clay and titanium dioxide to manufacture 80+ brightness paper. This, in turn, requires internal sizing agents to be used under alkaline conditions. Notably, the use of alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD), the so-called synthetic sizing agents developed in the 1930s and 1940s and available since the 1950s, is based on the pioneering work of Weisgerber (1) and Mazzarella (2). They are expensive and more difficult to use than rosin size. The purpose of this study was to look at the fundamental coordinate chemistry involved in sizing to extend the use of rosin sizing well into the alkaline range and to characterize the role of alum so that it might be made more efficient or replaced in rosin sizing.

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1. Formation of a coordinate complex

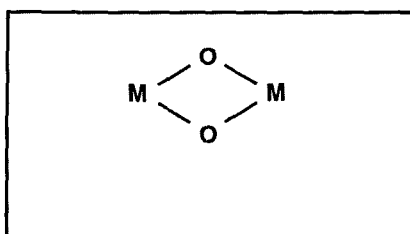
2. Formation of aluminum ion dimer by OH⁻ bridging

Theory of mordant action in rosin sizing

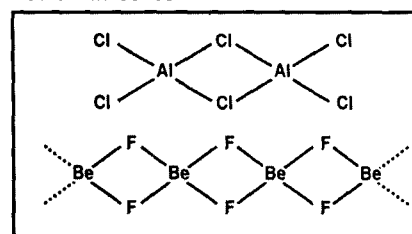
First, the term mordant will be introduced to describe the role of aluminum ion, or any other substance which has the same role as aluminum ion in rosin sizing. In the textile field, a mordant is a substance that fixes a dye to a material. A mordant works by combining with the dye to form an insoluble complex that fixes dye to the material. Mordants are metal atoms that attach to the dye at the oxygen and nitrogen atoms through formation of coordinate bonds. Actually, alum is a common mordant used in textile dyeing. This term describes the effect of aluminum ion in the paper sizing process more aptly than the general term "retention aid." For example, calcium salts will precipitate (and retain) rosin, but without concomitant sizing.

To understand the mechanism of rosin sizing, it is important to understand elementary coordinate chemistry. The first explanation of the actual nature of complexes is credited to the classic 1906 work of Werner, for which Werner received the Nobel Prize in 1913. Werner showed that neutral compounds were bound directly to metal atoms of complexes. Thus, $\text{CuCl}_2 \cdot 6\text{NH}_3$ is correctly written as $\text{Cu}(\text{NH}_3)_6\text{Cl}_2$. In general, coordinate complexes are formed upon the reaction of Lewis acids, compounds which accept electron pairs, with Lewis bases, compounds which donate electron pairs, to form the complex. The term ligand also denotes the species donating the electron pair(s). Coordinate covalent bonds are formed when one atom donates both electrons of the shared electron pair, whereas most covalent bonds are formed when each atom donates one electron to the shared electron pair. For example, acid-base reactions are coordinate chemistry reactions. The reaction of H^+ and OH^- to form the product H_2O proceeds as $\text{H}^+ + \text{OH}^- \rightarrow \text{H}:\text{OH}$, where

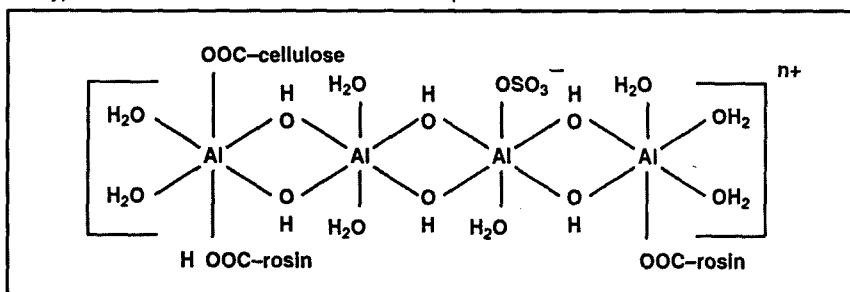
3. Example of an oxo compound



4. Example of anions that form multiple coordinate bonds



5. Hypothetical structure of aluminum rosin complex.



the electron pair is shared in the product. Many other reactions besides acid-base reactions are included as well. Figure 1 shows a classic example of the reaction of the two gases NH_3 and BF_3 to form the complex $\text{H}_3\text{N}:\text{BF}_3$, which is a white solid.

The Al^{3+} ion forms coordinate complexes with many ions or molecules in aqueous solutions. The aluminum cation has a coordination number of 6 in aqueous solutions. This means aluminum will react with six electron pairs of ligands. In the absence of other coordinating species, Al^{3+} forms a hydrated complex by reacting with 6 water molecules to form $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ with the octahedral shape shown as a reactant in Fig. 2. Because of steric (spatial) hindrance, generally only one pair of electrons from one atom is donated to a particular atom. Thus, while the oxygen atom of water has two free electron pairs, only one pair act with a particular aluminum cation. The oxygen atom of the OH^- ion, which has three unshared electron

pairs, shares only one pair of electrons with a particular aluminum cation. However, the oxygen atom of the OH^- anion is known to form coordinate bonds with two different coordinating cations and, thereby, form a hydroxo bridge; double bridges, involving two hydroxide groups as shown in Fig. 2 with aluminum as an example, are the most common (3). These bridges are crucial to rosin sizing with alum as they increase the size of the aluminum-rosin complex and decrease water solubility. At pH 5, as much as 90% of the aluminum is in the form of polymers, and at high degrees of hydrolysis the main species may be $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ (3); therefore, the average degree of polymerization varies with pH. Alcohols also form bridges with aluminum ions, although these tend to be hydrolyzed easily in water. Dimers of ferric ions complexed with OH^- are well known at pH 2-3, while highly condensed species occur at higher pHs (3).

The loss of the second proton from

water of the hydroxo bridges leads to the formation of oxo compounds, the double bridged species of which are almost always symmetrical (3) as shown in Fig. 3, where M is a metal coordinating atom.

An aluminum compound with a single oxo bond occurs at $\text{pH} > 13$ in dilute aqueous solutions; it has the formula $[(\text{HO})_3\text{AlOAl}(\text{OH})_3]^{2-}$ and occurs in the crystalline, potassium salt of this compound (3). Other ligands are of interest in rosin sizing. Carboxylic acids can coordinate with more than one metal ion to give nonpolar compounds; indeed, aluminum naphthenic acids were used as a gelling agent in "napalm" (3). Sulfate anion is capable of being unidentate, bidentate, chelating, or bridging.

Other anions can form more than one coordinate bond as well under appropriate conditions. In the liquid form of pure aluminum chloride, two chloride anions bridge two aluminum ions, while each of the other chloride anions form single bonds, so that aluminum chloride exists as dimers (4). Here aluminum has a coordination number of only 4 because of the large size of the chloride ion (3). Notably, the aluminum chloride dimers may be split by donor molecules such as amines to form $\text{R}_3\text{N}:\text{AlCl}_3$. Similarly (Fig. 4), beryllium fluoride solid exists as a polymer (3).

While much attention has been paid to the reactions in dilute aqueous solutions involved during rosin sizing, the equilibrium mixture of coordinated species in the press and dryer sections is much different, and probably much more important in the overall sizing process. Coordinate chemistry reactions in dilute aqueous solutions is important principally as a means of rosin and aluminum retention in the web. Many coordination compounds will form in the press and dryer sections where the concentrations of the species involved are relatively high as is the temperature. This partially explains why "aging" or "heat setting" of rosin is important in addition to rosin migration.

One can hypothesize rosin sizing with candidate mordants, with alum as an example, occurring in three steps. First, alum forms coordinate bonds with water, rosinate anions, hydroxyl anions, sulfate anions and other ligands present to form a relatively large complex of complicated

structure called the aluminum-rosinate complex, which is depicted hypothetically in Fig. 5. It is essential to keep in mind, however, that the aluminum-rosinate complex contains more than just aluminum and rosin, and may be even more complex and variable depending on the composition of the solution. The aluminum-rosin complex must have limited water solubility (achieved by increasing the size and reducing the charge by coordination of the aluminum cation with anions) so that it will adhere to fibers with weak bonds. If the complex is too stable [soluble] in water, the equilibrium with fiber complexing will be small and the rosin will not be retained. Alum at pH below 4 has very little sizing ability because the Al^{3+} ions have not sufficiently complexed with OH^- species. Therefore, the complex has high solubility and is not retained. While rosinate certainly coordinates with aluminum at pH 4, the complex is not retained on the fiber as it is at higher pHs.

In the second step water is removed from the sheet with retention of the aluminum-rosin complex. In the third step, the remainder of the water is removed and the temperature increased in the dryer section. This allows new, stronger coordinate bonds to form that are not possible in dilute, aqueous solutions. Elevated temperature is not necessarily required with some coordinating cations, but may speed up coordination reactions with other cations that may react more slowly (3). For example, work in our laboratory shows heating at 250°F for approximately 2 min is necessary to develop fully surface sizing with zirconyl acetate. As the concentration of the aluminum-rosin complex increases, additional coordinate bonds are allowed to form with cellulose fibers provided the pH is not too high. At high pH, OH^- groups occupy most of the available sites that might otherwise complex with functional groups of the cellulose fiber. The reason that the emulsion sizes are so effective at higher whitewater pHs is probably because they can effectively lower the pH during the drying of the paper near the aluminum-rosinate complexes.

Carboxylate groups on the surface of fibers, being anionic, would form strong coordinate bonds with the

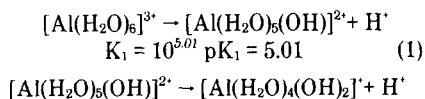
aluminum-rosinate complex. Besides carboxylate groups, another functional group available as a ligand on the surface of the fiber is the hydroxyl group of cellulose and hemicelluloses. Hydroxyl groups are available for hydrogen bonding or coordination but, of course, these are not as effective under papermaking conditions since it is known that pulps with higher concentrations of carboxylate groups are more effectively sized than pulps with lower concentrations or without carboxylate groups. Experience has shown that hardwoods are easier to size than softwoods, and dissolving pulps are not easily sized because of the low concentration of carboxylate groups (5).

The importance of coordinate chemistry must not be overlooked in any explanation of rosin sizing; yet only a few publications stress this relationship (6, 7), and these, only under dilute, aqueous conditions. On the other hand, the ionic interactions and the so-called "Stern's layer" are commonly found explanations of rosin sizing. This implies that the aluminum-rosin complex forms an ionic bond as an ion does in an ion-exchange resin. This cannot be the entire story since the zeta potential is only loosely related to sizing potential. Furthermore, heating of the sheet should have very little to do with sizing efficacy if this were true. Aging sheets causes an increase in sizing; this phenomenon points to coordinate chemistry reactions, which can be relatively slow. The failure of quaternary amines to act as a mordant in sizing (as will be shown in the second paper of this series) argues that this is not the case. Finally, ionic bonds are easily destroyed by water because of their high polarity; coordinate bonds are of much lower polarity.

The effect of pH on rosin sizing with aluminum is a central issue to rosin sizing. This is a result of the chemistry of aluminum, not rosin. Sizing with ferric ion is possible well below pH 4, but not possible with aluminum ion (8), and the present study will demonstrate rosin sizing above pH 8 in the absence of alum. Let us consider the acidity of a wide variety of candidate mordants for rosin sizing of paper in terms of coordinate chemistry.

Substitution reactions occur when one ligand is replaced by another, such as when a molecule of H_2O is

replaced by a rosin molecule, sulfate anion, etc. Metallic complexes of water may undergo hydrolysis, a type of substitution reaction that is equivalent to acid dissociation. For aluminum the first two acid dissociations are as follows:



The value of the second acid dissociation has little practical significance because of formation of the polyaluminum complexes mentioned previously. When the pH of a solution is equal to the pK_a of most acids, then both the acid and the conjugate base are present in equal amounts. This is a consequence of the Henderson-Hasselbalch equation of analytical chemistry. With acetic acid, which has a pK_a of 4.75 for the acid ionization, an aqueous solution of acetic acid at pH 4.75 has equal concentrations of HAc and Ac^- . With aluminum and other highly coordinating species the chemistry is more complex. The pK_a for the first ionization of aluminum is 5.01. Rather than the predicted 0.5 equivalents; however, it takes about 2.5 equivalents of OH^- per equivalent of aluminum to increase the pH to 5.01 in water. The reason is that competing reactions involving higher substitutions and polyaluminum complexes occur. (Since the monosubstituted aluminum ion product undergoes additional reactions with the hydroxide anion, the equilibrium in Eq. 1 is forced further to the right. Thus the pH is always lower than anticipated for a given amount of hydroxide ion added to alum.) It is interesting to note that maximum rosin sizing with alum as a mordant occurs at a pH near the pK_a of the aluminum ion. For this reason, the first acid dissociation constant, pK_1 , of a variety of coordinating metallic ions will be used to predict their mordant action in rosin sizing as a function of pH.

Only a few other metallic ions besides aluminum have been used and studied as mordants for rosin sizing of paper. The ferric ion, Fe^{3+} has been known in this role for a long time and was used in the United States during World War II when alum was not always available (8). One other important study (9) looked at a variety of ions including Fe^{3+} , Cr^{3+} , Cu^{2+} , Mg^{2+} ,

I. Properties of candidate species for mordants in rosin sizing in water at 25°C (10)

First formation constant					
Element	Cation	pK_1	SO_4^{2-}	Cl^-	Ac^-
<u>Divalent cations</u>					
Calcium	Ca^{2+}	12.8			4
Copper	Cu^{2+}	8.0		1	145
Magnesium	Mg^{2+}	11.4			6
Manganese	Mn^{2+}	10.59		9	$6.9 \cdot 10^9$
<u>Trivalent cations</u>					
Aluminum	Al^{3+}	5.01	Low	V. low	
Cerium	Ce^{3+}	~9	2500	3	48
Chromium	Cr^{3+}	4.0			63
Dysprosium	Dy^{3+}	8.10			
Erbium	Er^{3+}	7.99	3800		
Europium	Eu^{3+}	8.3			
Gallium	Ga^{3+}	3.4			
Holmium	Ho^{3+}	8.04	3800		
Iron	Fe^{3+}	2.83	110	30	1580
Lanthanum	La^{3+}	9.03	4400		36
Plutonium	Pu^{3+}	7.37	4570	15	
Yttrium	Y^{3+}	8.34	3800		34
<u>Tetravalent cation</u>					
Thorium	Th^{4+}	3.89	2100	24	

and Ca^{2+} , in addition to alum, at various pHs. In this study, alum gave good sizing at pH 5, $\text{Fe}_2(\text{SO}_4)_3$ gave good sizing at pH 3.6. CuCl_2 gave some sizing at pH 6.9, while others did not show sizing by the optical ink test. The pH values of maximum sizing for these elements compare to the first acid ionization constants, pK_1 , of Al^{3+} , Fe^{3+} , and Cu^{2+} , which are 5.01, 2.83, and 8.0, respectively (10). Ferric ion acts as a mordant with maximum efficacy at lower pH values than alum since it has a higher affinity for OH^- . On the other hand, copper (II) ion has a maximum efficacy at a higher pH than alum since it has a low affinity for OH^- in the formation of coordinate bonds. It stands to reason that divalent cations are not as effective since they complex with only two anions; bridging of each cation with two hydroxyl groups to form a polymer does not leave a cationic charge for additional complexing with rosin, cellulose, sulfate, etc. The other divalent cations probably did not give good sizing as they tend to form salts that have significantly higher solubilities than the copper salts and may not have retained the rosin. Furthermore,

using acetate as an indicator of rosin coordination, the formation constants of Fe^{3+} , Cr^{3+} , Cu^{2+} , Mg^{2+} , and Ca^{2+} are 1580, 63, 145, 6.3, and 4.0, respectively (10). The small affinity for forming coordinate bonds with rosinate in the cases of Mg^{2+} and Ca^{2+} also accounts for little sizing efficacy with these two ions. The exact pH of maximum efficacy as a sizing mordant is related to the pK_1 but, because of many competing reactions including formation of other complexes, has some variability. It is very difficult to describe all the possible reactions of coordination compounds of mixed species in detail, and it is probably unnecessary if the predominant reactions are known.

Results and discussion of elemental cationic mordants

If the hypothesis of the importance of coordinate chemistry in the action of mordants for rosin sizing is true, one should be able to find trivalent cations, with appropriate pK_1 values, which will give good sizing in the alkaline region. Coordinating cations are found among the transition and

II. Results of sizing with various mordants

Mordant	pH of sizing	Cobb size, g/m ² /2 min	HST ^a value (neutral), s	HST value (1% formic acid), s
Aluminum sulfate	4.5	24.5	410	120
	5.0	25.1	585	133
	5.5	24.1	382	101
	6.0	25.1	340	
	6.5	26.4	200	84
	7.0	soaked	12	6.5
Cerium sulfate	6.0	31.3	73	2.2
	6.5	26.1	260	2.4
	7.0	28.5	257	1.3
	7.5	30.1	177	1.1
	8.0	soaked	2	0.7
Cerium chloride	6.0	28.4	100	3.4
	6.5	25.8	300	3.0
	7.0	25.8	310	2.0
	7.5	32.9	100	0.9
Dysprosium sulfate	7.0	24.9	320	5.3
	7.5	25.2	300	3.1
Dysprosium chloride	5.5	29.8	116	3.2
	6.0	28.0	95	2.9
	6.5	24.5	284	2.8
	7.0	24.4	342	1.9
	7.5	25.5	300	1.7
	8.0	34.7	75	1.0
Erbium sulfate	6.0	27.7	165	5.2
	6.5	26.3	172	5.1
	7.0	23.2	350	3.8
	7.5	25.3	285	3.1
	8.0	25.3	273	2.3
Erbium chloride	6.5	28.1	200	4.6
	7.0	23.8	436	5.0
	7.5	25.0	366	2.8
Europium sulfate	6.5	25.4	205	4.2
	7.0	25.3	325	2.8
	7.5	29.0	235	1.4
	8.0		7	0.8
Gallium sulfate	3.0	42.3	62	7.9
	3.5	32.4	155	9.8
	4.0	27.2	280	12.5
	4.5	42.6	150	3.2
	5.0	43.2	135	4.6
	4.0 (2 hr reten)	26.5	285	100
Lanthanum sulfate	5.0	36.3	55	1.6
	5.5	31.0	75	2.8
	6.0	33.4	61	2.5
	6.5	28.0	113	2.5
	7.5	soaked	25	1.1
Lanthanum chloride	6.0	31.1	53	2.4
	6.5	26.7	136	2.5
	7.0	28.4	235	1.7
	7.5	35.4	100	1.1
(with no SO ₄ ²⁻)	7.0	soaked	10	1.3

^aHercules size test.

lanthanide series elements. Some candidate species are listed in Table I, without regard to commercial viability. Some of these compounds are extremely toxic!

While the use of plutonium as a mordant for rosin sizing is not being advocated, some important generalizations come out of this table. Sulfate has a much higher tendency than chloride for formation of coordinate bonds with cations. This is undoubtedly true for the aluminum cation as well, even though the interaction in dilute aqueous solutions is minimal. It probably becomes very important in the web during pressing and drying when the concentration of these species increases. Note that Table I gives equilibrium constants and says nothing about the reaction rates to achieve equilibrium.

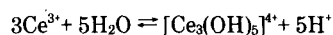
In a set of experiments, a variety of these species were tested as mordants and gave good rosin sizing (but generally were not as effective as alum). The maximum efficacy of each ion correlated roughly to the pK_1 of the metallic ion. For example when sizing was used with 12.5 lb of potassium rosinate soap solids and the molar equivalent of aluminum ion, see experimental section, as 20 lb anhydrous aluminum sulfate per ton of hardwood pulp, the results achieved with handsheets corresponding to 60 g/m² are shown in Table II (Of course, low Cobb size and high HST values indicate good sizing.)

The results of Table II taken with previous work suggest that the pK_1 is a good indication of the pH of maximum sizing efficacy. Any trivalent cationic coordinating element can be used as a mordant for rosin sizing. By looking up the formation constants in handbooks, one can now predict the suitability of a material as a mordant in sizing. In most of these cases, the chloride salt works better than the sulfate salt; with aluminum, of course, the sulfate salt sizes much better than the chloride salt. This is because sulfate has a very high formation constant with these elements (compared with that of aluminum ion) so that the sulfate ion displaces rosin and fiber carboxylate groups in the coordination reactions. Indeed, the solubility of cerium-group sulfates (La-Eu on the periodic table) is very low; the solubility of sulfates of the yttrium group (Y, Gd-Lu) are appreciable. No

experiments were conducted to maximize sizing efficiency by varying rosin addition levels and the reaction conditions since the actual sizing efficacy of these materials have very little commercial or theoretical significance.

The chemistry of gallium is very similar to that of alum. Gallium atoms form oxo bridges, but hydrolysis is very slow at 25°C (3). In all cases, except alum and gallium with long reaction time, 1% formic acid used in the ink results in rapid ink penetration. It is hypothesized that oxo bridges are formed with aluminum and gallium during rosin sizing to increase the size and stability of the complex, if sufficient time for hydrolysis is given in the latter case. The oxo bridges are known to be much more stable than the hydroxo bridges. Just as acetate complexes with the rare earth elements (see cerium, etc. in Table I), undoubtedly the formic acid results in ligand substitution reactions, destroying the hydroxo bridges between the metal atoms quickly, but the oxo bridges much more slowly. The neutral ink for HST tests showed all of the trivalent mordants to have approximately the same mordant action when compared at the most suitable pH of each.

The lanthanides are hydrolyzed in water to a much smaller extent than aluminum or even gallium (3). Hydrolysis increases with increasing atomic number of the lanthanide. The main equilibrium of Ce^{3+} involves hydroxo bridges between the cerium atoms and is probably (3):



Oxo bridging of the lanthanides is not likely under the conditions of rosin sizing. This fact is used to support the hypothesis that oxo bridging increases the stability of alum sizing toward 1% formic acid which is not seen with any of the lanthanide elements. The formation of oxo bridges during sizing was first hypothesized by Thomas in 1935 (11) in what remains today one of the most important papers on the mechanism of rosin sizing. This points out one often observed fact in sizing: the degree of sizing is very much dependent on the liquid from which sizing is measured. One might now say that the composition and concentration of the ligand in the liquid is what determines the

degree of sizing in sized paper.

One other observation was made in this study. It has been mentioned that some divalent ions have limited mordant action. Table I shows that divalent manganese cation has a very high affinity for carboxylate groups, while having a low affinity for hydroxide ions. One might anticipate very good rosin sizing action with this species; however, after experimenting with $MnSO_4$ under a variety of conditions, rosin sizing could still not be achieved. Using abietic acid instead of fortified rosin (to avoid chelation) could not induce sizing either. These experiments showed, that even with retention of both the cobalt sulfate and rosin, sizing did not occur.

Upon first examination of these results, one might conclude that, while the results are novel and interesting, there appears to be little commercial value in this method. Granted, there does not appear to be any trivalent cationic element available to replace the role of alum; however, certain cationic polymers are expected to have coordinate chemistry reactions similar to those of these elements. The results of this section led to the prediction of polymers ideally suited to mordant action in rosin sizing at elevated pH conditions (12). Furthermore, these results should apply directly to dyeing paper with acid dyes, retention of polymers and materials retained with polymers, drainage, and other wet-end phenomena.

Experimental

Thick stock (1.5% consistency) containing 20 g of hardwood pulp (ovendry basis) with a Canadian Standard freeness of 360 mL was taken and stirred. Rosin size (Stafor, Westvaco Chemicals) solution (1%) was added equal to 12.5 lb/ton pulp of potassium resinate solids and the mixture stirred for 5 min; the pH was approximately 7 at this point. Alum or an equal molar amount of alum substitute was added corresponding to 40 lb/ton of hydrated alum. For example, 0.024 g hydrated alum (per 1.2 g handsheet) with formula weight of 666.41 is equal to 0.072 milliequivalents (meq) of Al^{3+} ; 0.072 meq of cerium(III) chloride heptahydrate (formula weight of 372.59) is 0.0268 g per 1.2 g handsheet. The pH of the solution was adjusted

to the desired pH with NaOH or H_2SO_4 and mixed for 5 min. The stock was diluted to 8 L (0.25% consistency) with the pH of the water previously adjusted to the desired pH and stirred for 30 min. (Some samples used 2 h retention at 1.5% consistency to test reaction rates.) Approximately 500 mL of stock solution were added to 2 L of soft tap water at pH 6.8 (instead of 7 liters total, there were 2.5 L total) in the British sheet mold (BSM), and the handsheets formed quickly (TAPPI Test Method 205 om-88). 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. Cobb size values were determined by TAPPI T 441 om-90 and ink resistance on a Hercules size tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution and solution of the same concentration of ink made with distilled water. □

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