Analytical techniques for analyzing white pitch deposits

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Determining the origin of pitch contamination is crucial for solving the problem. Analytical techniques include gas chromatography, size exclusion chromatography, and nuclear magnetic resonance (NMR) spectrometry.

Analyzing deposits on paper machines and other equipment is important for determining the origin of the contaminant, for monitoring the effectiveness of combative measures and additives, and for other purposes. These deposits often contain many components that further complicate the picture. We studied the methods for separating and identifying components of paper machine contaminants. These methods included gas chromatography, size exclusion chromatography, and proton nuclear magnetic resonance (^{1}H NMR) spectrometry. Used together, these techniques allowed a precise characterization of mill residues.

The buildup of contaminants on paper machine wires and clothing and paper products is a significant problem. Paper mill deposits may be wood extractives appearing in the pulp (pitch), additives used in the papermaking process (rosin, defoamers containing fatty acids, salts of stearic acid, and so on), polymers and wax from secondary fiber sources, other contaminants, or mixtures of these. Contaminants from secondary fiber are causing more problems to the industry as the amount of paper being recycled and the amount of synthetic polymers in paper products both increase. The preferred generic term used for the cause of paper spotting and paper mill residue deposits is "white pitch deposits," regardless of the source of the contaminants—whether wood pitch, additives used in the process, or contaminants from secondary fiber.

Despite the severity of the problem of white pitch deposits, there is little information on analyses of these contaminants. Some useful papers have appeared recently on proton NMR spectroscopy (*1*), fourier transform infrared (FTIR) microscopy (*2*), pyrolysis-gas chromatography (*3*), and a variety of other techniques (*4*). However, there are some common analytical techniques available that are quite useful for characterizing mill deposits, techniques that have not been discussed in detail in the published literature. Among these are gas chromatography (GC) and size exclusion chromatography (SEC). Also, overall strategies for white pitch analysis should be considered.

There has been little work on comprehensive analysis of white pitch residues in conjunction with pitch abatement schemes or the use of pitch-controlling additives. For example, are all of the components of pitch decreased by additives such as talc, or are some components easier to control than others by a certain method? What additives contribute to the problem? Do sticky scavengers (*5*) work on all sources, or does it depend on the contaminant's structure and molecular weight? Fundamental research will have to be carried out in this area to reduce the difficulty caused by white pitch.

Results and discussion

We can divide the techniques for characterizing pitch into those that separate the components (involving chromatography) and those that do not. This distinction is important for white pitch deposits that are complex mixtures of contaminants. Two methods considered here that actually separate pitch constituents are gas chromatography and size exclusion chromatography. The other methods, in **Table I**, are used to characterize the complex pitch or individual constituents after separation by size exclusion.

Collecting and purifying the sample

The first step in white pitch analysis is to obtain samples. Sometimes the mill has a general buildup of contaminant on paper machine felts or wires that has caused a shutdown for cleaning or replacement. If the wire or felt is replaced, then a sample can be sent to the lab; if not, some of the material scraped from the wire is sent to the laboratory. In some cases, one may want to analyze several individual samples collected at one time or over a period of time to see if there are multiple sources.

Unless set by heat (as in paper spots), white pitch deposits are almost always soluble in nonpolar solvents such as toluene, chloroform, or methylene chloride, though solvents such as hexane are not polar enough for most components. Therefore, these deposits tend to be nonpolar

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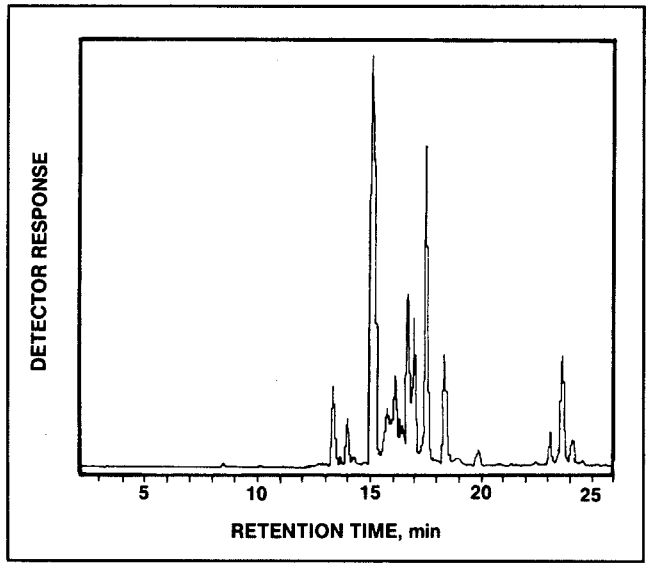
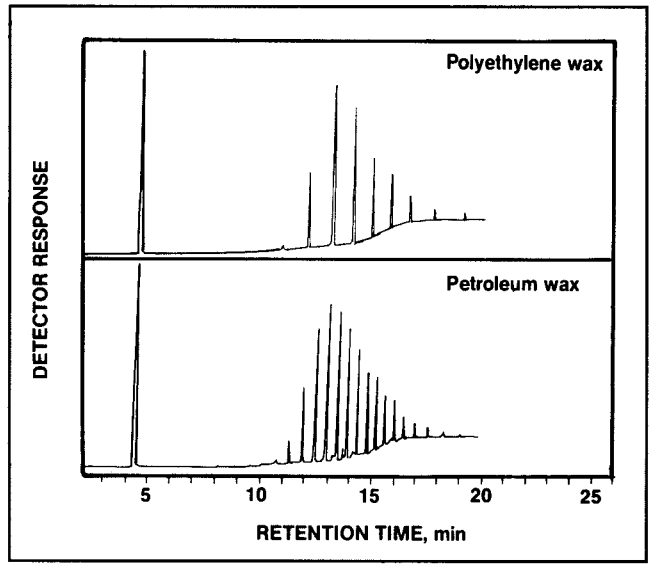
I. Summary of methods considered for white pitch analysis.

Method	*Features*	*Remarks*
Size exclusion chromatography	Separation by molecular weight; nondestructive	Soluble compounds; fractions can be analyzed separately
Gas chromatography	Separation and identification by retention time	Volatile materials (waxes, wood pitch, fatty acids, some additives, rosin)
Proton nuclear magnetic resonance spectroscopy	Identification of functional groups	Soluble compounds with hydrogen atoms; quantitative method
Fourier transform infrared spectroscopy	Identification of functional groups	All compounds; not quantitative

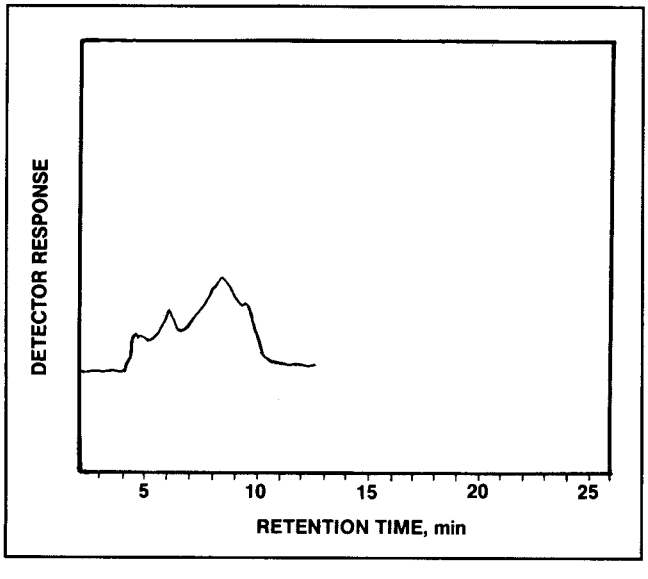
1. Analysis of typical trimethylsilylated tall oil sample from pine on a GC packed column showing fatty acids, resin acids, and sterols



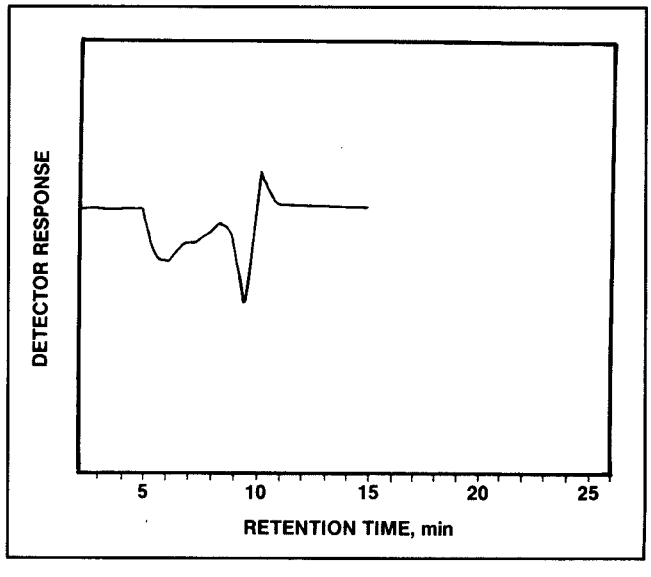
2. Analysis of paraffin and polyethylene waxes



3. Fractionation of a white pitch sample by size exclusion chromatography



4. Fractionation of the contact adhesive formulation by size exclusion chromatography



molecules themselves. When the residues of small sections of wires or felts are extracted with one of these solvents, followed by filtration of the solution and evaporation of the solvent in the filtrate, we obtain white pitch free of entrained fibers, talc, and other materials. This simplifies its analysis.

Gas chromatographic analysis

Gas chromatography analysis of pitch is limited to those components that can be made volatile at temperatures below about 300°C. It is useful for petroleum wax, extractives, and certain low-molecular-weight additives. For those compounds with polar groups such as R-COOH and R-OH (the fatty acids, resin acids, and sterols from the wood extractives, for example), it is necessary to derivatize the components to increase their volatility. A convenient, multipurpose derivative is the trimethylsilyl derivative; the formation of these derivatives is called "trimethylsilylation," or "silylation" for short. Silylation is a common, simple laboratory technique. The trimethylsilyl derivatives are formed as follows:

$$R\text{-}OH + (CH_3)_3\,Si\text{-}X \rightarrow R\text{-}O\text{-}Si\,(CH_3)_3 + HX \qquad (1)$$

Figure 1 shows a wood pitch sample separated on a packed column using ion monitoring (*6*). In this case, palmitic acid elutes at 13.4 min, margaric acid at 14.2 min, C-18 fatty acids at 15.2 min, resin acids from 15.5 min to 19.5 min, and sterols from 23 min to 25 min. In a particular mill, samples of pitch from each species of wood, commercial rosin, and other suitable materials would be analyzed for comparison with contaminants collected at the mill. In a related method, tall oil constituents were methylated with diazomethane prior to analysis by gas chromatography using a capillary column (*7*). Studies that give the composition of pitch from various species of wood are useful if one's mill uses those species; however, there is relatively little information available on capillary gas chromatography of wood pitch. Also, the fact that the composition of extractives changes during pulping and bleaching complicates the picture.

Various types of wax can be analyzed directly after hexane extraction of the white pitch. There are three important types of wax that can be distinguished:

1. Paraffin wax, a series of simple alkanes from C-25 to C-40
2. Wax made from ethylene, which contains even-number chains of simple alkanes
3. Microcrystalline wax, which has a higher molecular weight than paraffin wax and contains branching.

Figure 2 shows chromatograms of paraffin wax and polyethylene wax separated on a capillary column with naphthalene (the first peak after the solvent) as an internal standard.

Because gas chromatography separates the components and the components are identified on the basis of retention time, other constituents of pitch samples do not interfere with the analysis. Both qualitative and quantitative information can be derived, which would be impossible for spectroscopic methods. For example, the distribution of fatty acids in wood pitch (or from defoamers) can be used to characterize the species or source. Microcrystalline wax contains branched aliphatic moieties that can be distinguished from paraffin wax through the technique of gas chromatography. Also, hydrogenated resin acids used in hot-melt adhesives can be distinguished from resin acids from wood pitch or rosin sizing agents.

Some compounds coelute, meaning that they have the same retention time, which precludes gas chromatography as the method of analysis. For these, mass spectrometry can be used to determine the identity and quantity of the individual components. Take, for example, the trimethylsilyl derivatives of the C-18 fatty acids—stearic, oleic, linoleic, and linolenic acids. All of these acids coelute on packed columns, but their trimethylsilyl derivatives can be determined separately by monitoring the ions at 341, 339, 337, and 335 nm, respectively. (On capillary columns, stearic acid can be resolved from the other three components, having a slightly longer retention time.) Analyzing these separated materials by gas chromatography allows us to determine the presence in the contaminant of paraffin wax, certain other waxes, pitch originating from wood extractives (with much information on the actual or likely species of wood), defoamers containing fatty acids, calcium sterate used as an additive, and rosin added in the papermaking process.

Analysis by size exclusion chromatography (SEC)

SEC analysis is the only other convenient method available to actually separate the components of paper mill deposits. SEC columns are generally made of polystyrene cross-linked with various amounts of divinylbenzene to give certain pore sizes and, therefore, to separate mixtures by molecular weight (or molecular size). Large polymers cannot enter the small pores and are eluted first, a unique characteristic of SEC methods. Elution of polymers is monitored by a refractive index detector that detects all materials with approximately the same sensitivity.

A useful approach for some samples, though not used in this study, would be to use chloroform as the eluent (usable above 233 nm in the ultraviolet range), trap the individual peaks using a refractive index detector, and analyze the peaks on a scanning ultraviolet-visible spectrum spectrophotometer. With this approach, we can detect compounds such as polystyrene (260 nm), rosin and rosin derivatives (260–290 nm) (*4*), antioxidants, and stabilizers that absorb above 233 nm in the ultraviolet range.

Since size exclusion chromatography is a nondestructive procedure, the separated components can be collected in a fraction collector and recovered after solvent evaporation. Later, more analyses can be performed on the purified fractions. **Figure 3** shows a particularly complex white pitch residue with a complex molecular weight distribution that could be used to fingerprint the source; in this case, the contaminant is natural rubber *cis*-1,4-polyisoprene, as determined by ^1H NMR analysis.

Figure 4 shows the typical pattern for hot-melt adhesives. There is a resin peak at 10.04 (such as for modified wood resin acids or other compounds), a wax peak (negative refractive index) at 9.28, and a polymer peak, which in this case is a branched aliphatic polydisperse polymer with a molecular weight in the vicinity of 100,000. More often, hot-melt adhesives used in the pulp and paper

industry use ethylene vinyl acetate copolymer as the polymer. Components such as wax and polyethylene copolymers will be separated by this technique to obtain a detailed analysis of each component without cross interference.

General analysis of mill fiber samples

In reality, residue analysis is difficult, and there are unforeseen complications. For example, if these residues go through the bleach plant, we can expect modifications of the chemical structure to complicate their analyses. This was observed for natural rubber (*1*) and polystyrene (*3*). Our work on analysis of spots on paper indicates that wax can be extracted, but polymers cannot. The heat from the dryer section "sets" the polymer (probably as a result of crosslinking reactions) and prevents its extraction by solvents. Similarly, solvent extraction of oven-dried fiber samples gave less extract than that of air-dried fiber samples during a study of the efficacy of secondary fiber cleaning equipment. In general, temperatures above 40°C should be avoided when trying to isolate white pitch deposits.

Solvent extraction of dry fiber samples can be used to help solve residue problems before they occur. For example, the efficiency of secondary fiber cleaners in terms of white pitch removal can be checked by taking samples at appropriate points, drying the sample at room temperature with air circulation (such as in a laboratory hood), extracting the samples with solvent, and analyzing the residue after evaporating the solvent. For dilute fiber samples, rotary evaporation below 40°C is effective for concentrating the sample.

Analysis of actual mill residues

White pitch samples from 15 mills were collected and analyzed by the methods outlined. Stickies from secondary fiber often contain hot-melt adhesives. Hot-melt adhesives contain wax, resin, polymers such as ethylene vinyl acetate (EVA), or mixtures of these components with many possible combinations (*8, 9*). Many of our samples collected from mills showed characteristic proton NMR peaks of ethylene vinyl acetate (*4*), wax by gas chromatography, and a resin identified by gas chromatography or NMR. The relative composition of the EVA ran from about 5% to 75% vinyl acetate groups with different distributions of molecular weight.

Another sample analyzed by ^{1}H NMR spectroscopy was quickly identified as fatty acids with some silicone resin or oil and a small aromatic peak. The aliphatic-silicone functionalities give characteristic peaks in the region between 0.05 ppm and 0.6 ppm (relative to tetramethylsilane). In this case, at 0.07 ppm and 0.55 ppm, gas chromatography analysis showed one major peak corresponding to a C-20 to C-22 fatty acid; the exact identity could have been determined by mass spectrometry or by trying suitable standards, including suspect additives used at the mill.

There were some samples of hydrocarbon polymers. A sample from a mill using secondary fiber showed polyisobutylene with the characteristic ^{1}H NMR peaks at 1.1 ppm and 1.4 ppm, with a small peak at 5.3 ppm indicating residual unsaturation. Two other peaks at 0.89 ppm and 1.3 ppm were due to RCH_2R; since SEC gave one peak corresponding to a molecular weight above 200,000 daltons, the sample was probably an ethylene-isobutylene copolymer. A small amount of polymethyl methacrylate was also present. Another sample from a mill using 100% deinked, bleached secondary fiber for tissue and towels was *cis*-1,4-polyisoprene with the proton NMR spectra reported previously (*1*) with a SEC trace as shown in Fig. 3. A third sample was a polymer of polybutene with wax—a possible hot melt or contact adhesive formulation.

For mills not using secondary fiber, most paper machine deposits come from wood pitch or additives used in the process. In one case, we observed the residue to contain wood pitch, but another residue from the same mill was mostly rosin, presumably used as a sizing agent. Gas chromatography is the most effective tool for detailed analysis of wood pitch, whereas the other methods do not give much useful information on these complex samples. Even in such mills, polymers are sometimes found among the white pitch contaminants, indicating that an internal source of contamination must not be ruled out without proper analysis of the situation.

Experimental procedures

General sample preparation and ^{1}H NMR spectroscopy of the samples were carried out as detailed previously (*1*). Silylation is carried out by reacting 10–15 mg of deposit in a screw-cap vial with a septum with 1 mL of Tri-Sil/BSA in pyridine (Pierce) and heating at 70°C for 2 h. Heptadecanoic acid (1 mg) may be added prior to silylation as an internal standard (*6*). Separation as in Fig. 1 is achieved with a 3% OV-17 column (2 m long with an internal diameter of 2 mm), raising the temperature from 90°C to 300°C at the rate of 10°C/min. Detection was by mass spectrometry. A capillary column was also quite effective for silylated samples (*10*).

Wax analysis was carried out by dissolving 50 mg of residue in 0.5 mL of toluene. Hexane (2 mL with internal standard) was added to precipitate polymer. A portion of the decanted liquid was taken for gas chromatography analysis. Gas chromatography separation, as in Fig. 2, was achieved by a 30-m-wide bore (0.75 mm), glass capillary column with SPB-5 bonded phase (Supelco), using a temperature program of holding at 100°C for 4 min, raising at 16°C/min to 320°C, and holding for 4 min. Hydrogen was used as the carrier gas at 60 cm/min. Detection was by flame ionization.

Size exclusion chromatography was carried out using a 1000-angstrom pore size ultrastyragel column (Waters), with toluene as the eluent at 1.00 mL/min. A refractive index detector was used. Molecular size calibration was carried out with monodisperse polystyrene standards, sucroseoctaacetate, wax, and other materials.□

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