

Rosin soap sizing without mordants by immersion in size solution

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A REMARKABLE CHARACTERISTIC OF cellulosic fibers is their content of many hydroxyl groups. The existence of these hydroxyl groups in fibers is essential to papermaking. Without them, fibers would not be dispersible in water and papermaking would be impossible. Paper without hydroxyl groups would have little strength, since it is the hydrogen bonding of these groups that provides the foundation of paper strength. The inherent hydrophilicity of hydroxyl groups also renders the paper products very vulnerable to water, however. Sizing is therefore a necessity for many paper applications.

The most common purpose of sizing is to make the originally hydrophilic fiber surfaces relatively hydrophobic. Then it is possible to achieve a certain degree of water repellency. One way to achieve this goal is to apply an amphipathic (polar and nonpolar) material such as rosin size onto fiber surfaces. Ideally, the hydrophilic part of the amphipathic material should bind to the fiber surfaces, and its hydrophobic part should extend outward (1) to cover the fiber surfaces. When there is sufficient surface coverage, the paper can have good water repellency.

Previous work (2-5) from our laboratory showed that the bonding strength between rosin size and fiber components is critical to the effectiveness of sizing. Rosin size must bind to fiber surfaces through primary chemical forces such as coordinate bonds or other types of covalent bonds to effect sizing. Secondary chemical forces such as Van

der Waals forces and hydrogen bonds are insufficient to resist the attack of incoming polar fluids like water.

Rosin size is a nonreactive sizing agent, because rosin size cannot directly react with fiber components to bind strongly on fiber surfaces. This is the reason why mordants (2-5) are usually necessary in rosin sizing. Mordants such as alum and iron ions are chemicals that function to retain and chemically bind rosin size on fibers. If under certain conditions rosin size can retain and chemically bind on fibers without the presence of mordants, then rosin sizing without mordants should be possible. Sizing with synthetic sizing agents such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) does not require mordants. This is because direct reactions between size molecules and fiber components can occur. Such reactions must occur for a portion of the molecules to realize any sizing (6).

Other work (7) from our laboratory showed that esterification reactions between multifunctional carboxylic acids such as citric acid and 1,2,3,4-butanetetracarboxylic acid (BTCA) and cellulose can occur under certain conditions. Caulfield (8) reported similar results. Inorganic salts catalyze this class of esterification reactions. For example, Hodgson (6) reports that the presence of bicarbonate ion (HCO_3^-) is essential to the ability of AKD to function as an internal sizing agent. The reaction of carboxylic acids to form ester linkages probably occurs by the formation of acid anhydride intermediates. It is possible that some rosin attaches to fibers by a labile acid anhydride linkage. Since

ABSTRACT

Dipping handsheets in rosin soap solution and drying them with heat will achieve effective sizing. No alum is necessary. The drying conditions of the handsheets in both pre-dipping and after-dipping stages is critical. The concentration of rosin in the dipping solution is also critical for some pulps. Heat treatment can promote sizing in TMP and bleached softwood pulps but not in bleached hardwood pulp. Heating at higher temperature for more than one hour can develop good sizing even in control handsheets made from chemical pulps containing no rosin but not in the control TMP handsheets. Ester or some acid anhydride linkages may provide the bonding mechanism for the rosin size.

Application:

Direct esterification reactions between rosin acid and cellulose provide effective sizing of paper.

fortified rosin acid is a multifunctional carboxylic acid, there is reason to believe that direct esterification reactions between rosin acid and cellulose can occur under certain conditions. This is the basis of this work. Dipping handsheets in rosin solution and drying at room temperature or 121°C ensured the retention of rosin. Additional heat treatment at 160°C after drying with some samples promoted the possible reactions between rosin molecules and fiber components.

RESULTS AND DISCUSSION

Direct sizing in various pulps

Handsheets made from different pulps were simply immersed (dipped) in rosin soap solution for 45 s and then dried on a sheet dryer at 121°C for 3 min or in air after removing surplus liquid. No mordant was applied. Sizing was then tested on the rosin treated handsheets. Table I summarizes the results. The

Exp. no.	Pulp type	Handsheet drying	Rosin adsorbed, %	Drying after dipping	HST, s, neutral	HST, s, 1% FA ^a	Cobb size, g/m ² /2 min
1	Unbld. SW KP	Dryer	1.76	Dryer	4479	7623	28.4
2	TMP	Dryer	2.00	Dryer	6307	>10,000 ²	33.5
3	Bld. SW KP	Dryer	1.20	Dryer	244	415	32.2
4	Bld. HW KP	Dryer	1.35	Dryer	199	1597	51.6
5	Unbld. SW KP	Air	1.85	Dryer	2008	4606	34.6
6	TMP	Air	2.18	Dryer	230	475	Soaked
7	Bld. SW KP	Air	1.36	Dryer	4.8	36.2	Soaked
8	Bld. HW KP	Air	1.47	Dryer	0.4	5.1	Soaked
9	Unbld. SW KP	Dryer	1.85	Air	2746	4561	35.2
10	TMP	Dryer	1.89	Air	9.0	8.3	Soaked
11	Bld. SW KP	Dryer	1.14	Air	4.6	4.3	Soaked
12	TMP	Dryer	1.89	Air+Heat ^c	>10,000 ^b	>10,000 ^b	Soaked
13	Bld. SW KP	Dryer	1.14	Air+Heat ^c	7.6	7.4	Soaked

^a Formic acid ink
^b Test terminated at this point
^c Handsheets heated at 160 °C for 1 min after dipping rosin and air drying

I. Sizing results by direct size application with rosin soap dipping solution concentration at 1.0%

concentration of the rosin soap solution was 1.0%.

Table I shows that the handsheet drying conditions from which the pre-dipping handsheets were obtained or under which the after-dipping handsheets were dried have critical effects on the sizing results. When both pre-dipping drying and after-dipping drying were carried out on a dryer (121°C for 3 min), handsheets made from unbleached softwood kraft pulp (Unbld. SW KP) and thermomechanical pulp (TMP) possess high levels of sizing (No. 1 and 2). The Hercules Sizing Test (HST) value with 1% formic acid ink in the TMP pulp exceeds 10,000 s. This is a very high level of sizing. Handsheets made from bleached softwood kraft pulp (Bld. SW KP) and bleached hardwood kraft pulp (Bld. HW KP) also possess moderate sizing.

If pre-dipping or after-dipping drying is by air drying, handsheets from all pulps except Unbld. SW KP possess practically no sizing (soaked in Cobb size tests, No. 6–8 and 10–11). Although unbleached chemical pulp is an easily sized pulp, the experimental fact that even air drying after dipping rosin soap solution can give fairly good sizing (No. 9) is beyond what the existing theories can explain.

Since commercial mechanical pulps may contain rosin acids and fatty acids, these components may

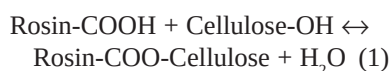
Rosin conc., %	Rosin adsorbed, %	HST, s, neutral	HST, s, 1% FA ^a	Cobb size, g/m ² /2 min
A. In Bld. SW KP handsheets				
0.5	0.60	3.0	2.4	Soaked
1.0	1.20	244	415	32.2
1.5	1.84	1.0	1.0	Soaked
2.0	2.41	0.2	0.4	Soaked
B. In Unbld. SW KP				
0.5	0.91	3227	5393	30.1
1.0	1.76	4479	7623	28.4
1.5	2.78	4706	7926	28.2
2.0	3.61	5173	8815	28.1

^a Formic acid ink

II. Sizing results with dipping solutions of varied rosin concentrations with dryer dried handsheets using dryer drying after dipping in rosin solution

contribute to the “self sizing” phenomenon sometimes observed in newsprint (No. 6).

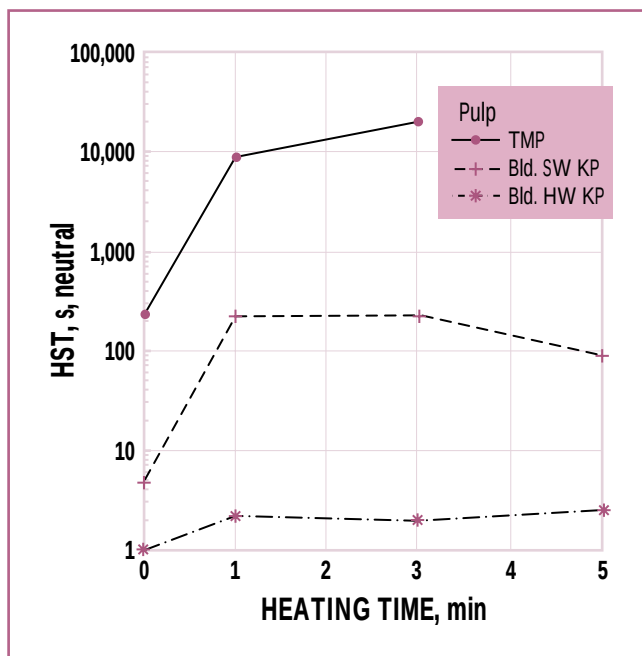
The most likely bonding mechanism that binds rosin soap size on fibers to affect the sizing in the above process is ester linkage. The following is a simple depiction of the esterification reaction between rosin acid and cellulose:



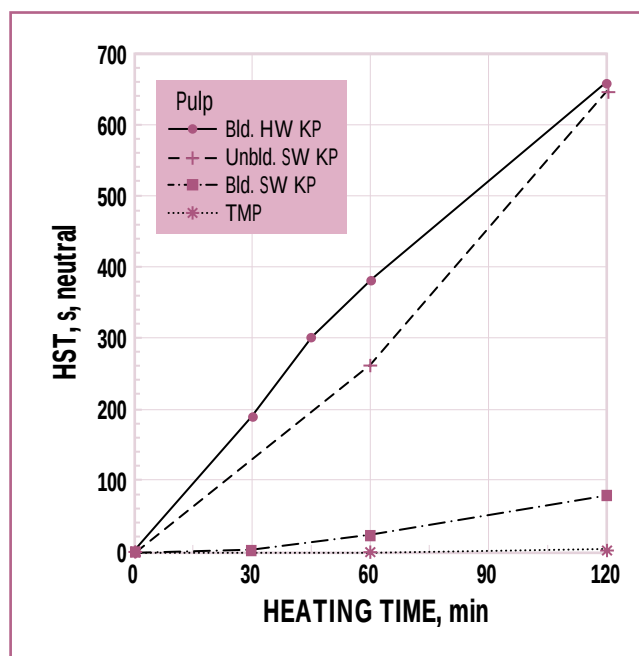
This mechanism can explain why dryer drying after dipping rosin can give much better sizing than air drying. The heat can remove the produced water molecules quickly, shift

the chemical equilibrium of Eq. 1 toward the right, and promote the esterification reaction. A similar explanation may demonstrate the fact that pre-dipping drying conditions are also critical in this sizing process—sizing is always much better when the original handsheets are obtained from dryer drying than when they are obtained from air drying. The dryer-dried handsheets will have a lower moisture content than the air-dried handsheets due to the hysteresis phenomenon (9). It is also possible that a surface activation reaction is occurring.

As in other sizing processes, different pulps demonstrated very different sizing abilities. Sizing in



1. Effect of heating treatment on sizing for air-dried handsheets dipped in 1% rosin sizing solution and air-dried again followed by heat treatment at 160°C as a function of time



2. Sizing in control handsheets without rosin with heat treatment at 160°C

unbleached pulp is much higher than in bleached pulps under the same conditions. This is a well known sizing phenomenon. As in rosin soap sizing with iron ions as the mordants (3), TMP was sized much more effectively than bleached pulps. Bleached softwood pulp was sized better than bleached hardwood pulp. These trends do not occur in the conventional rosin-alum sizing process (3). We did not consider the effect of inorganic salts as possible catalysts in the sizing reaction. Further work might explore deashing of pulps or the addition of inorganic salts.

Heat treatment of dipped and air-dried handsheets that originally showed no sizing has a profound effect on the sizing development in TMP pulp (No. 12, 10, and 6). Heating at 160°C for only one minute can promote the handsheets from no sizing (No. 10) to a very high level of sizing (HST values > 10,000 s) (No. 12). The same heat treatment seems to have little effect on the sizing development in Bld. SW KP (No. 11 vs. No. 13), however. Further work is necessary to explain this unusual phenomenon because it calls the mechanism into question. Discussion

below will report more work on the effect of heat treatment on sizing development.

Another extraordinary phenomenon shown in Table I is that the HST values with 1% formic acid ink are always higher than that with neutral ink in this sizing process. Earlier work (10) showed that formic acid has an accelerating effect on HST measurements in rosin-alum sized paper and little accelerating effect on HST tests in AKD sized paper. There has been no report that formic acid has a slowing effect on HST tests, however. Under some conditions, excess sizing agent can act as a surfactant and therefore lower the level of sizing (6). It is possible that unreacted rosin is less effective as a surfactant at low pH. This contributes to higher sizing levels with formic acid ink.

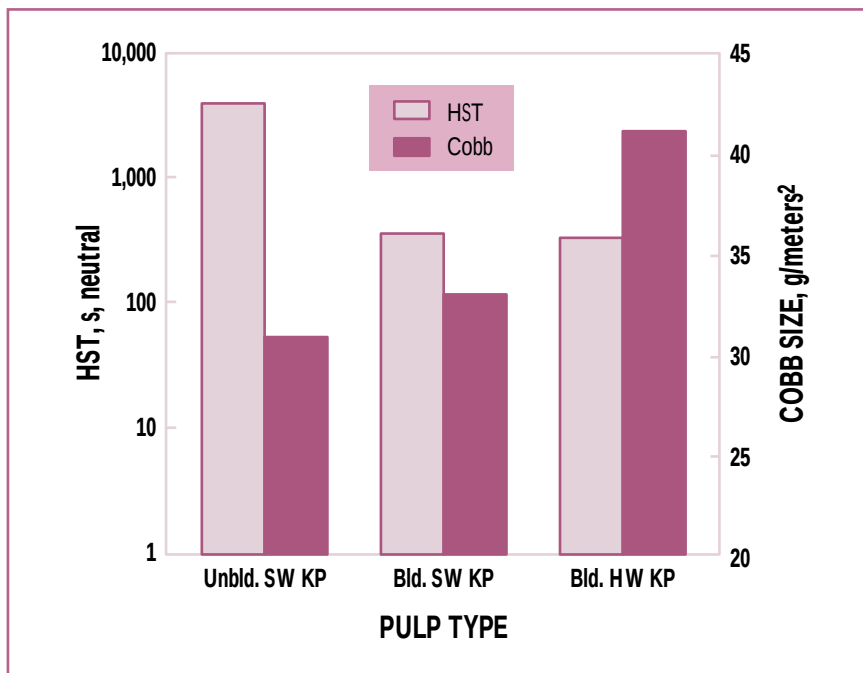
There is another unusual fact about this sizing process. Although the HST values show that the handsheets have high to very high levels of sizing, in many cases the Cobb size test shows that the sizing is only moderate. Cobb values seldom go below 25 g/m² in well sized papers made with these pulps. This indi-

cates that the ink penetration resistance of paper does not always coincide with the water pickup resistance. As an example, the sizing result with Bld. HW KP (No. 4) shows that the handsheets were almost soaked by water, although the HST value with 1% formic acid ink was 1597 s.

Effect of the concentration of dipping solutions

Table II shows the effects of the concentration of rosin solutions and rosin pickup on sizing. Commercial use of rosin size is approximately 10 lb/ton. The sizing results used dryer-dried handsheets with the handsheets dryer-dried again after dipping in rosin solution. Part A of the table shows that the concentration of the rosin soap solution has a critical effect on the sizing in Bld. SW KP. Only when the concentration of dipping rosin solution is 1% is it possible to achieve effective sizing. Lower or higher concentration cannot give good sizing. Excess sizing agent—acting as a surfactant—could lower the level of sizing.

The situation is very different in the case of Unbld. SW KP as Part B of Table II shows. A 0.5–2.0% concentration range of dipping solution has



3. Effectiveness of sizing with alternate size on dryer-dried handsheets dipped in 1% rosin solution and dryer-dried at 121°C for 3 min

KEYWORDS

Ester number, hand sheets, heat treatment, rosin soap, size, softwood pulps, submersion, surface sizing, thermomechanical pulps.

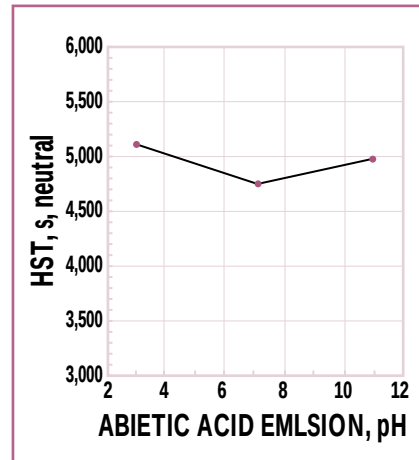
little effect on sizing. We cannot explain this phenomenon.

Effect of heating treatment on sizing

As Table I shows (No. 6–8), no sizing can be observed in air-dried handsheets made from TMP and bleached pulps after dipping the handsheets in a 1.0% rosin soap solution and drying on a dryer at 121°C for 3 min. Figure 1 gives the effect of heating time at 160°C on the development of sizing in rosin dipped and then air-dried handsheets. When further treating the dipped handsheets with heat at 160°C for just 1 min, Fig. 1 shows a very high level of sizing in the handsheets made from TMP and good sizing in the handsheets made from bleached softwood pulp. There is still no substantial sizing observed in the handsheets made from bleached hardwood pulp even after a longer period of heating.

We believe that heat treatment at 160°C can promote the esterification reaction between rosin size and cellulose and hemicellulose to develop the sizing in the handsheets. Previous workers (7, 8, 11, 12) reported that a similar heat treatment with catalysts can promote the esterification reactions between multifunctional carboxylic acids and cellulose. We are unable to explain the fact that a high level of sizing can develop quickly with heat treatment in the TMP handsheets but no sizing can develop with the same heat treatment in the more cellulose rich Bld. HW KP handsheets.

Even more interesting is the fact that good sizing can develop in control handsheets—using no sizing agent or any other chemicals—made from bleached or unbleached chemical pulps under prolonged heating at 160°C, as Fig. 2 shows. We observed no sizing in control handsheets made from TMP under the same heating treatment. While sizing can develop more easily in Bld. SW KP than in Bld. HW KP by dipping rosin, the opposite is true for the sizing development in the control handsheets by the prolonged heating. TMP pulps are less prone to



4. Effectiveness of sizing with abietic acid on dryer-dried Unbld. SW KP handsheets dipped in 1% abietic acid emulsion and dryer-dried at 121°C for 3 min

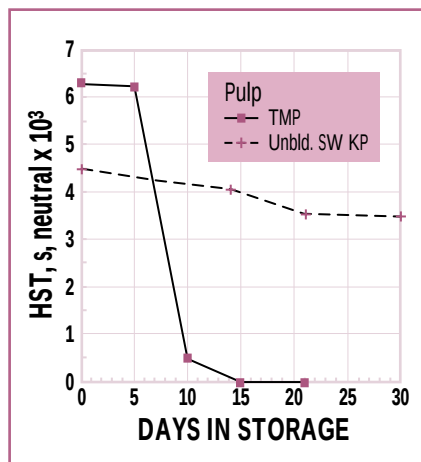
“hornification” than bleached chemical pulps.

Sizing can develop even more quickly in the control handsheets when heating at a higher temperature such as 180°C. We do not include those results here. Although the ink penetration resistances (HST values) of the handsheets are not very high in the blank handsheets after prolonged heating, the water pickup resistances (Cobb size tested but not reported) are quite high. This is opposite to the situations when sizing develops by dipping rosin.

Effectiveness with other rosin

The paper industry has used rosin soap size for almost 200 years but always as an internal sizing agent rather than a surface sizing agent. The dip treatment simulates internal sizing while avoiding the issue of retention. Dipping is different from surface sizing because dipping involves a low viscosity fluid in an unsized sheet that completely penetrates the sheet. Surface size uses high molecular weight material that remains on the surface of the sheet.

Is the sizing achieved by immersing paper in the size solution an unique phenomenon for the particular rosin size used or a common property for any rosin size? We designed the following experiments to answer that question.



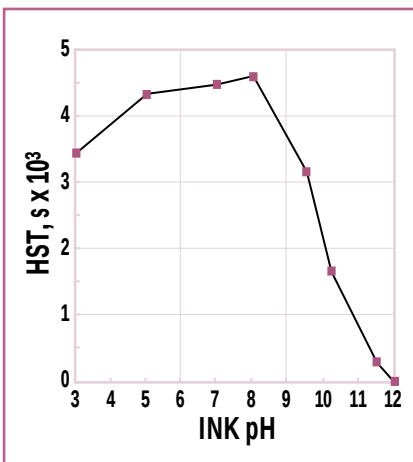
5. Fugitive sizing in dryer-dried handsheets dipped in 1% rosin solution and dryer-dried at 121°C for 3 min

Figure 3 shows the effectiveness of another commercially available fortified rosin soap size. After being dryer-dried at 121°C for 3 min, handsheets were dipped in a 1% solution for 45 s and then dryer-dried again after removing the excess solution. Compared to the results in Table I (No. 1, 3, and 4), we see that the second size (ammonium salt of fortified rosin) is as effective as the original one (potassium salt of fortified rosin).

Figure 4 shows that abietic acid can also achieve sizing in the same way. Abietic acid shows similar effectiveness. Since abietic acid is not water soluble, we dissolved it in a small amount of ethanol first and then diluted with water to make an emulsion. Changing the emulsion pH from 3 to 11 did not seem to have an appreciable effect on the sizing results.

Fugitive sizing

Fugitive sizing with synthetic sizing agents is a common phenomenon (13). The same phenomenon occurs in the dip treatment of handsheets with rosin soap size in some pulps. As Fig. 5 shows, after dipping in 1% rosin soap solution and drying at 121°C, handsheets made from TMP possessed very high levels of sizing in the first week. The sizing dropped dramatically afterward. The sizing almost completely disappeared after



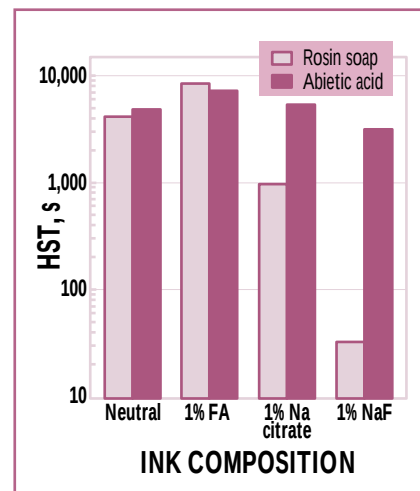
6. The effect of ink pH on HST measurement of Unbld. SW KP dryer-dried handsheets dipped in 1% rosin solution and dryer-dried at 121°C for 3 min

10–15 days. In the handsheets made from Unbld. SW KP and treated with rosin solution in the same way, the sizing lasts much longer. Again there is no explanation for the different behaviors among pulps.

HST measurement with different inks

Previous work (10) shows that ink pH and composition have great effects on HST values in rosin-alum sized paper but much less effect in AKD sized paper. Bonding in the former is much less resistant to acid and coordinating species in the test ink than the β -ketoester linkage of the latter. Measuring HST values with inks of different pH and compositions can help elucidate the bonding mechanism between size molecules and fiber components.

Figure 6 shows the effect of ink pH on HST values of handsheets sized by dipping in rosin solution. We obtained the ink solutions with different pH by adjusting the pH of the neutral ink with 1% HCl or 1% NaOH aqueous solutions. This sizing is resistant to acidic ink solutions. It is not true with rosin-alum wet-end sizing (10). This shows a difference in the bonding mechanism between the two rosin sizing processes. The new sizing method is not resistant to basic ink solutions. One would expect this, if the rosin forms an ester linkage.



7. The effect of ink composition on HST measurement of Unbld. SW KP dryer-dried handsheets dipped in 1% rosin solution and dryer-dried at 121°C for 3 min

Earlier work (10) reported that 1% sodium citrate has an appreciable desizing effect on rosin-alum sized paper and 1% sodium fluoride ink can soak the rosin-alum sized paper instantly. Both chemicals have little desizing effect on AKD sized paper. Citrate anions and especially fluoride anions have very high formation constant (coordination potential) with Al^{3+} . Therefore they can easily break the coordinate bonds that bind rosin molecules on fibers by a ligand substitution reaction. They cannot break the β -ketoester linkages that bind AKD molecules on fibers.

Figure 7 shows that 1% formic acid, sodium citrate, and sodium fluoride have little desizing effect on handsheets sized by dipping in 1% abietic acid emulsion. When sized by dipping in abietic acid, this result is a strong indication that the bonding between abietic acid and fiber components is a covalent linkage that resists coordination anions—mostly probably an ester linkage.

Figure 7 also shows, however, that 1% formic acid has no desizing effect, 1% sodium citrate has some desizing effect, and 1% sodium fluoride has great desizing effect on handsheets sized by dipping in rosin soap solution. We cannot explain this phenomenon, although sodium fluo-

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ride is slightly alkaline (pH approximately 7.4), since fluoride is a weak base. The 1% sodium citrate ink and 1% sodium fluoride ink were made in exactly the same way as the 1% formic acid ink except 2% sodium citrate solution and 2% sodium fluoride solution were used instead of the 2% formic acid solution.

SUMMARY

Dipping handsheets in rosin soap solution and then drying them with heat can result in effective sizing. No mordant is necessary in this process. Sizing with this method is easy in Unbld. SW KP and TMP handsheets but less so in handsheets made from bleached pulps especially bleached hardwood pulp. Sizing achieved with this method is quite fugitive in the TMP handsheets but is quite stable in Unbld. SW KP handsheets. Effective sizing is also possible by dipping handsheets in abietic acid emulsion.

There are many factors that can affect the sizing with this method. The handsheet drying conditions in both pre-dipping and after-dipping stages seem critical. Dryer drying at 121°C for 3 min in the two drying stages was indispensable in achieving effective sizing. Air drying in either stage will result in no sizing in the handsheets from all the pulps except for those of Unbld. SW KP. This method is highly dependent upon the sheet density.

The concentration of rosin in the dipping solution is also an important factor. While it is critical in the sizing of handsheets made from Bld. SW KP, it is much less in the sizing of handsheets made from Unbld. SW KP.

Heating the dipped handsheets that originally have no sizing because of air drying in one of the two drying stages at 160°C for only 1 min can promote a high level of sizing in handsheets from TMP and good sizing in handsheets from Bld. SW KP. The same or even longer heating treatment has no effect on the sizing development in the handsheets made from Bld. HW KP, however. Heating the control handsheets with no added size agent made from bleached or unbleached chemical pulps at 160°C or higher tempera-

ture for more than 1 h can also develop good sizing in them. The same heating treatment has no effect on the sizing development of blank TMP handsheets.

HST tests with inks of different pH and different compositions indicated that the bonding interaction between abietic acid and fiber components that affect the sizing is more likely an ester linkage. The bonding interaction between rosin soap molecules and fiber components is much less clear.

EXPERIMENTAL

Materials

The unbleached Douglas-fir kraft pulp had a CSF of 650 mL and a 40 mL permanganate 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 main rosin soap size used in this study was Stafor, and the alternate examined was Plasmine PLH-55. The abietic acid was a technical grade chemical.

Procedures

Handsheets of 60 g/m² basis weight were made according to TAPPI Test Method T 205 om-88 in the British Sheet Mold using a total water volume in the mold of 5.0 L rather than 7.0 L. We used the standard press cycle and dried the handsheets in a sheet dryer at 121°C for 3 min (dryer drying) or in a standard TAPPI room (air drying).

After conditioning in the standard TAPPI room (22.2°C and 50% relative humidity) for at least 2 h, the handsheet was weighed to the nearest 0.001 g and then dipped in a rosin soap solution or abietic acid emulsion for 45 s. The handsheets were removed from the solution or emulsion and put in the middle of four blotting paper sheets with application of slight pressure to remove the surplus liquid. The handsheet was immediately reweighed to the nearest 0.001 g. The handsheet was then dried in a sheet dryer at 121°C for 3 min (dryer drying) or in

a standard TAPPI room (air drying) as required.

The amount of rosin adsorbed in the handsheet was calculated by subtracting the conditioned weight of the handsheet from its weight after blotting, multiplying by the concentration of rosin in the dipping solution, and dividing by the conditioned weight of the handsheets.

After conditioning again in the standard TAPPI room for at least 2 h, Cobb Size values of the handsheets were determined by TAPPI T 441 om-90. Ink resistance was determined on a Hercules Sizing Tester according to TAPPI T 530 pm-89 to 80% reflectance values using 1% formic acid ink solution or a neutral ink solution. **TJ**

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