Efficient Resin Removal

Fast, efficient deresination of fully bleached market pulps can solve quality and runnability problems while reducing a mill’s overall production costs. – By Pierre Mouyal

Resins also affect the quality of other products converted from kraft hardwood market pulps. With fluff pulp, for example, debonders are typically added to increase absorbency. Resins react with these debonders, negatively impacting the overall quality of fluff pulp. When manufacturing fine paper or tissue, high resin levels show up as pitch, or undesirable specks in the sheet. Also, pitch can seriously contaminate a paper machine when it separates from the sheet furnish and deposits on rolls and other components in the wet end.

This article examines techniques mills typically use to reduce resin content in hardwood pulps, specifically the addition of surface active agents (surfactants) in the digester and as a “polishing” step by addition to the final caustic extraction stage in the bleach plant. As explained in more detail below, softwood pulps generally do not require the addition of surfactant-type deresination agents due to the formation of natural soaps during the pulping process.

This article further looks at the standard TAPPI method for extracting resins after bleaching of pulp to determine effectiveness of the surfactant addition, and to make corresponding rate adjustments. It also discusses an alternate “wet pulp” method that shows similar trends as the TAPPI Sohxlet extraction method but in only a fraction of the time, allowing much faster and more accurate adjustments in surfactant addition.

Softwood versus Hardwood Pulps. Generally, hardwood pulps cooked with the kraft process contain higher resin levels than softwood kraft pulps. In softwood pulps, a large portion of the resin (20% -30%) is in the form of free fatty acids, or resin acids (abietic acids), amounting to 20% to 50% of the ether solubles. These free fatty acids dissolve in the hot alkali environment of the kraft digester, and via a process known as saponification, form a detergent or surfactant (rosin soap) to emulsify the neutral portion of the resin.

Because hardwood resins contain few resin acids, large amounts are not removed by “natural” saponification during cooking and bleaching as with softwoods. Hardwood resins are mostly fatty esters, which are unsaponifiable. Emulsification by the addition of a surfactant during cooking in the digester and in the hot alkaline extraction stage of the bleach plant, is the only means for effectively removing these resins.

However, addition of a surfactant to reduce resin levels should not be confused with the use of nonionic surface active agents to increase pulp yield. These agents can be used to reduce resin content as well as to increase pulp yield, but not for both advantages at the same time.

As well documented in literature and patents, use of surface active agents to solubilize resins will actually reduce rather than increase pulp yield. A 1% -2% reduction in resin content (considered necessary with hardwood kraft pulps) is typical when using surface active agents for this purpose, but such application will effectively “mask” an otherwise 1% -2% gain in pulp yield.

Softwood vs. Hardwood Resins. Figure 1 shows the typical resins composition of hardwoods versus softwoods. In contrast to softwood resins, hardwood resins consist of fatty acids, esters, and unsaponifiables, and as noted above, hardwoods contain very little of the true resin acids of the abietic type. The hardwood fatty acids are largely unsaturated, consisting mainly of linoleic acid.

Unsaponifiables contribute appreciably to deresination dif-

![Indonesian acacia-mixed hardwoods contain very high levels of resins that are among the most difficult to remove.](image-url)
cultivates and pitch problems as they possess little hydrophilicity at all pH levels. The following Table 1 compares unsaponifiables with fatty acids and resin acids.

To measure the amounts of resins remaining in cooked and fully bleached hardwood kraft pulps, and thus determine the effectiveness of soap addition at the digester and in the bleach plant, as noted above, solvents are used to extract them in a Sohxlet extractor.

### Solvent Extraction Methods

Hardwood resins are usually soluble in specific organic solvents. Depending on the solvent used for extraction and the hardwood species, the amount of resins extracted varies considerably.

The most efficient method to extract organic resins from pulp is through single extraction in a Sohxlet extractor with a mixture of methanol and benzene. In addition to methanol-benzene, other solvents used for resin extraction include diethyl ether and methyl chloride. Methyl-benzene removes at least 1% more resins than the other agents (because those agents contain more phenols and other polar solvents). However, the methanol-benzene method is not always available because of environmental concerns.

Organic extraction is made after pulp has been cooked and bleached and is very time consuming. It is done many hours after a surfactant has been added to the digester (12 to 18 hours of lag time). Thus it is not a very efficient way to control surfactant addition to the process, and can result in large volumes of off-spec, non-premium pulp which typically is sold at discounted prices.

Another, much more “responsive” method is now being used to extract resins from the wet, unbleached pulp, immediately following cooking in the digester. Comparison of resin content in wet pulp with that in fully bleached, dried pulp shows a parallel trend, indicating that it is possible to make a correction to the rate of surface active addition when monitoring extractive levels. Results between the wet pulp (rapid extraction) and bleached pulp (Sohxlet extraction) are shown in Figure 2.

Typically, the rapid wet extraction method can be performed in an hour or less, representing a significant gain in the response time needed to make adjustments in surfactant addition at the digester and caustic extraction stage in the bleach plant. This can dramatically reduce the percentage of off-spec pulp production and/or savings in surfactant costs.

### Use of Surfactants

The effectiveness of a surface active agent is increased when phosphates are used in the formulation. Phosphates act as sequestering agents for calcium. They also prevent precipitation of the calcium salts of resins.

The use of nonionic surfactants such as nonyl phenol ethylene oxide condensation products is no longer permitted. This is especially true in Asia, a major manufacturer of hardwood market pulps. The Nordic Swan Ecolabel rule especially applies in Asia, when those pulps are exported to European markets. In the past years, formulators of digester additives using that chemistry have switched to different additives.

Emulsifiers added in the alkaline extractive stage (also called polishers) also cannot contain nonyl phenols ethoxylated agents, due to the same Nordic Swan Ecolabel rules. Use of nonyl phenols ethoxylated compounds has also created considerable foam in the alkaline bleaching stage.

Figure 3 shows the effect of acceptable digester additives on the level of organic resins in hardwood market pulps. In general, manufacturers of wood cellulose pulps want a resin level of less than 0.30%.

<table>
<thead>
<tr>
<th>Troublesome Rank</th>
<th>Deresination</th>
<th>Pitch</th>
<th>By-Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaponifiables</td>
<td>Difficult</td>
<td>High trouble</td>
<td>None</td>
</tr>
<tr>
<td>Fatty Acids</td>
<td>Difficult</td>
<td>High trouble</td>
<td>Valuable</td>
</tr>
<tr>
<td>Resin Acids</td>
<td>Less Difficult</td>
<td>Less trouble</td>
<td>High value</td>
</tr>
</tbody>
</table>

Table 1. Unsaponifiables are the most difficult to deresinate and are major contributors to pitch problems.