Rosin sizing with polyamine mordants from pH 3 to 10

Christopher J. Biermann
Assistant professor, Dept. of Forest Products, Oregon State University, Corvallis, OR 97331

ABSTRACT *After rosin sizing with elements that form complexes based on coordination chemistry was developed, sizing with rosin soap size with polyamines (meeting certain criteria) as mordants was predicted to be highly effective. While the use of polyamines to increase the level of sizing has been known, the theoretical basis for sizing and for the prediction of polyamines particularly suited for rosin sizing has not been known. In this laboratory, sizing at pH values ranging from 3 to 10 showed this method to be highly effective with appropriate polyamines. The most effective mordant was polyallylamine, which, even in the alkaline region, was extraordinarily more effective than rosin-alum sizing at pH 4.5. Furthermore, polyallylamine was a suitable mordant for rosin sizing up to pH 10. Although the polymers were studied at levels that may be too high to be used on paper machines, these results add a new dimension to the current knowledge of rosin sizing.*

KEYWORDS
Alkalinity
Mordants
pH
Polyamines
Rosin size
Sizing

Results reported in the previous paper (*1*) point to two important criteria for candidate materials to act as effective mordants in rosin in the alkaline region. (The term "mordant" as opposed to "retention aid" is defined in the previous paper.) First, the material should be a Lewis acid with the capability of forming coordinate complexes by accepting electron pairs. Second, the material should form a reasonably large complex. Besides the transition and lanthanide series elements, few compounds act as Lewis acids. This fact limits the choice of candidate materials with commercial viability for the pulp and paper industry. Among polymers and organic molecules, the choice is clearly limited to protonated polyamines that might act as Lewis acids. Therefore, in this study, amines were investigated as mordants for rosin sizing, with the important criterion that they develop as high a cationic charge density as possible in alkaline regions. It will be shown that the positive charge must be associated with a hydrogen atom to be effective; quaternary ammonium compounds have delocalized positive charges that appear to be ineffective.

Polyamides are used frequently in paper manufacturing as retention aids. These compounds become protonated (and therefore cationic) only at a very low pH, since they have very low pK_a values (-0.37 for acetamide, for example). Less than one in a hundred amide groups is protonated at pH of 2, and less than one in ten thousand amides is protonated at pH 4, much too low of a charge density for any mordant effect with rosin sizes. Polyamides and cationic starches have amine groups introduced into the polymer at low levels. In the case of cationic starches, this is typically at the level of 0.03 amines per anhydroglucose unit, giving an effective molecular weight of 5400 g/mol of amine groups. These groups tend to be quaternary ammonium compounds, and, as will be shown, their substitution is insufficient to affect rosin sizing directly.

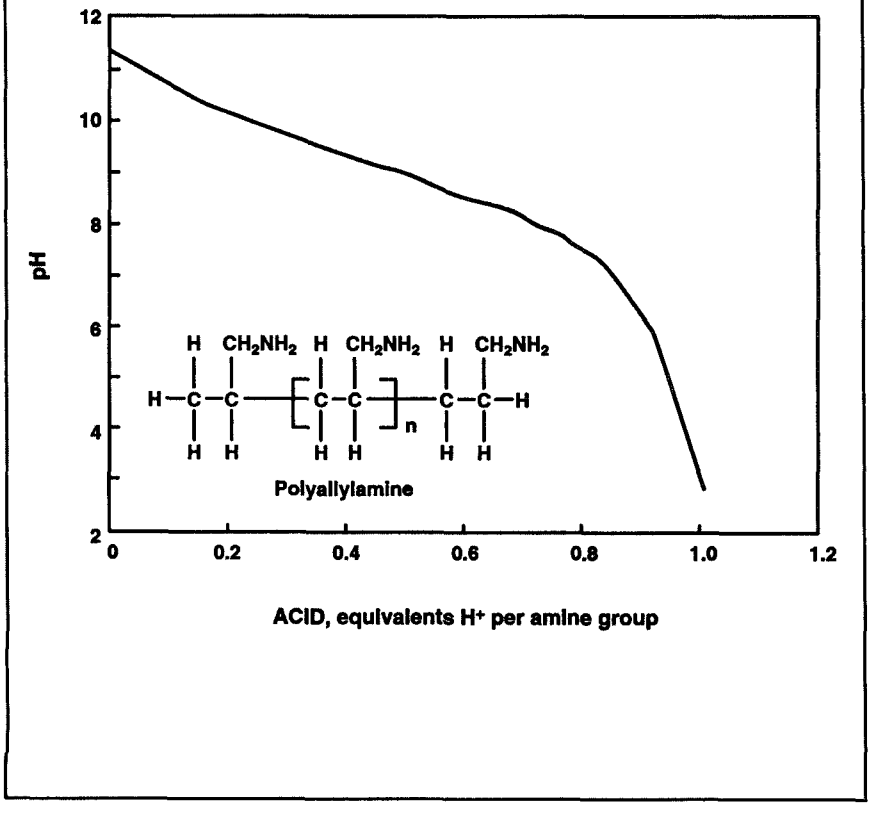
There is some qualitative information on the use of polyamines as mordants for sizing agents, but a theoretical basis on the mode of action has not been developed. The characteristics of polyamines that might be particularly efficacious have not been known until now. Consequently, ideal candidate polyamines have not been selected for study. Using a theoretical approach, a polyamine of unprecedented ability to induce rosin sizing at elevated pH values has been discovered. Polyamines are also known to increase drainage rates on the paper machine, improve retention of dyes and pigments, increase the sheet strength, and result in cleaner white water. Here too, for the same reason sizing is improved, I expect the polyamine used (polyallylamine) to achieve spectacular results, although these advantages are not considered in this study.

One of the earliest references on sizing with polyamines involves the use of alkylenimine resins, including polyethylenimine (PEI), to size in the

I. Acid ionization constants for representative protonated amines and an amide (8)

Compound	Structure	pK_1	pK_2	pK_3
	Monoamines (monoprotonated)			
Ammonia	NH_3	9.24	...	...
1-Butylamine	$CH_3(CH_2)3NH_2$	10.61	...	...
Diethylamine	$NH(CH_3CH_2)_2$	10.93	...	...
Triethylamine	$N(CH_3CH_2)_3$	10.72	...	...
Trimethylamine	$N(CH_3)_3$	9.80	...	...
Pyridine (aromatic)	$C_5H_5NH_2$	5.23	...	...
Piperidine (cyclo)	$C_5H_{11}NH_2$	11.11	...	...
	Diamines (diprotonated)			
Hydrazine	H_2NNH_2	0.27	7.94	...
Ethanediamine	$NH_2(CH_2)_2NH_2$	6.85	9.92	...
Propanediamine	$NH_2(CH_2)_3NH_2$	8.49	10.47	...
1,4-Butanediamine	$NH_2(CH_2)_4NH_2$	9.35	10.82	...
1,6-Hexanediamine	$NH_2(CH_2)_6NH_2$	9.83	10.93	...
	Triamines (triprotonated)			
Diethylenetriamine	$NH_2(CH_2)_2NH(CH_2)_2NH_2$	4.42	9.21	10.02
	Amides (monoprotonated)			
Acetamide	CH_3CONH_2	-0.37	...	...

1. Acid titration of polyallylamine (with structure)



presence of calcium carbonate (2). PEI was used later to size with 2-haloalkyl sulfones, sulfoxides, and sulfides (3). Notably, polymers of diallylamine with quaternary amines were used as wet strength and retention aids (4), but they were not studied in regard to sizing. Another polyamine, polyvinylcycloamine, was used by Strazdins (5) with fortified rosin soap size and alum to size paper. A self-substantive sizing agent was made by Leffler (6) by reacting triethylenetetramine with fortified rosin size to form a polyamide-polyamine stable from pH 4 to pH 9. It would be useful to try this approach directly with a polyamine to reduce the relative amount of polyamide groups. More recently PEI-alum combinations have been explored in the rosin sizing of paper up to pH 8.5; this system also gave increased paper strength (7).

Theory and background

Acid dissociation of protonated amines can be written as follows (with R as an alkane or H atom):

$$R_3NH^+ \rightleftarrows R_3N + H^+$$

Protonated amines have pK_a values on the order of 4-12, with aliphatic monoamines having values on the order of 10-11. **Table I** shows the pK_a values for various amines used here as representative compounds. The efficacy of polyamines as mordants for rosin sizing in terms of amine protonation becomes an important issue (1).

Using triprotonated diethylenetriamine as an example and applying the Henderson-Hasselbalch equation, we find that the approximate deprotonation with increasing pH is as follows:

1. As the pH is increased to 4.42, one half of the protons will be removed from one amine.
2. As the pH is increased to 9.21, all of the protons will be removed from one amine, and one-half will be removed from the second amine.
3. As the pH is increased to 10.02, only one-half of one of the amine groups will be protonated.

Additionally we will consider the model compound the penta-protonated tetraethylenepentamine with successive pK_a values of 2.98, 4.72, 8.08, 9.10, 9.67, respectively.

Table I shows some trends I will make use of to explain the sizing action of amines. First, the pK_a values of protonated primary, secondary, and tertiary amines are all approximately the same. With diamines, it is apparent that the protonation of the second amine group is strongly dependent on how far it is from the first amine group. With separation by two carbon atoms, the second amine to be protonated is greatly hindered from protonation (ethanediamine with pK_1 = 6.85 compared to 1-butylamine with pK_1 = 10.61); with separation by three carbon atoms, there is hindrance (propanediamine with pK_1 = 8.49); and with separation by four carbon atoms, there is slight hindrance (1,4-butanediamine with pK_1 = 9.35). In the latter case, both amines are mostly protonated below pH 9. With diethylenetriamine, the two outer amines are protonated below pH 9, but the inner one does not appreciably protonate unless the pH is below 5. In general, with amines of the type NH_2-$(CH_2CH_2NH)_n$-CH_2 CH_3, only every other amine is protonated in the pH range of 5 to 9. Note that this is the form of polyethylenimine (PEI); titration of PEI with HCl verified this behavior (data not shown).

On the other hand, with polyallylamine (PAA), - $[CH_2CH(CH_2NH2)]_n$ - with the structure shown in **Fig. 1**, the amines are separated by five carbon atoms, and essentially all the amines are protonated below pH 7. Since the pK_a of the protonated amine is approximately 9, this material should be an excellent mordant under alkaline conditions. Unlike alum, the material is already polymerized, so the role of OH^- to aid polymerization is not important. Thus this material should be a good mordant up to a pH of about 9, but it should also be good at very low pH values as well. The weight of one monomer of PEI is 43, while that of polyallylamine is 57, which is not a large difference considering that the separation of amines is two carbon atoms in the first case and five in the second case. (To summarize, at neutral pH PEI has 86 g/mol of protonated amine, while PAA has 57 g/mol protonated amine.)

Figure 1 shows the titration curve of polyallylamine. Over 80% of the amines are protonated at pH 7, about 50% of the amines are protonated at pH 9, and about 20% of the amines are

II. Results of using various mordants for rosin sizing

Trial	*pH*	*Amount added, lb/ton*	*Hercules size test, s*	*Notes*
			Alum	
1	4.75	12.2	13	...
2	4.75	16.7	29	...
3	4.75	33	105	...
4	4.75	33	200	1 L water in BSM
			Polyethyleneimine (PEI)	
5	10.2	16	0	3 lb/ton sulfate ion
6	8.6	16	0	3 lb/ton sulfate ion
7	6.7	16	35	3 lb/ton sulfate ion
8	7.5	6.7	73	...
9	7.1	6.7	100	...
10	7.1	6.7	180	3.3 lb/ton poly(styrene sulfonate)
11	7.1	6.7	150	3.3 lb/ton carboxymethyl cellulose
12	7.5	3.3	76	6.6 lb/ton alum
13	8.0	6.7	260	3.3 lb/ton alum
14	7.1	6.7	0	3.3 lb/ton pyrophosphoric acid
15	6.45	5	60	...
16	7.4	5	19	...
17	7.4	5	47	with 80 lb/ton Na_2SO_4
18	3.4	5	34	...
19	7.4	5	19	(air dried overnight)
20	6.4	5	19	(air dried overnight)
21	7.1	3.3	5	...
			Polyacrylamide	
22	5.0	16	0	...
			Egg albumin	
23	3.6	33	10	...
			Poly (1,1-dimethyl-3,5-dimethylene piperidinium chloride)	
24	6.5	13.3	6	...
			Polyallylamine (PAA)	
25	7.0	4.1	400	
26	7.0	4.1	3	with 3.3 lb/ton poly(styrene sulfonate)
27	7.0	4.1	40	used abietic acid instead of rosin
			Diethylenetriamine	
28	6.5	6.7	0	...
			Poly(lysine)*	
29	6.5	8.0	1.4	...

*Molecular weight = 70,000+, 146 g/mol primary amine.

protonated at pH 10. Compare this to PEI, for which less than 50% of the amines are protonated at pH 7. PEI has the additional disadvantage that only 40–50% of the amines are primary, as 20–25% are secondary and 20–25% are tertiary amines; presumably steric hindrance would reduce the efficacy of sizing.

Results and discussion

Various experiments were carried out to test the efficacy of various polyamines as mordants in sizing paper. In the first set of experiments, hardwood pulp was used to make handsheets in the British sheet mold with a basis weight of 60 g/m^2. Pulp at 1.4% consistency was treated with 9 lb/ton potassium rosinate soap solids. The pulp was then treated with additives such as filler or a second mordant and was finally treated with the mordant listed first in **Table II** with stirring for 5 min between additions. The stock was diluted to 0.25% prior to making the handsheets. The British sheet mold was completely filled (7 L), unless otherwise specified, prior to handsheet formation at 0.017% consistency without delay. Hercules size test values were determined at 80% reflectance using 1% formic acid, dye solution. Each determination presented here is the result of two HST tests on a single handsheet.

Table II shows several important factors for effective rosin sizing that have been discovered. The degree of sizing effectiveness seems to be related to the charge density of the protonated polyamine. This, in turn, is dependent on the pK_a and structure of the polyamine. A certain minimum size is required of the overall complex, which probably has to do with overall retention on the sheet. PEI gave good results but, as predicted, not nearly as good as those obtained with PAA. Alum (Trial 13 compared to Trial 8) increased the mordant action of PEI at the higher pH values, where neither material was effective alone. Only part of this action can be explained on the basis of sulfate anion (Trial 17 compared to Trial 16). As expected, polyacrylamide offers no mordant action on its own. Diethylenetriamine (Trial 28) gives no sizing because it is a very small molecule. It does complex because it interferes with sizing (Trials 39 and 47 in **Table III**). Additional experiments with diethylenetriamine in which it and rosin were sprayed onto wet sheets, to ensure retention, led to handsheets with no sizing. These results show that amine-based mordants for rosin sizing must have a fairly high molecular weight (on the order of 40,000 or less, since that was the original weight of the PEI and crosslinking PEI did not increase sizing action) in addition to a high charge density. Even high-molecular-weight poly(lysine) (Trial 29) with a moderately high charge density of 146 g/mol of primary amine led to only weak sizing.

Sizing is not merely a consequence of the positive charge, since the quaternary ammonium compound (Trial 24) offers very little sizing. With quaternary amines, the charge is too delocalized to allow the formation of coordinate bonds. Pyrophosphoric acid, a chelating agent, destroys sizing (Trial 14), indicating that coordinate chemistry reactions are important. The PEI was more effective at higher pH values than was alum. Heat setting of PEI does not seem to be necessary (Trials 19 and 20 compared with Trial 16). Some other experiments, not listed, showed that the crosslinking of the PEI with adipoyl chloride does not appreciably alter the sizing efficacy; the PEI is already a sufficiently large molecule. Analyses of the white waters of several of these trials indicate that the PEI is highly retained, but much of the rosin is not retained.

The extraordinarily favorable result with polyallylamine (Trial 25, at 400 s) prompted an additional series of experiments with this material (Table III). As expected, it gave the most effective mordant action of anything investigated in this study.

PAA mordant was effective in a wide pH range of 3 to 10 (Trials 44–49) at very low levels of addition compared to the level of alum necessary. On an equal mass basis, PAA is about 20 times more effective at pH 7.5 as alum is at pH 4.75. While aging did not generally make a large difference in several samples tested, it did make a very large difference in the polyallylamine at very high levels of addition (Trials 42 and 43), which gave phenomenal sizing results. Interestingly, while alum contributed to sizing at pH 7.5 (Trials 37 and 38 compared with Trial 47), it took away sizing at pH 9 (Trial 45 compared with Trial 44). At pH 9, the alum may be too anionic (while the PAA is less cationic because it is less protonated) to allow sizing.

The levels of PAA used in this study are considerably higher than typical additions of high-molecular-weight polymers such as polyacrylamide. When polyacrylamide is used at levels above 0.5 lb/ton after the low-density screens, the system will overflocculate; when it is used before the low-density screen, up to 2 lb/ton may be used. However, polyacrylamide often has a molecular weight of 500,000 or higher; polyamines for sizing could be on the order of 10,000.

Polyamines do not need to complex with OH^- to form large rosin complexes, because they already exist as polymers. The degree of sizing effectiveness seems to have more to do with the amines being protonated. It is not merely a consequence of the positive charge, since the quaternary ammonium compound did not cause significant sizing. However, mere hydrogen bonding is possible with the unprotonated amine, and the unprotonated polyamine undoubtedly is retained. Therefore, the mordant action of polyamines is probably due to the formation of weak coordinate bonds with the protonated amine groups of the polyamine. While quaternary ammonium compounds are often used to make polymers such as polyacrylamide and starch cationic, one must wonder if the introduction of primary amines would improve some of the characteristics of these polymers.

For the purpose of elucidating the importance of carboxylate groups on the pulp fibers, some other pulps with lower carboxylate groups were tried. **Table IV** shows these results.

With Douglas-fir bleached pulp, polyallylamine was about as effective as alum sizing. With TMP pulp, the polyallylamine was not as effective. This indicates that polyallylamine is not forming hydrogen bonds with the cellulose fibers as much as anchoring to the exposed carboxylate groups of fibers. As a result, polyallylamine offers a significant improvement over alum with hardwood pulp but less improvement with other types of pulp. Much more work needs to be done in this and other areas, however.

Using only 1 L of water in the British sheet mold increased the

consistency from 0.017% to 0.12%. The pulp was diluted from 0.25% consistency, and, although the time in the British sheet mold was on the order of 10 s, using only 1 L of water improved the sizing appreciably (Trial 31 compared with Trial 30 and results of Table IV with bleached Douglas-fir pulp). It is reasonable to assume that a weak complex will dissociate under dilute conditions.

PEI costs about US$ 7.50/lb and has the effect of yellowing white sheets when added on the order of 5-10 lb/ton. PAA is similarly priced and does not cause sheet yellowing but is not FDA approved. The polymerization of allylamine (covered by Japanese patents) is difficult and does not go much beyond a degree of polymerization of 14; when performed in conjunction with diallylamine as a crosslinking agent, high molecular weights can be obtained after 90 h. Residual monomer (0.2%) remains after polymerization, which might be a health concern when food contact is a factor. This is not to say that polyallylamine cannot be synthesized by an alternative route to achieve a safer product. This is also not to say that it might not be used in other countries besides the United States.

Future work in this area will explore many possibilities. For example, many reactions during sheet drying are made possible by adding sizing agents to the size press. This method should allow systems to be employed that would not be feasible otherwise because of limited wet-end retention. Careful consideration of coordinate chemistry at the size press should enable new surface sizing agents to be developed that exhibit outstanding efficacy. Size press pickup could be reduced, decreasing drying costs considerably. Compounds based on zirconium have been used for a number of years. Compounds of titanium, hafnium, boron, and others hold much potential. Mixtures of compounds such as polyamines with metal salts that are less acidic than aluminum could improve sizing in the alkaline region. The possibilities are almost endless.

Experimental procedures

Thick stock (1.5% consistency) containing 20 g of hardwood pulp (oven dry basis) with Canadian standard

III. Results of polyallylamine for rosin sizing

Trial	pH	Polyallylamine, lb/ton	Hercules size test, s	Notes
30	6.7	3.4	320	24.0 g/m² Cobb size
31	7.0	3.1	800	1 L water in BSM
32	6.5	4.1	780	...
33	7.0	4.1	1180	1 L water in BSM, 6.7 lb/ton alum
34	7.0	4.1	...	28.9 g/m² Cobb size
35	7.0	4.1	980	3.3 lb/ton alum
36	7.0	4.1	720	6.7 lb/ton alum
37	7.5	4.1	550	3.3 lb/ton alum
38	7.5	4.1	835	6.7 lb/ton aluminum chlorosulfate
39	7.5	4.1	100	20 lb/ton diethylenetriamine
40	7.5	2.0	14	3.3 lb/ton alum
41	7.5	2.0	43	6.7 lb/ton alum
42	6.5	12.2	265	21 lb/ton rosin solids
43	...	...	2500	Same sample with aging for 2 months
44	10.0	4.1	34	...
45	9.0	4.1	1	6.7 lb/ton alum, 1 L water in BSM
46	8.5	4.1	315	...
47	7.5	4.1	361	...
48	5.0	4.1	520	...
49	3.0	4.1	86	...
50	7.5	4.1	520	10 lb/ton rosin
51	7.5	2.0	3	1 L water in BSM
52	7.5	2.0	2	1 L water in BSM, 3.5 lb/ton rosin
53	7.5	4.1	50	1 L water in BSM, 58°C
54	7.8	4.1	120	1L water in BSM, 330 lb/ton $CaCO_3$, wire side down
55	7.8	4.1	2	Same sheet as No. 54, wire side up
56	7.0	4.1	0	Oleic acid instead of rosin

BSM = British sheet mold.
Rosin solids at 7 lb/ton unless otherwise noted.

IV. Sizing with other pulp species

Mordant	Amount added, lb/ton	pH	Hercules size test, s	Notes
		Douglas-fir, bleached		
PAA	4.1	7.5	14	...
PAA	4.1	7.5	91	6.7 lb/ton alum
Alum	17	4.7	68	...
Alum	17	4.7	131	1 L water in BSM
PEI	4.1	7.5	43	6.7 lb/ton alum
		TMP, softwood		
PAA	4.1	7.5	1	...
PAA	4.1	7.5	7	6.7 lb/ton alum
PAA	4.1	7.5	14	13.3 lb/ton alum
Alum	17	4.7	34	...
PEI	4.1	7.5	5	6.7 lb/ton alum

BSM = British sheet mold.

freeness of 360 mL was taken and stirred. Rosin size (Stafor, Westvaco Chemicals) solution (1%) was added equal to 9 lb/ton pulp of potassium resinate solids (except the results of Table III, which were obtained using 7 lb/ton), and the mixture was stirred for 5 min. The pH was approximately 7 at this point.

Alum or alum substitute was added as specified per ton of pulp. The solution was adjusted to the desired pH with NaOH or H_2SO_4 and was mixed for 5 min. The stock was diluted to 8 L (0.25% consistency) with the water previously adjusted to the desired pH. Approximately 500 mL of stock solution was added to soft tap water at pH 6.8 in the British sheet mold, and the handsheets were formed without delay (TAPPI T 205 om-88).

The first 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% relative humidity for 1 h unless otherwise specified. Cobb size values were determined by TAPPI T 441 om-90, and ink resistance was performed on a Hercules size tester according to T 530 pm-89 to 80% reflectance values using 1% formic acid ink in all cases.

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. Polyallylamine was listed as high molecular weight (Aldrich, Milwaukee, WI).□

Literature cited

1. Biermann, C. J., Tappi J. 75(3): (1992) p. 223.
2. Landes, C. G. and Reynolds, W. F. Jr., U.S. pat. 2,698,793 (1955).
3. Monsanto Co., British pat. 1,113,039 (1968).
4. Emmons, W. D. and Merritt, R. F., Can. pat. 999,300 (1976).
5. Strazdins, E., Can. pat. 1,008,609 (1977).
6. Leffler, K. T., Japan pat. 110,726 (1981).
7. Chizhov, G. I., Ivanova, V. A., Bodrova, V. M., and Khovanskii, V. V., Mezhvuz. Sb. Nauch. Tr., Khim. Tekhnol. Drev. Tsellyul. (Nepenin, Y. N., Ed.), 1983, p. 17.
8. Dean, A., Lange's Handbook of Chemistry, 13th edn., McGraw-Hill, New York, 1985, Ch. 5.

The mention of trade names or commercial products does not constitute endorsement or recommendation for use by the author or Oregon State University.

Received March 19, 1991.

Accepted Aug. 20, 1991.