

Investigation of the mechanism of paper sizing through a desizing approach

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ABSTRACT: A series of chemicals were employed to investigate the chemical properties of size-fiber bonds in different sizing systems. The bonding strength has been proved to be dependent upon the type of bonding. In rosin-alum size the size bond is indirect (through an aluminum coordinate complex), which is vulnerable to attack by acid, alkali and, especially, aluminum-complexing ligands, in which ligand substitutions take place and determine the rate of ink penetration in the Hercules size test (HST). Alkyl ketene dimer (AKD) can react with cellulose to form direct β -keto ester bonds. This covalent bond is strong enough to resist the attack of acids or bases, and it is almost inert to these chemicals. However, if a small amount of alum is used in AKD sizing under acidic conditions, two types of size bonds are formed. Therefore, different HST values will be observed depending on what ink is used. A hypothesized mechanism regarding ligand substitution has been proposed and verified indirectly. We suggest a surfactant, such as Tween[®], be used to accelerate testing of calcium carbonate filled sheets in place of formic acid, which is clearly inappropriate with this use of the HST test. This simple desizing approach provides important information on sizing mechanisms and will benefit new sizing agent research as well as routine process control.

KEYWORDS: Bonding strength, citrates, surfactants, dimers, ketenes, mordants, rosin size, sized papers, sizing tests, sizing, sodium fluoride.

of water repellency can be achieved in paper products. Normally, an amphipathic material is applied to achieve this goal. The hydrophilic part of the amphipathic material should bind to the fiber surfaces, and the hydrophobic part should extend outward to cover the fiber surfaces. When sufficient surface coverage is reached, the paper will have suitable water repellency.

It is apparent that to achieve effective sizing in any internal sizing system, the following basic requirements must be met (1, 2):

1. The size precipitate must have relatively high hydrophobicity.
2. The size must be well retained on fibers.
3. The retained size must be distributed throughout all fiber surfaces.
4. The size precipitate must be strongly bound to the fiber surfaces so that the bonding will not be broken down by fluids.

The importance of high hydrophobicity, good retention, and uniform distribution of size molecules to explain the various sizing phenomena and to improve sizing techniques has been fruitful (1, 3). On the other hand, the importance of bonding between size precipitates and fibers has not been well addressed. Anchoring is an ambiguous word frequently used to describe this bonding process. However, the relationship

The objective of internal sizing is to make the originally hydrophilic fiber surfaces relatively hydrophobic so that a certain degree

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I. HST values for rosin sized paper with different concentrations of formic acid ink

<i>Formic acid, %</i>	<i>Surface tension, dyn/cm</i>	<i>HST values, s</i>	<i>Ink pH</i>
0	73.0	225.7	7.00
1	62.7	138.8	2.20
5	60.8	76.2	1.79
10	59.3	33.8	1.49

between the bonding strength and sizing effectiveness has never been clearly specified. The bonding strength is a critical matter not only for sizing development, but also for the performance of the sized products in service. Completely understanding the bonding characteristics in different sizing systems will provide us fundamental information about sizing mechanisms and help us to understand some unsolved problems in sizing classification, size testing, and in the search for new size agents.

In the paper industry, traditional rosin soap sizing is often called acid sizing since it normally works at pH 4.5 in the paper machine wet end. Alkyl ketene dimer (AKD) is called neutral or alkaline sizing because it is applied at pH above 7. However, the pH difference is not the fundamental difference for these two types of sizing systems. Actually, rosin could be used at neutral or even at alkaline conditions (4). The fundamental difference is in the bonding mechanisms that hold the sizing agents onto the fibers. From this point of view, direct sizing or indirect sizing would be the suitable terminology for this classification. In the indirect rosin soap sizing system, alum usually is the necessary additive and forms polyaluminum ions in solution first, which then react with rosin to form rosin aluminate. This cationic substance can be retained with the anionic fibers and bond to the fiber as the sheet is dried. Aluminum serves as a bridge linking both rosin molecules and fibers. In the direct AKD sizing system, AKD

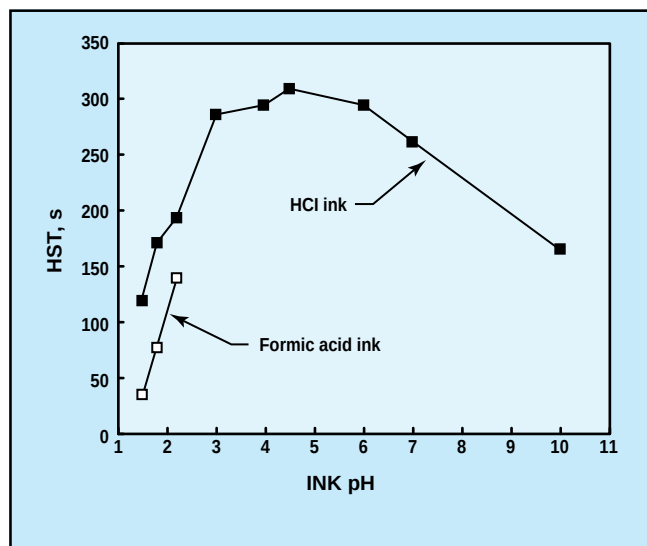
molecules are generally believed to react directly with the cellulose hydroxyl groups and form covalent ester bonds with fibers (5, 6).

The actual bonding mechanisms, the chemical properties, and the bond strengths of the size-fiber bond in the final paper still remain controversial. For example, electrostatic forces are often alleged as the main force in rosin-alum sized paper since the positive polyaluminum complex could attract the negative rosin and negative fibers (7, 8). This may be a good explanation for size retention but not for sizing development. Sizing development is another interaction, which should provide the size with enough strength to resist possible attack by water or other liquids. We hypothesize that electrostatic forces, hydrogen bonding, or Van der Waals forces would be too weak to withstand the attack of water. We have proposed the hypothesis that coordination bonds are the most likely linkage in the rosin-alum-fiber bonds. Aluminum acts as a mordant, while rosin and fiber act as ligands in the size complex (9). Even though the β -keto ester linkage is the widely accepted bond for AKD size, there are still reports claiming that the AKD molecules are physically trapped in the sheet (10) or anchored into fibers by hydrogen bonding (11). The critical point of these arguments actually is about the chemical properties of size bonding. If there are fundamental chemical differences in the size bonds, there should be remarkable differences in their behavior when they are exposed to water, and especially to the chemi-

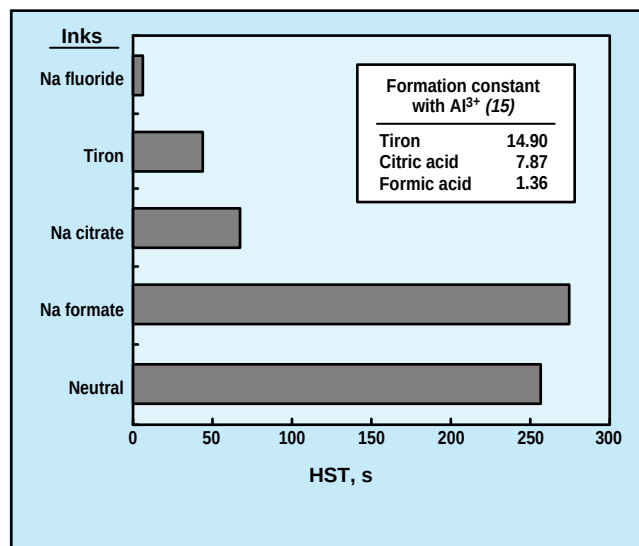
cal additives in the sizing test ink designed for testing various types of bonds.

The Lucas-Washburn equation has been frequently used as the basis for the explanation of sizing development and sizing test results. In the sizing process, sizing agents cover the fiber surface with a lower energy film. The aqueous liquid will form a higher contact angle on the surface, which will obstruct water from wetting and penetration. During the sizing test, we normally assume that this contact angle is constant, so that the liquid viscosity and surface tension are ascribed as the major factors in controlling the rate of liquid wetting and penetration (12). The lower the surface tension of the testing ink, the smaller the contact angle that will be formed, and the greater the rate at which the testing ink will penetrate through the paper. To speed up the sizing test for some hard sized paper, some penetrants with lower surface tension than water can be used (to decrease the contact angle). Formic acid in the Hercules sizing tester (HST) has been claimed for this purpose. However, the liquids to which the paper is exposed during its use are various. The process of liquid penetration involves not only the surface interaction, but often the chemical interaction between components of the liquid and the size-fiber bond, which may break these bonds. Thus, the orientation of the size molecules on fibers will be altered, the surface properties of the fiber will be changed, and the contact angle will vary with time as the size molecules are released from the fibers. In the extreme situation, the size agent will be detached from the fibers. Under these conditions, the Lucas-Washburn equation is no longer applicable, and the chemical stability of the size bond will play an important role in determining the rate of ink penetration. This important issue, which has been overlooked in the past, is the basis in our desizing

1. Effect of ink pH on HST values of rosin alum sized papers



2. Results of different desizing agents on rosin alum sized paper



approach to investigate the mechanism of paper sizing.

In the desizing approach, a variety of ink solutions are formulated to test a variety of sized papers on the HST. It is the purpose of this paper to try to infer the mechanism of different sizing methods from their responses to different test fluids. The specific interactions between these chemical inks with rosin-mordant-fiber bonds or size-fiber bonds will demonstrate the importance of the bonding strength to sizing performance and clarify the principal difference between direct sizing and indirect sizing. This method will provide us more realistic and valuable information about the sizing mechanism than some other complex and unrealistic analytical techniques. Based on this information, we may make a reliable prediction of the paper sizing performance in service. This will also benefit our search for new sizing agents.

Results and discussions

The Hercules sizing tester is a widely used instrument which measures the rate of liquid penetration into paper. For a given sized paper and a controlled environmental condition, the penetration rate is primarily determined by what ink is used. Neutral

ink and formic acid ink are the standard inks used for this method. For some experimental handsheets hard-sized with rosin, use of these two different types of inks can result in 5–50 times differences of HST values (9). The use of formic acid seems to be based on historical use without much knowledge of why it shortens the test time. The only explanation in the literature is that formic acid has a lower surface tension than water so it can accelerate the liquid penetration into the paper (13). It is not difficult for us to disprove this statement with a simple experiment.

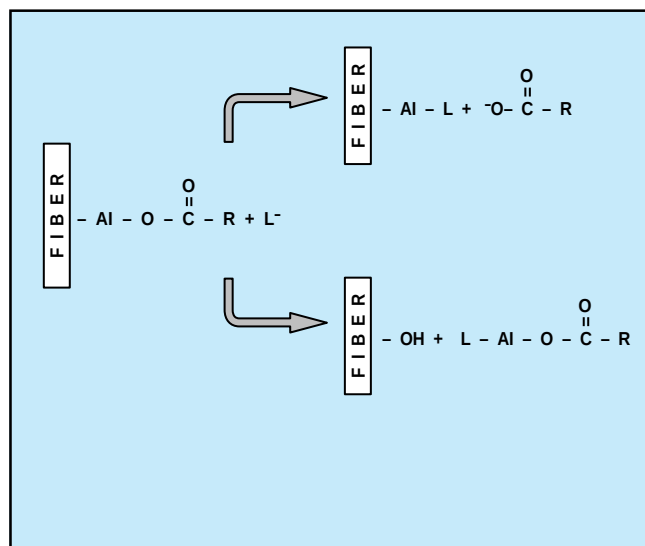
Different concentrations of formic acid inks were employed for this investigation. **Table I** lists the actual values of ink surface tensions and their HST values on the same rosin-alum sized handsheets. There is not much difference in the surface tensions of these inks, especially among those inks containing formic acid, while their HST values differ greatly. Therefore, formic acid must work by a mechanism other than lowering the surface tension. The relatively strong acidity of formic acid ink is worth considering; the pK_a of formic acid is 3.75 at 25°C.

In order to obtain data about the pH effect, hydrochloric acid was used for comparison with formic acid. Sodium hydroxide was used to give ink

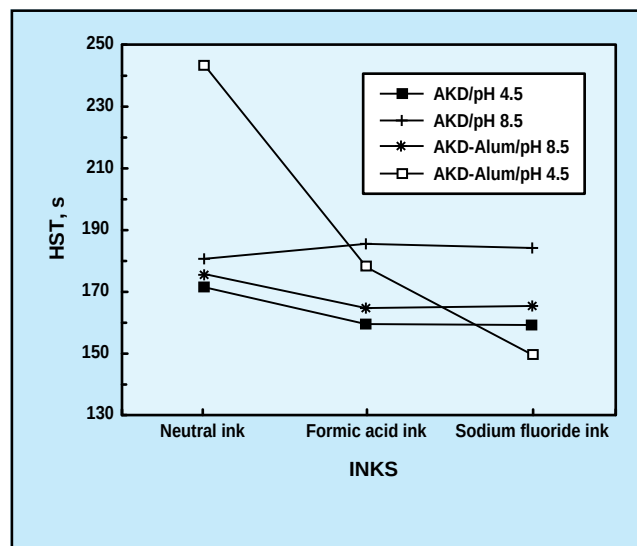
with higher pH values. **Figure 1** shows that ink pH does greatly affect its penetration rate, especially at the extreme acidic and alkaline conditions. The best HST value was reached when the ink pH is 4.5, which is also the optimum pH where rosin sizing can be effectively developed. Is it a coincidence, or is some important factor involved? We have pointed out that at pH 4.5 aluminum is in the form of a polynuclear complex, which is an effective mordant with the capability to bind with the ligands from rosin and fiber components (14). When the pH is below 3, aluminum will exist in the form of trivalent Al^{3+} ; when the pH is near 7, aluminum will be in the form of insoluble $Al(OH)_3$. They both are noncomplexing forms without any capability for size anchoring. If the ink pH causes the aluminum complex to change to these noncomplexing forms, the size precipitate would be broken. We suggest that the change of ink pH, initiating the change of the aluminum complex and resulting in the separation of the size bond, is the most important reason for the effect of formic acid on liquid penetration. We can provide more direct evidence for this assumption.

In order to clearly demonstrate the size bonding mechanism in the rosin-alum system, we selected a se-

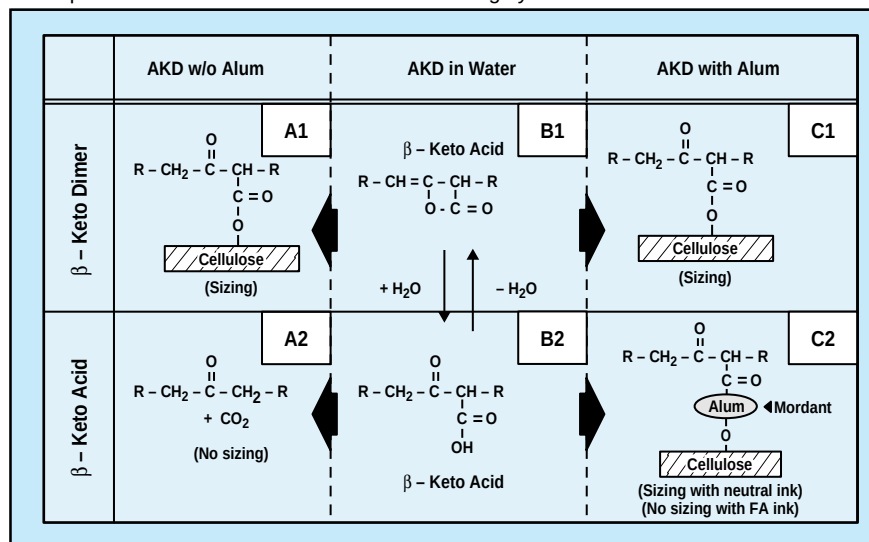
3. Two possible substitution reactions in the desizing process



4. Effect of desizing agents on AKD sized paper



5. Proposed mechanism of reactions in AKD sizing system



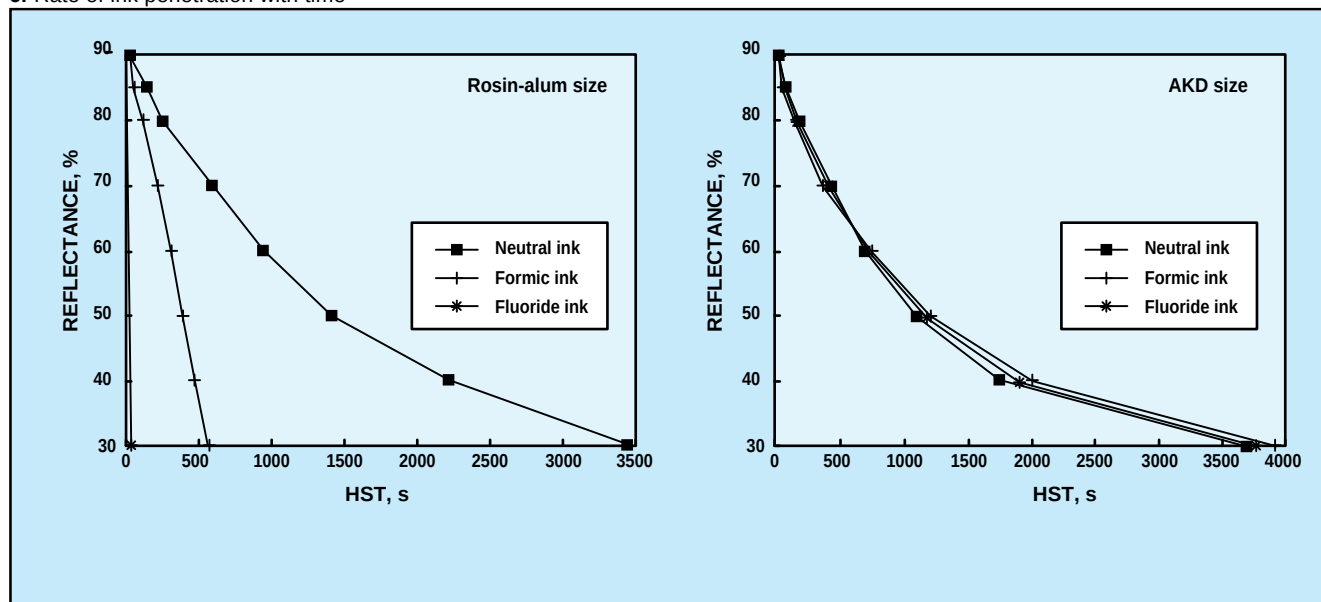
ries of ligands having different affinities for aluminum, which act as chemical penetrants, to formulate various test inks for HST testing. **Figure 2** shows the HST results and the desizing ability of these penetrants on rosin-alum sized paper at the same molar concentration (0.22 M, the same concentration as 1% formic acid) and the same pH (7.0). Their formation constants with aluminum (15) are also listed for reference. Even though these constants could not be used for quantitative comparison, they clearly demonstrate that the higher the formation

constant with aluminum, the stronger the effect of the penetrant on the desizing process. From the view of coordination chemistry, they all follow the reaction of ligand substitution—the stronger ligand replaces the weaker ligand of carboxylates from rosin or fibers, resulting in part or all of the size agent separating from the fibers or from rosin molecules. **Figure 3** depicts two of these possible reactions. Since sodium formate contains the ligand as formic acid but does not demonstrate desizing ability under these conditions, there is no reason to expect

that ligand substitution reactions take place in the process of HST testing with formic acid. As stated before, pH is the critical factor influencing the penetration rate of formic acid ink on rosin size. Citrate is a strong chelating agent to aluminum; it exhibits a greater effect than formate on ink penetration. The citrate chelating ability to aluminum ions was also demonstrated by the fact that a small amount of citrate in pulp resulted in a great loss of sizing because the high affinity of citrate ties up the aluminum ions (16). Since fluoride is a hard base with very high formation constants with aluminum (the successive pK values of the formation constants are 6.10, 11.15, 15.00, 17.75, 19.37, and 19.84), it gives sodium fluoride a special affinity for aluminum and demonstrates the strongest influence on the ink penetration into the rosin-alum sized paper (15).

The existence of coordination bonds in the rosin-alum-fiber complex is the basis for these aluminum-complexing ligands carrying out ligand substitution. If the size bond does not contain coordination bonds, one would not expect these ligands to exhibit desizing effects with the HST test. Paper sized with AKD is a good material with which to test this hypothesis. In **Fig. 4**, for paper sized

6. Rate of ink penetration with time



with AKD only, these desizing agents have very little effects on the ink penetration. If AKD was anchored by hydrogen bonding, one would expect a low pH to have an effect on the size performance. The effect of formic acid on calcium carbonate filled papers is only a measure of the reaction of acid with carbonate, which destroys the structure by the formation of carbon dioxide gas.

However, when AKD sized handsheets were formed with 0.5% alum, a very different phenomenon was observed. When paper is sized at pH 8.5, alum is somewhat detrimental to size. On the other hand, when paper is sized at pH 4.5, the highest HST value was obtained by neutral ink and the lowest value was observed with fluoride ink.

These "abnormal" phenomena can also be explained from the mechanism of size bonding and the theory of the coordination chemistry of aluminum. It is well known that AKD can react with water to form the unstable β -keto acid, which will decarboxylate to form keto if there is no retention aid. Therefore there are two types of AKD in the pulp system, the major type is the β -keto dimer (**Fig. 5B1**) and the minor hydrolysis product is β -keto acid (**Fig.**

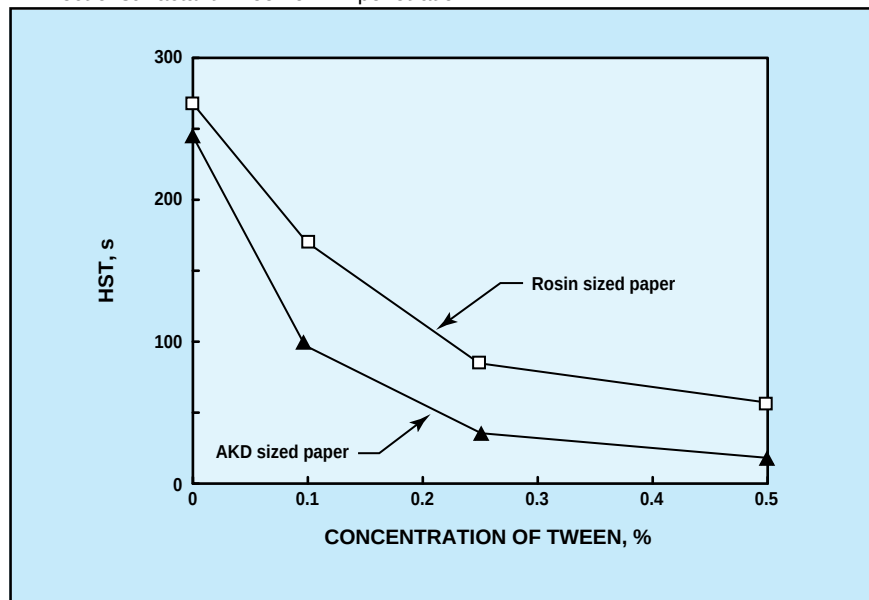
5B2). The former can react with fibers directly to form the strong β -keto ester bond (**Fig. 5A1** and **5C1**), providing the paper with long time stability in exposure to water, acid or other chemical inks. The latter can be retained on the fibers if there is a suitable retention aid, such as polyaluminum from alum at pH 4.5 in the presence of alum. It can bind to fibers through a mordant similar to the rosin-alum-fiber bond in rosin size. AKD is likely bound by two different mechanisms at pH 4.5. One is the direct ester bond (**Fig. 5C1**); the other is the indirect coordinate bond (**Fig. 5C2**). The existence of this indirect bond is indicated by the fact that neutral ink gives a much higher HST value than formic acid or fluoride ink (**Fig. 4**). With neutral ink, both types of bonds will be effective in sizing, but only the ester-bond size provides the effective resistance to ink penetration with fluoride or formic acid. Since only the strong ester bond exists in the other sizing conditions, there is no appreciable difference in their HST values by neutral or fluoride inks. On the basis of these results, we believe that alum has a small negative effect on AKD sizing at normal alkaline condition. It may have some ben-

efit to water drainage. However, the addition of alum should be controlled to the lowest possible level, or it may induce more AKD to hydrolyze, reducing the effective resistance of the size to chemical attack (17). However, under some conditions, particularly low pH, alum may improve AKD sizing against neutral ink.

One of the advantages of the HST size test is that one can observe the rate of ink penetration into paper. The bonding difference between rosin size and AKD size is also reflected in their reflectance-time curves shown in **Fig. 6**. For AKD sized paper, the neutral ink and fluoride ink both penetrate at the same rate throughout the test. For rosin size, the rate of penetration of fluoride ink is much higher than that of neutral ink. The size bond itself appears to be an important factor controlling the penetration rate in rosin alum size. Fluoride ink almost soaked the paper immediately while neutral ink seems to follow the Lucas-Washburn equation.

From the above discussion, one can see that rosin and AKD sizes have substantial difference in their size bonds. The β -keto ester bond is very strong and almost inert to acid and other chemicals. This strong

7. Effect of surfactant Tween on ink penetration



bond provides one of the advantages of AKD size over rosin size. In rosin soap sizing, fortified rosin has been demonstrated to give better performance than conventional rosin size. However, this improved performance is achieved only from its multi-functional groups, which allow the size to be more easily retained and more evenly distributed on the fiber surfaces. The size bond is still a coordination bond, which has relatively weak chemical stability. Good sizing agents normally must have a high degree of chemical inertness toward the impinging liquid. Therefore, if research on rosin sizing could lead to a new bonding mechanism for the rosin-fiber bond, it would be a revolutionary change and greatly extend the usefulness of this inexpensive, stable sizing material. This possibility should not be ignored.

Actually, the surface tension of the ink does have an effect on its rate of penetration, and it becomes important if one can reduce the ink surface tension drastically. We used the nonionic surfactant Tween 20™ (ICI Americas Ltd.) to demonstrate this effect. The surface tension of 0.1% Tween 20 neutral ink was 30.0 dyn/cm. Inks with different concentrations of surfactant were employed

for HST testing of rosin and AKD sized paper. **Figure 7** shows that the higher the level of addition of surfactant to the ink, the faster the liquid penetration. Notably, both the indirect coordinate rosin-alum bond size and the strong direct ester-bond AKD size were found to be affected by the surfactant in a similar fashion. This is mainly attributed to the lower surface tension of the ink, which reduces the contact angle of ink with paper. Ink containing a surfactant may be used to replace the formic acid ink for quick HST tests of AKD sized paper with calcium carbonate fillers since interference from the formation of CO₂ is avoided.

Conclusions

Substantial differences between rosin alum size and AKD size bonding mechanisms were demonstrated by their much different responses to a series of chemical penetrants. Indirect rosin-alum-fiber size is formed through coordination bonds, which are stable in water at neutral pH, but can be greatly affected by acid, alkaline, and other chemicals. Ligand substitution was the major cause of this desizing process. AKD can react with cellulose and form direct β-

keto ester bonds with fibers. This strong covalent bond is almost inert to acidic and alkaline solutions. Even the strongest aluminum-complexing ion, fluoride, has no effect on the ink penetration. However, if alum is used along with AKD sizing at low pH, there can be two types of bonds formed between the size and the fiber, the major direct ester bond and the minor indirect coordinate bond. Therefore, neutral ink will result in much higher HST values than formic acid or other penetrant inks. The use of alum in AKD sizing systems for its other positive effects on drainage and retention should be carefully considered since alum's preferential attraction to AKD molecules could reduce the effective strong covalent bond in the final size. The surfactant Tween 20 can be used as a penetrant to accelerate the testing of hard sized papers, which will reflect the real rate of ink penetration without interference with the size bond itself.

Experiments

Handsheets formation

Pulp: Softwood bleached kraft pulp was beaten to 380 mL CSF in a double-disc refiner. Handsheets (60 g/m²) were prepared from this kraft pulp, tap water and rosin soap size solution or AKD emulsion in the British Sheet Mold (TAPPI Test Method 205 om-88). All handsheets were pressed in the standard press cycle and conditioned at TAPPI standard conditions (72°F and 50% RH) for one week before being tested.

Rosin size: Fortified rosin soap at 1% solids based on dry pulp as a 0.1% solution (Stafor®, Westvaco Chemicals) was added to thick stock (1%). The stock was stirred and adjusted to about pH 4.5 (unless indicated) with HCl (2%), then 2% alum (based on dry pulp) was added. The pH was adjusted again, and the stock was stirred for another 5 min and diluted to 0.2% with tap water. The

Sizing

pH of the pulp slurry was adjusted again before the formation of handsheets.

AKD size: AKD (0.3%) based on dry pulp (Hercon®, Hercules Inc.), as a 12.5% emulsion, was added into thick stock (1%). The stock was stirred and adjusted to pH 8.5 with NaOH (2%). For AKD-alum, 0.5% alum was then added after 1 minute, pulp pH was adjusted to 8.5 (or 4.5 as mentioned). The stock was diluted to 0.2% with tap water, and the pH was adjusted again to the set value before the formation of the handsheet.

HST testing

1. Neutral ink and 1–10% formic acid inks were prepared according to TAPPI Test Method T 530 pm-89.
2. The penetrant inks were prepared to equal molar concentration of 1 % formic acid (0.22 M) and ad-

justed to pH 7 for testing, except as specified.

3. Surfactant ink: Tween 20 from ICI Americas Inc. (HLB value is 16.7) was used to prepare concentrations of 0.1%, 0.25%, and 0.5% in the ink.
4. Ink penetration test: The HST was set for 80% reflectance for all normal penetration tests. The reflectance was changed with time in those cases where reflectance is shown as a function of time.
5. Surface tension measurement: The surface tensions of all inks were measured with a DuNouy tensiometer (CSC Scientific, Fairfax, VA). Calibration was carried out with the known surface tension of pure water. 

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