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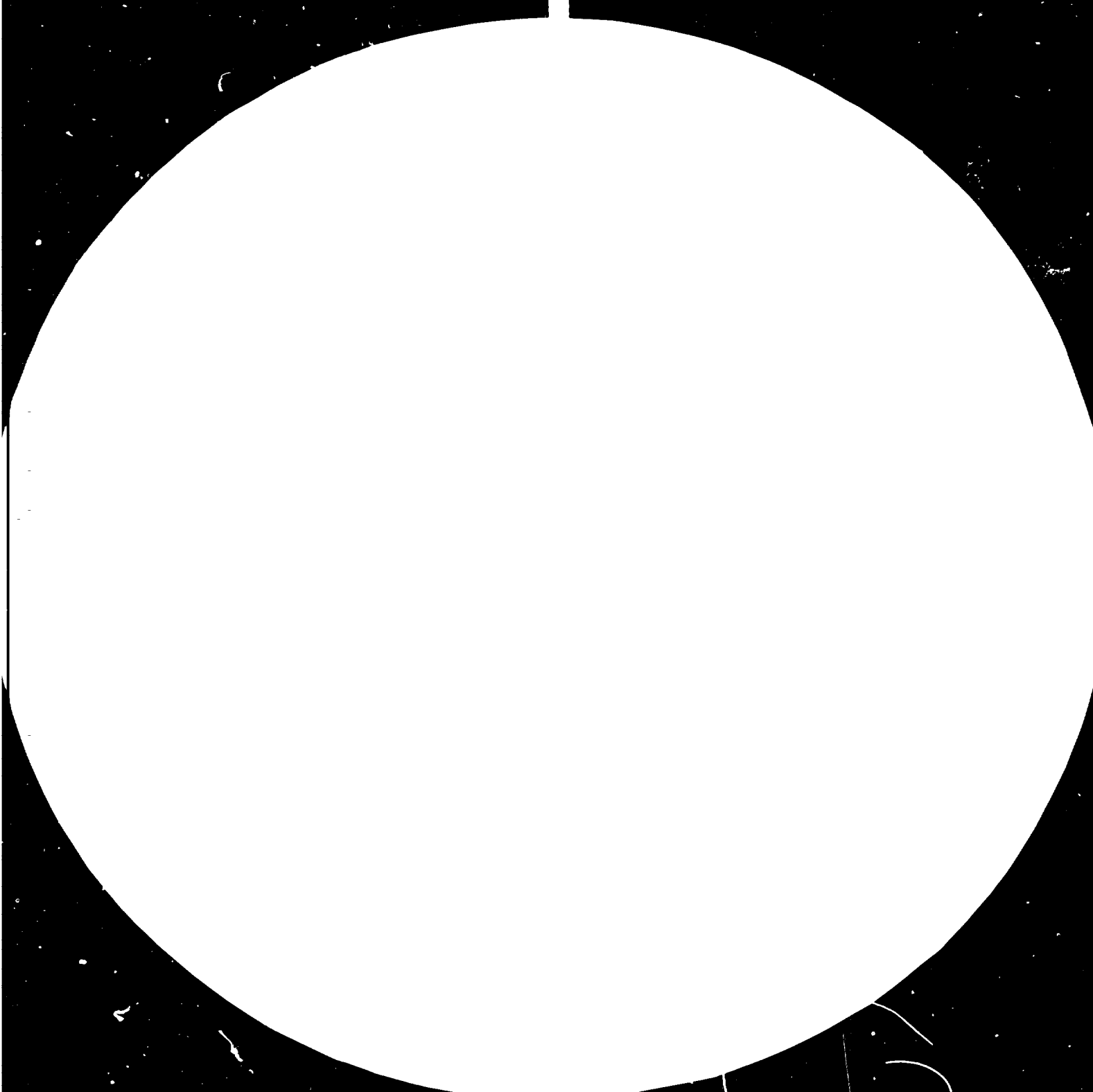
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PITCH CONTROL\*

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Pitch deposits cause the biggest headaches and their costs are painfully obvious, when they occur in paper machines. Deposits on wires and felts can cause production losses for cleaning downtime, and shortened wire and felt life leads to increased downtime for clothing changes. Specks, spots, holes and sheet breaks due to pitch cause loss on downgraded production. There are also hidden costs associated with pitch deposits. Pitch deposits are excellent breeding grounds for anaerobic sulfate-reducing micro-organisms. These microorganisms cause pitting, corrosion, and odor problems. Blinding of wires due to pitch deposits leads to decreased washer efficiency. Organic constituents of pitch will increase defoamer demand.

Pitch deposits are the most common organic deposits in paper systems. Most pitch contains more than just naturally-occurring wood resins. Kraft pitch contains large amounts of fatty and rosin acids, and their corresponding calcium, magnesium and sodium salts. It may also contain natural organics (non-ionic organics) such as sterols (complex alcohols), natural waxes and natural fatty alcohols.

Sulfite pitch is slightly different from kraft in that the sulfite cook is not as severe as the kraft, and the natural fats from the wood may not be fully broken down. Sulfite pitch contains fatty and rosin acid and may also contain glyceride esters (partially broken-down fats), as well as sterols, sterol esters, waxes, fatty alcohols and fatty alcohol esters.

Groundwood pitch is different from kraft and sulfite in that there is no cooking involved to break down the material fats. These natural fats (triglyceride esters) will be the major component of a groundwood pitch deposit along with minor amounts of sterols, esters, waxes and fatty alcohols.

Other organics which can be involved in pitch problems are those which are brought into the system as additives. Rosin size, synthetic sizes, strength additives such as modified starches, urea formaldehyde, melamine formaldehyde and others can present problems if they are not properly retained in the sheet. Most defoamers have some ingredient in their formulations that have deposit-forming tendencies. The hydrocarbon oil carriers used in most wash aids can be found in pitch deposits. Fatty alcohols, fatty amides, glyceride

esters, and other organics are common anti-foam additives. Defoamer fatty acids have a very high potential for causing problems in many systems.

#### MECHANICS OF PITCH DEPOSITION

The organic components of pitch are usually found in the form of crudely dispersed particles (colloidal form) or unstable solutions or emulsions. Changes in operating conditions such as temperature, electrolyte content, or pH can cause agglomeration and precipitation of pitch deposits.

At a temperature above 120°F, resins normally remain well dispersed or solubilized. At lower temperature, the soluble pitch resins tend to precipitate from solution.

Many pitch deposits contain inorganic minerals such as  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . These minerals make up as much as 30% (by weight) of some pitch deposits; they are generally found in the deposits as either carbonate crystals ( $\text{CaCO}_3$ ) or as insoluble mineral soaps of fatty acids.

$\text{CaCO}_3$  crystals tend to act as sites upon which pitch can agglomerate. The crystals have been likened to bricks on which the organic resins act somewhat like mortar to build pitch agglomerates.

Where  $\text{Ca}^{++}$  reacts with resin acids to form molecule soaps, deposits are caused because the soaps tend to both precipitate and destabilize the dispersed unsaponifiables.

Calcium can be introduced into the system at several points:

- \* Calcium inherent in wood and bark
- \*  $\text{CaCO}_3$  carryover from white liquor
- \* Calcium introduced from fresh, hard alkaline process water
- \* Calcium from machine and sewer room white water

Pitch deposits seldom occur when pH is below 6.5 or above 10.5. A pH outside this "dangerous" range inhibits organic pitch compo-

ment deposition, while pH's inside this range greatly favor the deposition of both organic and inorganic pitch components.

At the higher pH, the fatty and rosin acids exist as soluble sodium acid salts that are unlikely to deposit themselves and also act as natural surfactants to help stabilize dispersed unsaponifiables. If the pH of the pulp slurry is lowered into the dangerous range, the acid salts revert to free fatty and rosin acids. These free acids are almost insoluble, and are thus very likely to precipitate or deposit. They are relatively tacky or sticky, and thus have a greater tendency to deposit on surfaces when subjected to shear. Finally, the free acids can not act on surfactants to help stabilize the other crudely dispersed neutral organic pitch components. Thus the pitching potential of the system is greatly increased when pH falls into the dangerous zone.

At much lower pH, many of the organic resins lose most of their tackiness and become more glassy and brittle. These less tacky materials generally have a lower tendency to deposit under shear.

System pH also affects the mechanics of pitch deposition by influencing the way the resins react with calcium. Outside the dangerous pH range, calcium has little effect on the pitch potential of resins. Above pH 10.5, the resins are generally well solubilized and dispersed so that they are not affected by either  $\text{CaCO}_3$  or  $\text{Ca}^{++}$  soaps. Below pH 6.5,  $\text{CaCO}_3$  does not form, and calcium soaps are much less likely to form.

#### OPERATING VARIABLES INFLUENCING PITCH DEPOSITION

Pitch is at first introduced into the paper making system as organic extractables or resinous materials that can occur naturally in wood. The amount of resinous material in wood varies with the species. For instance, softwoods generally have higher levels of resinous materials than do hardwoods. However, hardwood pitch deposits, when they do occur, are often more difficult to treat than softwood deposits because they contain more unsaponifiables (sterols, waxes, fatty alcohols). These unsaponifiables, in neutral

organics are not easily solubilized in the pulping operation or by most chemical treatment.

The nature and quantity of pitch-forming organics in a pulp are also related to the type of pulping process. In kraft pulp organic fats and fatty acids are converted (saponified) to fatty acid salt and glycerine. These fatty acid salts act as natural surfactants that tend to solubilize and disperse many of the other pitch-forming wood organics in the cooking liquor. These solubilized and stabilized organics are more easily removed from the pulp during brown stock washing. However, Kraft mills can have pitch problems in spite of the fact that the alkaline process makes many of the organic resins self-emulsifying. If the concentration of neutral organics in the wood is high, as it is in many hardwoods, there may not be sufficient acid salt present to keep the neutral organics dispersed or in solution. Subsequent pulping operations and chemical treatment of the pulp are apt to modify both the chemical composition and the physical properties of these dispersed pitch resins.

Sulfite pulping, an acid process, is performed at a lower temperature than kraft process and therefore the level of neutral organics present in sulfite pulps is relatively high. Further, the acidic pH of the sulfite process inhibits the conversion of the wood fats to fatty acid salts. - These unsaponified fats exist as free fatty acids, which are almost insoluble in water. Sulfite liquors contain large amounts of pitch-forming resins in an unstable dispersed state, and are carried out throughout the paper making system. Minor changes in the chemical or physical environment of the pulp will cause them to fall out as pitch deposits. The fact that sulfite cooking conditions are less severe than kraft cooks can lead to "mechanically generated" pitch. Many of the wood ray cells containing large volumes of pitch resins may pass through the digestion process relatively undamaged. Later mechanical processing, such as beating and refining, can rupture the walls of these ray cells, releasing free resins that form pitch deposits.

Mechanical pulp (groundwood pulping) is often subject to severe pitch deposition problems. The mechanical action of grinders



releases pitch-forming resins from wood and disperses them in the process water. Since there is no cooking involved in groundwood pulping, none of the wood fats can be broken down to acid salts to act as natural emulsifiers for the neutral organics present in the resin, and again, as in the sulfite process, groundwood pulp is subject to continued release of resins in subsequent mechanical operation.

In addition to natural wood resins, many organic components of common system additives can be found in pitch control. Wash aids and defoamers often contain large amounts of hydrophobic fatty acids and hydrocarbon oil carriers. These hydrophobic components are attracted to the hydrophobic wood organics and can destabilize the natural pitch dispersion.

While wash aids and defoamers are seldom the cause of pitch deposits, they can, when applied incorrectly, increase the pitch-forming potential. The presence of saturated fatty acids, hydrocarbon oils, fatty amides, etc. in the analysis of a pitch deposit is a key indicator that system additives are contributing to the pitch problem.

The nature and quantity of pitch deposits that may form are greatly influenced by the types and quality of pulp washing used. Good pulp washing at brown stock washers can help minimize pitch deposition by removing many of the pitch resins from the pulp before they have a chance to cause problems. If relatively cold shower water is used in washing, it will cause poor drainage and can cause pitch deposition. The ideal temperature for washer shower water is about 140°F. The hardness and alkalinity of the wash water has a great influence on the ability of washers to remove pitchy resin from the pulp. High  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  may cause formation of calcium and magnesium salt. The "M" Alkalinity (carbonate and bicarbonate alkalinity) of the wash water can influence the degree of  $\text{CaCO}_3$  crystal formation.

In sulfite mills, the variables involved in pulp washing have less influence on pitch deposition at the washers in sulfite mills than in kraft mills. Low temperature wash water is unlikely to

be a cause of pitch deposits because sulfite resins are not soluble. Likewise, the hardness and alkalinity of the wash water have less effect on deposit formation in sulfite mills because of the acidic pH's in the system.

Pulp bleaching can affect the quantity and nature of pitch deposits because bleaching, like washing, provides an opportunity to remove resinous material from the pulp. The caustic extraction stage presents the greatest opportunity for resin removal in the bleach plant. The hot alkaline condition in kraft mills (temperature above 200°F, pH above 11) allow the resin acids to exist as soluble fatty and resin acid salt. This increased solubility allows for relatively easy wash-out of organics from the pulp. Since caustic extraction filtrate is sewerred in many mills, the stage is excellent for eliminating many pitch components from the paper making system. Despite the fact that extraction is the best bleaching stage for pitch removal, pitch deposits are often seen at the extraction washers. These deposits are almost always the result of excess  $\text{CaCO}_3$  entering with the shower water and acting as pitch.

Hypochlorite bleaching is notorious for its ability to create pitch problems in a bleach plant. The moderate temperature and pH's typical of this stage (100°F, pH = 9) are in the middle of the dangerous pitch-forming range. Calcium hypochlorite bleaching tendency to form  $\text{CaCO}_3$  and insoluble calcium soap can contribute to agglomeration of pitch deposit.

#### COMMON METHODS OF CONTROLLING PITCH

##### 1. Pitch Absorbent

Talc is rather unusual material because the large flat surfaces of its plate-like structure are hydrophobic, while the edges are hydrophyllic. The hydrophobic pitch particles are attracted to and absorbed by the hydrophobic talc surfaces. The exposed hydrophyllic edges of the talc stabilize the emulsified particles in solution. These supposedly innocuous particles are then carried through the paper making system with the pulp fibers and finally

out of the system with the finished sheet. Talc when it works does a fair job of controlling pitch deposits. However, required dosages are high and many mills have found the product difficult to handle. Further, claims by talc suppliers that 80-100% of the talc entering the system leaves the system with the final sheet seemed to be inflated. Many mills have also found out that they experienced severe deposits of talc/pitch agglomerates. These deposits occur when the recirculating water becomes saturated with talc. Treated clays have been used for pitch control in the same manner as talc. Again, results with clay have been mixed.

## 2. Surfactant

A surfactant is a molecule having both hydrophobic and hydrophilic portions in its structure. This coating can stabilize when sufficient surfactant has been added to a system to fully stabilize it. A critical micelle concentration must be present. Anything less than this will lead to agglomeration of pitch particles, decreasing emulsion stability and increasing the pitch deposition potential. It is often not economically feasible to add enough surfactant to the paper system to reach a critical micelle concentration, and thus many weak surfactants have failed as pitch control agents.

## 3. Chelating Agents

Chelating agents tie up soluble cations through the formation of complex ions. Polyvalent cations such as calcium and magnesium or aluminum can be removed from the system in this manner. When treated this way, these ions have lost their damaging effects through insoluble salt formation and surface charge destabilization. Several problems with chelating agents make them all impractical to use. Stoichiometric amounts are required; For instance, if 100 ppm of calcium were to be chelated, about 300-400 ppm of EDTA would be required. Further, chelating agents are not specific for individual ions. Finally, a chelating agent is useful in controlling pitch only if the mineral ion being tied up is the basic cause of the pitch deposit. Calcium or magnesium may be a significant portion of the volume of a particular pitch de-

posit, but it may not be necessarily the cause of the pitch deposit.

#### 4. Calcium Stabilizers

Calcium stabilizers or calcium modifiers work by adsorbing on microcrystals of  $\text{CaCO}_3$  and causing the crystals to distort. The distorted  $\text{CaCO}_3$  crystal can not grow to its normal size and thus has a tendency to redissolve, releasing the crystal modifier and allowing it to do its job all over again on another microcrystal of  $\text{CaCO}_3$ . Crystal modifiers are usually applied to alkaline stages of pulping and bleaching to prevent the formation of  $\text{CaCO}_3$  precipitate. However, when alkalinity reaches a certain level, crystal modifiers can no longer prevent gross precipitation. When applied properly, crystal modifiers can often produce excellent results in eliminating those pitch deposits caused by excess  $\text{CaCO}_3$ , or in reducing the volume of those deposits containing  $\text{CaCO}_3$  but not directly caused by  $\text{CaCO}_3$ .

#### 5. Dispersants

Dispersants work by keeping pitch particles from agglomerating through increasing the net surface charge and electrical repulsion of the pitch particles. However, dispersants can fail in pitch control if the pitch resins are subjected to concentrations of  $\text{CaCO}_3$  large enough to overcome the effect of dispersants. In such a case, the precipitating  $\text{CaCO}_3$  crystals overcome the dispersancy effects, and pull the resins into deposits. A pitch control program using only dispersants on the paper machine will eventually prove ineffective unless a good retention program is used to counteract the dispersancy and attach the pitch resin to the fiber sheet leaving the system. Dispersants added to the system build up in the recirculating water and lead to eventual failure.

#### 5. Alumina

Combination of alum and sodium aluminate is used to control deposits by attaching pitch particles to the fiber. The major drawback to alumina is its potential for easy abuse. Too much alumina

can drive the paper machine pH so low that pitch particles will float on top of the stock. This can cause loss on downgraded production because the pitch particles will fill the felts. Alumina residuals in the paper machine white water sometimes used in washers or bleach plant showers can have a detrimental effect on pitch control.

The Alumina will reduce the amount of pitch that can be washed out of the system at these points by attaching the pitch to the fiber. This leads to a higher level of pitch going with the fiber, and this additional pitch load may cause trouble later at the paper machine.

#### 7 Retention Aids

Polymeric retention aids are the most effective means of attaching resins to fiber. They improve retention not only of fibers in the sheet, but also of pitch in the fiber.

Polymeric retention aids do have limitations. If no dispersant is present in the system, a polymer will cause pitch resins to agglomerate.

#### PULP AND PAPER DEPOSIT ANALYSIS

The proper use of a deposit analysis can be very helpful in defining the cause of a problem in a particular application. A typical pulp and paper deposit analysis is broken down into four basic sections: a loss on drying at 105°C, loss at 300°C, analysis of the 800°C ash, and laboratory comments on other tests.

Analytical keys useful for laboratory analysis are:

1. High loss at 105°C

A sample which has a high loss at 105°C could indicate some of the following:

- \* Water and moisture
- \* Slime and microorganisms
- \* Chemical slime (alumina gel)
- \* Synthetic polymer gel
- \* Volatile organic solvents

2. Items which would be indicated by a high loss at 300°C:

- \* Fiber (paper in felt)
- \* Slivers and shives
- \* Starch
- \* Plastics
- \* Retention acids
- \* Rubber and latex
- \* Adhesives, glues, hot melts
- \* Lignin residues
- \* Carbon and soot
- \* Wet strength resins
- \* String, twine, cloth
- \* Oxalate deposits
- \* Acid ether extractable organics

3. Calculated combinations for inorganic materials that are found in the deposit. Proper ratios of elements will give information to account for the different types of filler materials and mineral deposits.

4. Extractable organics

The common constituents of acid ether extractable organics are as follows:

Pitch

1. Fatty acids
2. Rosin acids
3. Neutral acids
4. Fatty alcohols
5. Natural waxes
6. Sterols

Antifoams or wash aid constituents

1. Fatty acid and alcohols
2. Hydrocarbon carriers
3. Surface active materials
4. Silicon oil
5. Fatty amides

Waste paper constituents

1. Oil and grease
2. Wax
3. Asphalt
4. Synthetic latexes, coatings, rubber
5. Adhesives
6. Dyes

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