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# A REVIEW OF KRAFT PULP DERESINATION AND PITCH PROBLEMS

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# ABSTRACT

Knowledge on the oleophilic, resinous, extractives of wood with their relevance to pulping, paper making and paper properties is summarized.

The main physical and chemical features of the two types of wood resin - the one in resin canals and the one in parenchymatous cells, mainly within the ravs are to the above mentioned theme. reviewed in respect These also analyzed with special features are reference to alkaline deresination and pitch problems.

Difficulties in washing out resin after kraft pulping due to the effects of ionic strength and Ca-ions are discussed as well as deresination in bleaching operations.

Present pitch problems in paper making and control are reviewed. Effects of wood resin measures on paper properties e.g. deposits in laser printers and smell or taste in board for liquid containers are discussed.

#### INTRODUCTION

Pitch troubles, which some decades ago were mainly associated with sulphite pulp, today also arise in kraft mills and with kraft pulps. In Scandinavia, this is of a considered as a combined effect number of factors. shorter wood storage, an increased use of spruce e.g. with Pine (Pinus (Picea abies) compared sylvestris) in softwood kraft and the addition of minor amounts of birch (Betula verrucosa). Further, the process water systems

have become more closed both within the pulp mill and the bleaching plant and, in an integrated mill, with respect to the paper mill. The development of wider and faster paper machines has also increased the sensitivity to breaks and in both a technical adhesion problems and economical The more frequent use of high yield pulps and the sense. development of new paper grades and paper products have occasionally generated new forms of pitch troubles. There is thus today a very real interest in wood resin and its reactions during pulping, bleaching and papermaking.

This paper reviews present knowledge of wood resin, pulp deresination and pitch problems including pitch control. In particular, it presents the results of more recent studies on kraft pulp deresination.

# RESIN IN WOOD

#### Definitions

The sapwood and heartwood of a11 softwood and hardwood species contain a minor amount of low molecular weight, organic material of an oleophilic, mainly non-polar nature and of low solubility in water. This material is commonly referred to as wood resin. Important wood resin components are free resin and fatty acids, esters of fatty and other alcoholic compounds, acids with glycerol e.g. sterols, sterols and also free fatty alcohols and triterpenes. Within the sapwood these components occur in resin canals, resin pockets and parenchyma cells. Also present, but usually concentrated within the heartwood, are phenolic substances, some of which are significantly more soluble in water than the above mentioned substances. Tn this discussion, phenolic substances are not included in the term wood resin. Fig. 1 gives some examples of common wood resin components.

In laboratory work, wood resin is often defined by the choice of solvent - with a particular dielectric constant - and the procedure used for the extraction. The drying procedure determines the loss of volatile resin components, such as the terpenes, which make up about 15-20% of the wood resin in pines. The term "pitch" is sometimes used in this summary synonymously with wood resin, especially when discussing deposits and pulp and paper production problems.



Fig 1-Example of wood resin components.

### Canal Resin and Parenchyma Resin

Wood resin can be classified according to its occurrence There are fundamental differences in wood. between canal resin and parenchyma resin and between sapwood and heartwood resin with regard to both physical accessibility and chemical composition.

Resin canals are tubular intercellular spacings which occur both vertically and horizontally as a communicating system in the wood of some conifers. They are largest and most frequent in pine (Pinus) but occur also in the genera larch (Larix) Douglas spruce (Picea), and fir In Tsuga, Abies and Sequoia species, resin (Pseudotsuga). canals are normally absent in wood, but they may be produced by injury to the tree (1,2). Similar canals are the gum canals in some tropical hardwoods, e.g. the gum canals in the bark of Hevea brasiliensis.

Most of the parenchyma cells occur in the rays but a amount, easily seen in hardwoods, do occur as minor The parenchyma cells make up vertical rows in the wood. the living cells of the sapwood. The resin components of parenchyma cells are therefore apparently, to some extent, involved in the metabolism of the living wood, whereas only as wound secretion material to canal resin serves against fungal attack. Thus the chemical protect composition of the canal resin in conifers can be expected to differ from that of parenchyma resin. An experimental comparison on Picea abies (3) indicates that of the total resin, the canals contain most of the free fatty and resin acids with resin acids predominant and also some esters, while the parenchyma resin contains most of the glycerol esters, the unsaponifiable components and the waxes. Thus. the sterols, which are believed to be biologically active and which belong to the unsaponifiable resin components, although partly esterified, are found within the parenchyma cells. In agreement herewith, the resin in the sapwood of northern hardwoods, which only occurs as parenchyma resin, contains only negligible amounts of free fatty acids and no resin acids. The canal resin or oleoresin of softwoods also contains volatile turpentine components, which in pine constitutes about 25% of the weight of the oleoresin (1).

There are obvious differences between the parenchyma resin and the canal resin with respect to their behaviour pulping processes, in pulp deresination and in pitch in control (4). After acid and alkaline pulping or after a mechanical defibration process, the canal resin is physically exposed. Even if the resin is still undissolved, its surface is easily accessible for chemical This may lead to pitch troubles but also reactions. The parenchyma resin, facilitates deresination. on the other hand, is protected by hydrophilic cell walls. provided these walls are not mechanically or chemically damaged in pulping or in a subsequent mechanical and/or chemical treatment. Thus the alkaline dissolution of resin from undamaged parenchyma cells requires the diffusion of dissolved resin material out of these cells.

The alkaline dissolution of canal resin is also facilitated by the fact that it contains most of the free resin and fatty acids. The soap anions thus formed make possible the dispersion and the solubilization of those resin components, which are per se alkali insoluble. Hence, a pulp deresination of parenchyma resin is facilitated if a large proportion of the total pulpwood resin is originated from the canals. See also under "Wood Resin During Kraft Pulping".

Of importance for deresination is also the structure of the ray parenchyma pits, their size, the proportion of the cell wall area which they occupy and their cell wall thickness. In chemical deresination and delignification of these cells, the reagents and the reaction products must diffuse, in and out of the parenchyma cell, via the pits with their remnants of primary wall. The relative area and the distribution of the pits in the cell walls affect the resistance of the parenchyma cells to mechanical damage and thereby affect the release of the resin. The pronounced difference in this respect, between Pinus, with a mean relative pit area of 50% of the ray parenchyma cell area (5) and Picea, where the pit area is only 5% (6), is thought to be one of the reasons for the slower chemical de-resination of sprucewood pulp.

In the sapwood of northern hardwoods all the resin occurs in parenchyma cells. These parenchyma cells make up a considerable part of the hardwood volume. The completely parenchymatous rays in hardwoods extend from 10% of the species to 40% wood volume in the Betula for certain In addition, some hardwoods Quercus species. also contain a significant amount of various types of vertical rows of parenchyma cells (2). The parenchyma cells also have а higher lignin content than the tracheids which. in combination with their resinous material, makes them more resistant to the pulping reactions (7). As an example, the wood of Picea abies, holds 3% by weight of ray parenchyma, with a lignin content of 43%, compared with a lignin content of 26% in the tracheids (8).

# Heartwood Resin

In heartwood, not only the tracheids, but also the parenchyma cells are dead. In some species, before dying, these cells greatly increase their production of resin and/or phenolic compounds which in softwoods then become

Thus, distributed throughout the wood structure. in coniferous heartwood, wood resin also exists in normal tracheids and contributes to the clogging of the bordered pits. The increase in resin content in heartwood compared with sapwood is about 100% for several Pinus species and 5% in some Picea and Abies species. can amount to about This imparts an increased microbiological resistance to the heartwood, which otherwise because of its lower moisture compared sapwood, would be more easily content to extractives of pines also include attacked. The heartwood special fungicide phenolic substances such as pinosylvin. other hand, for Picea abies the resin content in 0n the heartwood was found to be somewhat lower than that in the without any large differences in the qualitative sapwood composition (9).



Fig 2—Formation of heartwood in hardwoods.

To the left: Secretion of resin from parenchyma cells into vessels.

To the right: Thylosis formation, wherein the walls of the parenchyma cells expand and clog the vessels.

From M. M. Chattaway (10).

Hardwoods produce heartwood in two different ways (10). Either by clogging the vessels with thyloses or by resin secretion into the vessels. Thyloses are formed bv expansion of the ray parenchyma cell walls to block the vessels physically. An example is shown in Fig.2. Hardwoods, with ray parenchyma pits greater than about 6 microns in diameter, usually produce thyloses, whereas those with smaller parenchyma pits, secrete resin into such as Betula verrucosa, a wood belonging vessels. Birch the latter somewhat complicated to type, with rav pits of about 4 microns in diameter, is rather parenchyma resistant to chemical pulp deresination. On the other hand, tremula and beech, Fagus sylvatica, aspen, Populus both with thylosis formation and ray parenchyma pit sizes of 8-10 microns and 17-20 microns respectively are fairly accessible to chemical pulp deresination.

#### Chemical Composition and Physical Aspects

The content of wood resin and its composition varies significantly between different wood species. Some examples are given in Table 1 (11,12). There is also a variation both between individual trees of the same species. depending on the age of the tree, genetic factors and growth conditions e.g. climatologic and geographic factors, and within a tree between root, stock and branches. Generally a more slowly growing individual has a higher resin content (13).

Northern hardwood species such as birch and aspen usually have a larger resin content than southern hardwoods, which to some extent, store starch instead of fatty material in their parenchyma cells (11). the Both fatty material, the glycerides, and the starch are partly considered as a reserve food supply for the living tree, Consequently, in most wood species the amount the sapwood. of glycerides in the heartwood is very low.

	Pinus sylvestris	Picea abies	Betula verrucosa
(% of dry wood)	2.5 - 4.8	1.0 - 2.0	1.1 - 3.6
component (% of ether extract)			
(% OI ether extract)			
Neutral substances	48	63	91
unsaponifiables fatty acids, esterified	8	20	32
	40	43	58
Fatty acids, free	18	10	6
Resin acids, free	34	25	0

<sup>1)</sup>includes glycerol esters, sterol esters, free alcohols etc.

Table 1. Content of wood resin (11) and its composition (12) for some Scandinavian wood species

The chemical composition of wood resin has been investigated for a great number of species. As an example the composition of heartwood and sapwood resin in Picea abies is given in table 2 (9). Fig.3 shows the radial variation of wood resin composition in Pinus sylvestris (14).

The acids in wood resin are long chain fatty aliphatic monocarboxyl acids with a carbon chain length from 10 to 24 carbon atoms. Most abundant are the unsaturated acids such as oleic acid with one double bond (Cl8-1), linolic acid with two double bonds (Cl8-2) and pinolenic acid, an isomer of linolic acid with three double bonds (C18-3). In Table 2 these three acids make up 80% of the triglyceride fatty acids. The saturated acids. palmitic acid (C-16) and behenic acid (C-22) are reported from 14 to 24% of the fatty acids to constitute in Scandinavian birches (15).

The chemical composition of the resin retained in the pulp varies with the pulping process and has an important influence not only on pulp deresination but also on pitch problems, through such physical properties as resin viscosity, ionic groups for electrical charge and means to stabilize by electrical charge.

#### Resin in Bark

Resin in bark has been studied less than that in in Scandinavia wood. Of special importance is the verv high triterpene content of birch bark. In the outer bark of birch (Betula alba, B. platyphylla, B. verrucosa) 25 to 35% of betulinol has been found. The average resin content in birch bark is 10 - 12%. Betulinol (cf. Fig.1) is crystalline, with a melting point at about 260°C, and alkali-insoluble and therefore very difficult to remove by alkaline pulping. Since birch, especially in wintertime in a cold climate, is hard to debark, substantial amounts of betulinol enter the pulp mill and this substance is often found to be a dominant component of pitch deposits.

Component	Sapwood	Heartwood
Fatty Acids	6.77	3.29
triglyceride-	5.54	1.67
mono- and diglyceride-	0.57	0.80
other esterified	0.66	0.53
free	+ ''	0.29
Resin Acids	1.21	0.95
Sterols	1.00	0.94
free	0.20	0.29
esterified	0.80	0.65
Triterpene Alcohols	0.13	0.13
free	+	0.02
esterified	0.13	0.11
Diterpene Alcohols	0.32	0.22
free	0.26	0.22
esterified	0.06	+
Diterpene aldehydes	0.08	0.07
Alkyl Ferulates	0.12	0.19
Glyceryl Residues <sup>2)</sup>	0.36	0.22
Total, mg/g dry wood	10.0	6.0

1) + = less than 0.01 mg/g wood

2) Approximated calculation assuming equal amounts of mono- and diglycerides and a mean fatty acid MW = 280

Table 2. Petroleumether extractives in mg/g dry wood in Picea abies. Samples from one tree. From Ekman (9).



**Fig 3**—Total extract and amount of some resin components as a function of the number of annual rings from the centre. Data for Pinus sylvestris according to Assarsson (14).

#### WOOD SEASONING

T+ is well known that the seasoning of wood reduces pitch troubles, especially in sulphite and mechanical pulps. However, since seasoning is economically unfavourable, the general trend today is towards а just sufficient raw material buffer. A special system, for seasoning chips with moist air at  $50 - 60^{\circ}$ C for one or a few days to accelerate wood resin seasoning reactions, has been introduced (16).For sulphite pulp, а special mechanical treatment of the pulp, followed by alkaline washing (17), has been developed in order to reduce the importance of wood seasoning.

The reactions of resin during wood seasoning have been studied for e.g. black spruce (Picea mariana), jack pine (Pinus banksiana) and trembling aspen (Populus tremuloides) (<u>18</u>), and for Norwegian spruce (Picea abies) (<u>19</u>).

The results show that 1) the total amount of wood resin is decreased, partly due to oxidative and metabolic reactions i.e. a continuation of life functions in the still living parenchyma cells. This decrease is most pronounced during the first month when the decrease in total fatty acids in piled chips can amount to 50% (19). Volatile components such as terpenes are partly lost . 2) Fats and waxes are hydrolysed. The decrease in bound fatty acids in the same period was about 70%. Part of this decrease might also be due to autoxidation and microbiological of attack. Α total disappearance triglycerids in pine, spruce and aspen sapwood after 2 months storage in the form of 2cm thick discs, has been reported (18). 3) The autoxidation of unsaturated compounds introduces more hydrophilic groups, thereby changing the resin solubility both in water and in organic solvents. The oxidation can proceed all the way to the end products CO<sub>2</sub> and H<sub>2</sub>O.

form When wood is stored in the of logs and when stored in especially they are water the above-mentioned reactions are strongly suppressed by the lack of oxygen and by low temperature. In a chip pile the

temperature is substantially raised by the heat of reaction from the oxidation processes and depends on pile size and ventilation.

The decrease in total wood resin content and the hydrolysis of fats and especially of waxes facilitates the deresination, especially for sulphite and mechanical pulp but also for kraft pulp. For pine kraft there is however such positive effect on the pulp deresination by chip no storage (20), since pine resin is initially low in waxes and other neutral components. On the other hand, the decrease in tall oil yield is substantial. The general loss in total wood weight during storage must of course also be considered when calculations are made.

# WOOD RESIN DURING KRAFT PULPING

#### Solution Properties of Resin and Fatty Acids

Resin and fatty acids are examples of amphiphilic compounds often called surfactants. They have а hydrophilic. polar carboxy1 group and а hvdrophobic nonpolar hydrocarbon moiety. Comprehensive reviews of the association behaviour and micelle formation of amphiphilic compounds are given in the literature (21,22).

During kraft pulping, resin and fatty acids are converted sodium soap anions, with high water to solubility. Fig.4, the As shown in solubility in pure both sodium oleate is about 18% for water and sodium At this high concentration, the soaps are abietate (23). dissolved in the form of micelles, e.g. spherical aggregates built up by a large number of soap anions, arranged so that the hydrophobic carbon chains are located inside the sphere while the hydrophilic carboxyl groups form the surface of the sphere in contact with the water low concentrations, the soaps are dissolved as phase. At monomers and maybe dimers. the concentration at which the association of soap anions to micelles starts, is called the CMC (Critical Micelle Concentration) and is specific At the CMC, the solubility for each soap or soap mixture. of the soap is drastically increased. The CMC for sodium oleate is about 1 mmole/1 (24) and for mixed resin acids,

e.g. "wood rosin", about 12 mmole/1 ( $\underline{25}$ ). Mixtures of different fatty acids and/or resin acids form mixed micelles. In mixtures of sodium oleate and sodium abietate the highest solubility was achieved at a molar ratio of 1:1 of oleate to abietate ( $\underline{23}$ ).

The solubilities of the resin and fatty acids are strongly affected by the ionic strength of the solution, as shown in Figure. 4. Of interest, with respect to kraft pulping, is the very low solubility of the sodium soaps at high ionic strength. At  $60^{\circ}$ C, the solubility of a mixture of sodium oleate and abietate falls rapidly at a sodium concentration of about 0.8 mole/1.



**Fig 4**—The influence of NaC1 concentration on the solubility of sodium abietate, NaAb, sodium oleate, NaO1 and NaAb/NaO1 (molar ratio 1:1) at 60°C. From Palonen, Stenius and Ström (23).

Of importance for the deresination of kraft pulp is also the capability of the soap micelles to solubilize otherwise water-insoluble hydrophobic substances inside the micelles. This is the principle of all washing. One the normally used addition of tall oil, e.g. a example is mixture of fatty and resin acids, to the digester during birch kraft pulping. This addition results in a lower resin content in the birch pulp after washing. The hirch wood resin holds a high amount of neutral components with a low solubility per se in the cooking liquor. The amount of naturally formed from soaps the birch resin. is insufficient to solubilize these components.

sodium soaps, calcium soaps are very In contrast to insoluble in water and often coagulate to big aggregates. As an example the solubility product Ks, in pure water of only  $10^{-17.4}$  and of calcium oleate calcium palmitate is 10-15.4 kraft pulping, the calcium ions also (26). During take part in several other equilibrium reactions e.g. with carbonate ions and with the ion exchanging groups of the This is kraft fiber or the dissolved lignin. discussed later.

#### Kraft Pulping

During kraft pulping, the free fatty and resin acids are dissolved as soaps. Further, the glycerol esters as well as some of the waxes are hydrolysed to form anions and respectively glycerol and other alcohols (e.g. sterols). Α complete hydrolysis of the glycerol esters requires а content certain residual alkali in the cooking liquor (27). Some of the waxes are however very resistant to hydrolysis and remain unchanged but can be solubilized alkali-insoluble together with other compounds e.g. hydrocarbons, sterols, fatty alcohols etc.

When the pulp leaves the digester, the combination of prevailing temperature, normally about  $90^{\circ}$ C, and ionic strength, normally about 1.2M, restrict the solubility of the fatty and resin acid soaps. A well-known phenomenon, is the accumulation of wood resin, as a separate phase, in the first stage of a filter washing line. When wood resin, being insoluble in the black liquor, first follows the pulp



**Fig 5**—Dissolved wood resin (p.ether extract) in black liquor from kraft pine and kraft spruce cooking as a function of the black liquor temperature. The dashed horizontal lines indicate the maximum possible concentration of wood resin in the black liquor based on wood extration. Data for freshly felled, unseasoned trees.



**Fig 6**—Wood resin (p.ether extract) in kraft pulp after laboratory washing as a function of the ionic strength of the washing liquor. Residual alkali after washing with pure water is 19 kg Na $_{2}^{2}O_{4}^{\prime}$  ton in the pine pulp and 12 kg/ton for the spruce pulp.

to the second washing stage, where - as a consequence of the lower ionic strength - it is dissolved and transported back to the first stage by the counter-current washing liquor. Here it is re-precipitated and so on. This effect is most pronounced in the pulping of wood species with a high resin content such as pines. A solution, sometimes used, is the withdrawal of the soap layer formed to the tall oil system.

following experiment indicates, Our that this situation in the beginning of the washing line, is not equivalent to that during cooking (28). At the end of a kraft cook, at 170°C and during the cooling down, samples of the black liquor were withdrawn. The solubility of the resin components in the black liquor was found to decrease significantly with decreasing temperature as shown in Fig. 5. Data refer to laboratory cooking of fresh pine and spruce wood to final kappa-numbers of 30 and 32 respectively. Efficient alkali was 20%, sulfidity 25% and wood:water the ratio 1:4. The broken lines in the figure indicate the maximum possible concentration of wood resin in the black liquor based on wood extraction. Resin analyses in black liquor were made according to Akerlund and Frejman (29). Apparently a major part of the resin components are dissolved at the digesting temperature in spite of the high ionic strength. Accordingly, a first above 100°C, such as in washing is most efficient the Hi-Heat washing zone of a continuous digester or in a pressurized diffusion washer.

#### Kraft Pulp Washing

In the filter washing line, the most important parameter effecting wood resin dissolution, is the ionic strength within the liquor phase. This effect is easilv demonstrated by laboratory washing with liquor containing added NaCl, as in Fig. 6 (28). A high ionic strength decreased the solubility of the fatty and resin acid soaps which are therefore adsorbed to the fibers.

The effect is more pronounced for the pine pulp with the higher resin content of pine wood. Figure 6 also illustrates that spruce pulp, after normal washing with pure water, holds more wood resin than a pine pulp due to the less favourable chemical composition of its resin and the much smaller pores in its parenchyma cells.

decrease in solubility at a high ionic Although the strength is very temperature dependent in the concentrated black liquor, the effect of temperature after dilution in laboratory washing, appears to be much less. Onlv а slightly positive washing effect was noted between  $20^{\circ}$  and 90°C (28). The time of contact between the fibers and the washing liquor at 60°C had little effect, the washing efficiency being the same after 2 min as after 24 h. This means that in washing the diffusion of wood resin out of fibers is not a limiting factor. This could be the interpreted as meaning that only a minor part of the resin is still enclosed in the parenchyma cells. This enclosed resin cannot of course easily be washed away. The resin content. of a well washed unbleached kraft pulp. is normally about 0.1% for pine, 0.3 - 0.4% for spruce and up to 0.4 - 0.6% for fresh birch wood.

The chemical composition of the wood resin in a kraft pulp, before and after laboratory washing, has been determined and is exemplified in Table 3 (28). It would also be of great value to know in which form this residual resin is retained in the washed pulp. Most of the resin probably consists of calcium soaps of fatty acids and of neutral substances partly enclosed in the parenchyma Only a minor amount of resin, following the pulp to cells. paper mill, is dissolved in the water phase.

		from digester		after washing	
	in wood	in black liguor	in fibers	resin retai in pulp	ned
Component	g/kg pulp	g/kg pulp	g/kg pulp <sup>1)</sup>	g/kg pulp	%
fatty acids		4.0	4.5	0.9	9
resin acids		2.8	1.7	0.1	2
sterols		3.2	0.3	0.9	25
undetermined		4.0+(9.0) <sup>2)</sup>	0.7+(1.0) <sup>2)</sup>	0.6	
Total p.eth- er extract	(24)	14	8	2.5	11

1) excluding resin dissolved in retained liquor

 free sulphur formed on acidification of liquor and following these extractives

Table 3. The chemical composition of the petroleum ether extractfrom a spruce kraft pulp before and after laboratorywashing

Fig. 7 illustrates how the fines fraction from a birch kraft pulp, mainly consisting of parenchyma cells, holds over 60 % of the pulp resin (15).

Deposits in the brownstock washing and screening departments are usually built up of calcium soaps of fatty acids and calcium carbonate (30). When birch wood is used, betulinol from birch bark is often a major component.

a slightly acid washing water in the last The of use washer, is said to decrease the pitch deposition in the following pulp operation (31). A mild acidification of the pulp breaks the calcium soaps and reduces the calcium content of the pulp very significantly. However, below a 7, the fatty acids then are present in their ъΗ of about acidic, unionized form, having a very low water solubility.



**Fig 7**—The distribution of fibers by size and the contents of extractives of the different fractions of birch sulphate pulp. From Paasonen (15).

Therefore it is important that most of the sodium soaps are washed away before such an acidic washing stage, in order not to be re-precipitated as resin on the fibers.

Wood resin enclosed in parenchyma cells can be activated by mechanical treatment, released and e.g. in alkaline refining. Thereafter additional washing has а Since the major part of positive effect. this resin consists of neutral components, the addition of a dispersent e.g. nonionics in such washing may be necessary.

Naturally, one of the important factors for efficient deresination, is a good function of the pulp washing equipment producing a high solids content and possibly some mechanical action on the parenchyma cells.

#### Calcium - An Important Parameter

Calcium soaps often constitute a major part of pitch deposits in the washing and screening departments. T-+ seems likely that part of the resin in the pulp enters the in the form of calcium soaps, especially of Calcium soaps of resin acids are generally paper mill in fatty acids. pitch deposits even though they are also absent in such water-insoluble. 0ur insufficient knowledge of the formation of possibilities these soaps and the of their behaviour summarized influencing are below. Magnesium and barium soaps behave in a similar way but are present in much smaller concentrations.

wood, which contains about 600 to 800 mg Usually the calcium per kg dry wood, is the main calcium source in kraft pulping. The white liquor often adds only about 50mg/kg wood, but up to the same amount the wood with as inadequate white liquor clarification. The bark contains five to ten times as much calcium as wood, e.g. 3000 to 5000 mg/kg.

It is not known in which form calcium exists in the wood. In the cross section of a pine tree, the calcium and likewise the magnesium and manganese contents are reported to be highest in the cambium  $(\underline{32})$ . They are also somewhat higher in the heartwood than in the sapwood. The calcium content is slightly higher in the parenchyma cells and in the resin canals (32).

During kraft pulping and washing, calcium ions take part in several equilibrium reactions. Calcium carbonate precipitates during cooking. Most of the carbonate enters with the white liquor but some carbonate ions are also during formed cooking (33). The calcium concentration in the cooking liquor increases during cooking due to dissolution of calcium from the wood. After reaching a maximum of about 60ppm. the calcium concentration again decreases probably due to calcium carbonate precipitation (33).

Calcium mainly follows the pulp - not the black liquor - as do also magnesium and barium (34). The calcium ions can be bound to the ion exchanging groups of the kraft fiber. As an example, Fig.8 shows the amount of calcium pulp as a function of the kappa number and bound to kraft unbleached kraft pulp the calcium ρH. For an content normally increases slightly during pulp washing (30).The calcium content after washing is about 1.5 - 2.0 kg/ton (=38-50 moles). If this calcium content is compared with a normal wood resin content - that is after washing;





about 1-3 kg/ton (about 3.5-10.5 moles) of which only a part is resin and fatty acids - it is clear that most of the calcium is transported in other forms than as calcium soaps. However, this does not exclude that most of the fatty acids can be transported as calcium soaps.

the stream from the digester to the paper mill, Tn parameters affecting the discussed equilibrium reactions change continuously, washing e.g. liquor pH. ionic temperature, the concentrations of carbonate, of strength, sulphate lignins, of resin components and of dissolved calcium. Tt is а tedious, but important task. to the complexity of disentangle the system in order to quantify calcium and its reaction with other components. As an example, the presence of kraft lignin, has been shown inhibit the precipitation of calcium oleate to (31).a dispersant of Ca-soaps, as was function as Lignin may washing. shown earlier in sulphite An alternative explanation is that the calcium ions are bound to the lignin.

# WOOD RESIN DURING BLEACHING

To avoid pitch problems during bleaching and to reduce the bleached pulp resin content, the most important step is a successful deresination during washing of the unbleached pulp. Herefore, the differences between wood species and the positive effect of wood seasoning are usually most apparent.

reaction of wood resin, with The main elemental the addition of chlorine to the unsaturated chlorine. is compounds. This means, that the total weight of the boow resin is increased during chlorination and that the resin content of the bleached pulp is often higher than that of the washed, unbleached pulp for the following reasons : 1) Chlorinated fatty acids have а lower alkaline water unchlorinated. 2) In solubility per se than model experiments, chlorinated fatty acids have also been shown to be less efficient in solubilizing neutral compounds in alkaline extraction steps than unchlorinated (35). 3) Chlorinated neutral compounds such as chlorinated sterols or steryl ester are more difficult to solubilize in the subsequent alkaline extraction step than unchlorinated (35).

If, before the extraction step, some of the chlorine is replaced by chlorine dioxide such as in a D + C or D/Cstep, the chlorination of the extractives is decreased. 0n a mill scale, a mixture of chlorine and chlorine dioxide is normally used today. This reduces the resin content of the bleached pulp. Recently, for birch kraft bleaching, no such positive effect was found on a laboratory scale (36). However, when the surface area of the extractives was increased, the positive effect of chlorine dioxide was very clear after alkaline extraction. The explanation given was a difference in the production of resin surface area on the mill and laboratory scales. In contrast to chlorine, chlorine dioxide is unable to penetrate into the solid extractives phase; it reacts only on the surface of the extractives (36).

In birch pulp bleaching, none of the other bleaching agents such as hypochlorite, peroxide, oxygen and ozone were able to penetrate the wood resin, but some of them, especially low-pressure oxygen and ozone. gave а considerable reduction in resin content. High pressure oxygen treatment did not reduce the resin content, probably due to the magnesium carbonate added, which might bind resin (36).

In the bleaching of sulphite pulp (37), the increased substitution of chloring with chlorine dioxide reduced both the resin content of the bleached pulp and its chlorine content. A bleaching sequence, starting with oxygen or ozone followed by chlorine dioxide, seemed to combine low resin content with both good pulp quality and minimum effluent problems.

In closing up the water system in the bleaching solubility properties of the wood resin must be plant, the considered. If acidic water is used to neutralize the effluent from the alkaline stage or vice versa, the once-dissolved resin is re-precipitated. For this reason dispersants should be added to the pulp when it passes from the alkaline to the acidic bleaching stage to prevent reprecipitation of large specks or resin deposition. The use of talc in this position will bind the resin to the pulp, which might be necessary to eliminate severe problems

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with pitch deposition. Problems caused by deposits, clogging pipes and other equipment problems might also have to be prevented by keeping temperatures and other conditions constant.

For sulphite pulp, a mechanical treatment followed by alkaline washing, has proved very efficient for deresination  $(\underline{16})$ .

For mechanical pulps, such as TMP and CTMP, bleaching with hydrogen peroxide is often used, normally without a subsequent washing. On acidification, the dissolved resin is then reprecipitated on the fiber surface, which mav reduce the fiber-to-fiber bonding capacity and thereby lower the paper strength and initial wet web strength. Τn the introduction this case. of a washing step seems logical. For food container board - where smell and taste are important - such subsequent washing steps are in use in some mills.

# RESIN DEPOSITION AND PITCH PROBLEMS IN PAPER MILLS

Different mechanisms by which wood resin is transferred from the pulp to the surfaces of the process equipment have been analysed (<u>38</u>) and summarized recently (39) and will not be discussed here.

The risk for resin deposition in the paper mill depends on the following factors:

- The relative amount or concentration of easily accessible wood resin and other oleophilic material in the system, especially in the white water system e.g. as fines.
- Chemical, surface chemical and physical properties of the easily accessible wood resin.
- 3. Physical and surface chemical properties of the solid surfaces within the system and of paper machine parts, including solid surfaces such as pulp fibers, fillers, slime etc.

4. Chemical and some physical conditions in the white water and pulp suspension.

The risks associated with factor 1) may be reduced by a good retention of resin particles and fines in the web, i.e. a low content in the white water, and by the addition of specific absorbents for resin, such as talc with a large surface area.

The risks associated with factor 2) may be reduced by the attainment of a high positive charge on the resin particles, both to facilitate their retention on the originally negatively charged fibers, and to develop mutual repulsion forces between resin particles to prevent aggregation and coagulation. A rather high or a rather low viscosity of the resin is an advantage in order to reduce stickiness. This can be achieved by varying its the temperature and by the addition of softeners or solvents, such as kerosene etc.

The risks associated with factor 3) may be reduced by smooth and hydrophilic surfaces with a low reactivity towards resin and fatty acids on sensitive parts of the machinery, which also means metals with a low metal ion acitivity, i.e. with low corrosivity. If possible, these deposition sensitive surfaces should repel resin particles, which means that they should have the same charge as the particles, such as glass and ceramics. Fibers and fillers on the other hand should absorb the resinous particles, which means that they should be of contrary charge. Slime should not be allowed to exist and deposit, since it may combine with resin in the deposits as well (40).

With respect to factor 4) it is advantageous to have a low air content in the system to prevent concentration of resin by flotation. A suitable and constant temperature in the system, preferentially a low pH in the white water and the absence of divalent cations are also an advantage. as is the presence of polyvalent cations to stabilize resin with positive charge and cause its retention in the web as well. For some papers, such as tissue, anionic and nonionic low foaming surfactants can stabilize resin and facilitate its removal from the system. A high temperature increases the rate of resin coagulation and deposition, but reduces the resin viscosity, so that coagulated or deposited resin particles flow off again under the shear forces in a pulp suspension (38).

If pitch problems occur, action according to one, mentioned several or all of the above measures is Stabilizing suitable. chemicals or resin-absorbent chemicals naturally must be added at appropriate places before coagulation has taken place. The stabilisation of resin particles by positively charged aluminium sulphate. requires fairly low pH and cannot be combined with alkaline sizing. Aluminium ions are often not sufficient even under the more neutral conditions used today for the production of liner etc. Cationic low molecular weight polymers must therefore be used e.g. in combination with multicomponent retention aids. Calcium carbonate may absorb resin and fatty acids prevalent in the system.

The retention of resin and fines from the white water must be kept high enough to prevent problems, because of fluctuations in the system. Local measures, e.g. on a press roll, might include a change of wood resin or deposit viscosity at this place to permit the doctor blades to keep this roll clean. Fungicides may have to be added the or The body of sensing elements, such raw water chlorinated. as for flow and consistency, should have а smooth. inactive, hydrophilic surface, such as ceramic. The same can hold true for other very sensitive surfaces in the should have a large negative charge. system. Fibers With any addition of chemicals to the system the necessary retention of wood resin with the web must be taken into account.

Over one or two decades, positive features in respect pitch problems have been e.g. higher white to water temperatures, less air in systems, high pressure showers, more open felts made from textile fibers of less surface charge, stainless steel in all the system, double doctors against press rolls with an inbetween shower, higher solids the first open draw and where the wet webs touch the in press roll, less sulphite pulp and more mechanical and pulp. Negative features have occasionally been new pulp grades or wood species, increased white water closure, a more neutral or alkaline white water system, lower grammages reducing the overall wet web strength.

Due to this development, pitch problems have generally moved further along the paper machine from wire and felt deposits to adhesion on press rolls, on the first dryers, occasionally also onto breaker stacks and machine calenders or on the dryer hood, caused by condensation of volatile resin components.

example of problem-solving One recent mav be mentioned. Pitch deposits were observed on the central roll of a twin press followed by the first open draw and a third press, when a steam box was placed in front of the second nip. These deposits prevented the use of the steam in spite of double doctors against the central roll box with an inbetween shower. The injection about once per shift of a few liters of kerosene into this shower water enabled the steam box to be used without web breaks. An exception was the lowest grammage run on this machine where the additional adhesion of the wet web against this central roll could not be overcome without an increasing number of breaks.

It may be mentioned that a good knowledge of the solubilities and properties of resin components and especially of the various resin soaps is often the key to the chemical analysis of pitch problems (41).

# EFFECTS OF WOOD RESIN ON PAPER PROPERTIES

Some paper quality problems can be due to resin and pitch problems. Specks of resin are well known. The lifting of fibers in the paper surface may have been caused bv a resin film adhering to a press roll or drying cylinder. A high resin content on the fines reduces the bonding of these fines within the paper web, both when wet and when dry, and may promote linting etc. in the printing press.

Smell and taste problems in food boards are often due to resin components, which are volatile or split off as volatile degradation products on oxidation of resin

components. An example is aldehydes from unsaturated fatty acids. Improved washing or deresination of pulp and of recycled waste are then a necessary remedy.

In xerographic or laser printing, the hot print fixation roll, called the "fuser roll", easily vaporized sufficient resinous material from mechanical pulps to prevent their use in papers for such printing operations. Otherwise, clogging and deposition parts of in the This problem has to be solved equipment occurs. for mechanical pulps, and is occasionally also a problem for high resin content bleached hardwood pulps. One remedy is to transform prevalent fatty acids and fatty acid esters into aluminium soaps, the volatility of which is very low.

Well-known is the self-sizing of paper during storage, which is caused by a vapour phase redistribution of paper resin components, so that they cover most of the fiber surfaces. This problem is most evident in absorbent paper products. The friction coefficient of paper is also reduced by this redistribution of fatty material.

In bleached pulp, the residual resin is often the source of residual chlorine, which on aging can split main off as hydrochloric acid and thereby increase the rate of and embrittlement of paper (11). degradation the The brightness stability of a paper can also greatly be its resin components. This is especially true affected by when certain metal ions, such as Fe, Cu, Cr etc. have reacted with the resin or fatty acids present.

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# **Transcription of Discussion**

**A Review of Kraft Pulp Deresination and Pitch Problems** by M. Björklund Jansson, E.L. Back and M.I. Tufvesson

#### Dr. P.F. Nelson APM, Victoria, Australia

Have you any experience of the effect of an in-line (i.e. blow line) refiner on the state of dispersion of resin in Kraft black liquor from a continuous digester, especially on the tendency for deposition of resin on equipment?

M. Bjorklund Jansson No, I do not have an information on that particular subject.

Dr. L. G. Odberg STFI, Stockholm, Sweden

You showed a slide which corresponded to the beginning of the washing process, in which we saw calcium oleate precipitated. I think that it should be pointed out that since there is so much sodium there, the sodium liquid crystal precipitates before calcium oleate.

**Bjorklund Jansson** In the beginning, we have the liquid crystalline phase of the sodium soaps, but when the sodium concentration decreases, we do not have that precipitation any longer and instead the calcium soap begins to precipitate.

# Prof R.H. Atalla IPC, Appleton, U.S.A.

I would like to make a comment about the eccentricities of calcium which I referred to earlier in the week. During our study, we looked at some theoretical calculations on the calcium ion. It is the ion that immediately precedes the first transition series. The d-orbitals begin to decline substantially in energy and begin to approach the level of the p-orbitals which gives it the unusual power to chelate with many components in wood, not just the cellulosic components, but many of the substituted lignin fragments and obviously the resins. This has been known for some time, but the reasons for it have not been well understood. I think this is something that bears further investigation.

**Bjorklund Jansson** Dr. Allan in Canada and ourselves have been doing some model experiments, showing that if you are precipitating calcium soaps and if you add Kraft lignin, the precipitation will be restricted.