Understanding of Pitch Deposit Phenomenon in Virgin Mills

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In pulp and paper industry, closing of water loop to reduce fresh water consumption has become a world wide trend today. The closure of white water systems leads to build up of various organic and inorganic components causing deposition along the papermaking process, which appear to adversely affect the runnability on the paper machine and quality of the end product. The problem has been found to be more serious in the virgin mills using wood as raw materials containing more resinous materials. Different wood components are released from the fibres during pulping and bleaching into the process water of the paper mill. These components are present in process water in the form of dissolved and colloidal substances (DCS), which are mainly hemicelluloses, lipophilic wood extractives, lignans, pectins and lignins etc. Dissolved and colloidal substances can be carried over to the paper machine, where they can interfere with papermaking process.

The present paper highlights the work carried out by CPPRI at CTP, France on **Understanding the Problem of Pitch Deposit Phenomenon in Virgin Wood based Mills** in India. The study is concluded in two parts. Part I highlights the behavior of native colloids on pitch deposit formation and is presented in this paper. The part II covers modification colloidal pitch during pulping and bleaching stages, which will be presented in one of the forthcoming seminars of IPPTA.

INTRODUCTION

Closing of water loop has become a worldwide trend in Paper Industry not only as a measure for water conservation but also to reduce the effluent treatment cost. As a consequence of the system closure, the mills are facing serious problems of deposition along the paper making process due to increased buildup of various organic and inorganic components, which in turn adversely affects the quality of finished product.

Wood extractives deserve serious consideration because of their potential adverse effect on various aspects of pulp and papermaking. Wood extractives comprise about 1-5% of the weight of wood but the problems they cause in open systems are disproportionately much larger than their concentrations. These problems are expected to aggravate due to reduced water usage. When some dissolved solids in the white water system reach a certain concentration, they begin to precipitate and interfere with papermaking. Below 10 m^3/t, the concentration of dissolved solids increases very rapidly. In virgin kraft mills, the woody extraneous material is carried over along with pulp causes deposition of tacky material, which is known as pitch.

Pitch is a composite material that exists in bark and/or wood in nature for protection against microbial attack. The reasons for solidification could be either due to oxidation or polymerization. In general, Pitch is a low molecular weight, oleophilic materials extracted from wood chips in neutral, nonpolar, organic solvents. Pitch occurs in pulp and commonly deposits on machines during papermaking. The pitch consists of resin acids (softwoods), fatty acids (hardwoods), triglycerides, unsaponifyable matter (like sistosterol) in addition may have lignin, hemicellulose and divalent cations etc, and other compounds not well characterized.

Composition of Pitch Deposits

Chemically pitch are saponifiable and unsaponifiable compounds. The saponifiable pitch components which are mainly fatty acids and their salts dissolve or hydrolyze at a high pH during alkaline stages in the bleaching process whereas the unsaponifiable pitch deposits are fatty acid ester, waxes, di- and tri- glycerides, fatty alchohols and sterols, which are conducive to pitch deposition because they are sticky in nature and do not readily hydrolyze, causing a significant portion of the unsaponifiable material to remain in the pulp during papermaking process.

Another form of pitch deposition is the metal soap deposition due to presence of dissolved multivalent metal ions in the hardness of water reacting with anion of the soap of a fatty acid or resin acid according to the equation.

$$\underset{\text{(Metal Ion)}}{M^{n+}} + \underset{\text{(Soap Anion)}}{nSoap^-} \longrightarrow \underset{\text{(Metal Soap)}}{MSoapn}\downarrow$$

Mechanism of Pitch Deposits

Hydrodynamic or mechanical shear can destabilize the colloidal pitch emulsion, causing pitch to agglomerate and deposits to form. Similarly, sudden temperature drops, pH shocks, or the introduction of water hardness ions (e.g., from fresh water inlets or showers) can also cause deposits by destabilizing the colloidal pitch emulsion. Inorganic salts such as calcium carbonate can catalyze pitch deposition by acting as the "bricks" for the "mortar-like" pitch. Calcium ions in the white water can react with fatty and resin acids, forming insoluble, tacky calcium soaps.

Pitch Problem in Indian Context

In the last 2-3 years the problem of pitch deposition has also been observed in some of the virgin wood based mills. The severity of the pitch deposition is more pronounced, in the mills where the water circuit is closed to maximum. Keeping in view the seriousness of the problem as a future threat to virgin wood based mills, CPPRI initiated a project on **Pitch & Deposit Control** and carried out extensive research at CTP, France in the area of understanding the nature of pitch

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behavior in indigenous wood species and its control aspects.

In the present paper, the findings of the first part of the studies i.e. understanding the problem due to native colloids present in wood is undertaken. The paper highlights the findings of the R&D work carried out by CPPRI at CTP, France. The present study is focused on the comparison of native colloidal wood resin in different wood species.

MATERIALS & METHODS

Following wood species were selected for stiudies

- Vaneer Waste
- Cashew nut
- Accacia
- Eucalyptus
- Bamboo

The chips were subjected to refining to generate effluent containing native colloids, which were characterized for Turbidity, TDS, COD, Cationic Demand, Conductivity and pH.

To study the colloidal instability salt aggregation test was performed with electrolyte addition such as $CaCl_2$ followed by turbidity measurement.

RESULTS & DISCUSSION

Comparative Assessment of Release of Colloidal & Dissolved Materials

The results shown in **Table 1** give an assessment of the release of colloidal and dissolved substance in Vaneer Waste, Eucalyptus, Accacia, Bamboo & Cashew Nut.

The results indicate that Vaneer Waste and Bamboo induces lower release of colloidal substances, as indicated by low turbidity levels (109.2 & 78.1) compared to other species, however, the release of soluble & colloidal substances determined through COD (2600 & 4500 ppm) and TDS (2.4 & 3.7 gpl) is high. In case of Accacia, Eucalyptus and Cashew Nut both the release of colloidal substances and soluble & dissolved substances is high.

Table 2 depicts the ratio of dissolved / colloidal materials which is responsible for colloidal stabilization. Higher the ratio better is the stability.

The results show Vaneer Waste and Bamboo has higher ratios (24 & 57), which implies that it is colloidally stable. Indeed higher soluble content means higher soluble carbohydrate content and part of these carbohydrates may be adsorbed at the surface of the colloidal particles inducing the formation of a protective layer which will avoid agglomeration of the colloids.

Table 2: Cod / Turbidity Ratio For The Different Species

Species	COD / Turbidity ratio
Vaneer Waste	24
Eucalyptus	10
Accacia	11
Bamboo	57
Cashew nut	17

Assessment of Electrostatic Destabilization of Colloids

Colloidal instability is evaluated by increasing the ionic strength of the water. The consequence is a reduction of the zeta potential of the particles, which may then agglomerate if not well sterically stabilized.

Fig. 1 shows the evaluation of zeta potential and turbidity of colloids from Accacia.

The results show decrease in zeta potential values (between 5 mv and 10 mv) and simultaneously a large decrease in turbidity value measured after centrifugation, which indicates a considerable aggregation of colloidal particles with increase ionic concentration. To have an effective comparison an aggregation index was defined as the variation of turbidity (expressed in percentage) occurring between 0 and 300 mM $CaCl_2$.

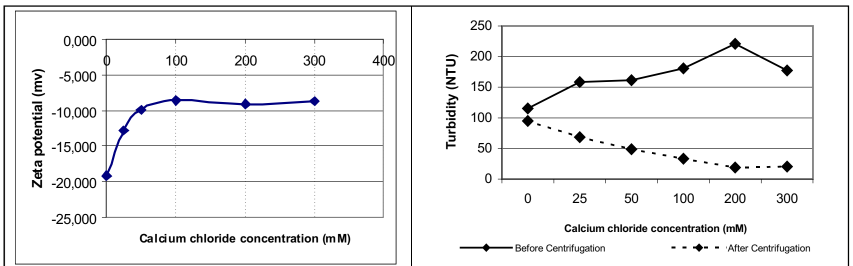

Figure 1: Evolution of zeta potential and turbidity versus calcium chloride concentration

Table 3: Aggregation Index

Species	Aggregation Index with $CaCl_2$
Vaneer Waste	33
Cashew nut	79
Eucalyptus	17
Accacia	78
Bamboo	15

The results of aggregation index are summarized in **Table 3.**

The results indicate that Vaneer Waste (33) Eucalyptus (17) and Bamboo (15) show low aggregation index, which attributes to better stability of colloids. It is interesting to note that despite of low dissolved / colloidal ratio (10) a better colloidal stability is observed in case of Eucalyptus. This may be due to the nature of soluble carbohydrates present in Eucalyptus species.

Table 1: Release Of Colloidal And Dissolved Materials From The Different Wood Species

Species	Colloids	Soluble + colloids			
	Turbidity (NTU)	COD (mg/l)	TDS (g/l)	CD (meq/l)	Conductivity (µs/cm)
Vaneer Waste	109.2	2660	2.4	0.33	380
Eucalyptus	542	5105	-	0.76	321
Accacia	284	3335	2.2	0.6	487
Bamboo	78.1	4500	3.7	0.07	469
Cashew nut	375	6260	4	2.41	475

Assessment of Potentially Precipitable Soluble Substanc - -es

This indicates generation of new colloids or suspended matter originating from precipitation of soluble substance. The precipitation index is calculated by addition of $CaCl_2$ and measuring turbidity before centrifugation. The index was defined as the variation (expressed in percentage) of the turbidity observed between 0 mM and 300 mM. The

Table 4: Precipitation Index

Species	Precipitation Index with $CaCl_2$
Vaneer Waste	102
Cashew nut	163
Eucalyptus	151
Accacia	62
Bamboo	47

results are depicted in **Table 4.**
The results indicates that precipitation index is low for Bamboo (47) and Accacia (62) compared to Vaneer Waste (102), Eucalyptus (151) and Cashew Nut (163) which implies that the soluble components of Eucalyptus & Cashew Nut are more sensitive to precipitation compared to Bamboo & Accacia as shown by Precipitation Index.

Table 5 summarizes the synthesis the results obtained for the 3 parameters studied.

Table 5: Synthesis Of Results Obtained For The 3 Parameters Studied

Species	Native wood colloid release (turbidity at 0 mM)	Colloids stability face to Ca (Aggregation index)	Precipitable Dissolved substances with Ca (Precipitation index)
Vaneer Waste	52	33	102
Cashew nut	188	79	163
Eucalyptus	260	17	151
Accacia	115	78	62
Bamboo	34	15	47

It is concluded among the five species that

(i) **Bamboo** produces the native colloids and dissolved substances having the lowest detrimental impact supported by low release of colloids, good colloidal stability and low to medium potentially precipitated dissolved substances.

(ii) **Vaneer Waste** behaves similar to Bamboo with lower release of colloids and having good colloidal stability. However, compared with Bamboo it has higher proportion of potentially precipitated dissolved substances.

(iii) **Eucalyptus** can be considered as intermediate species because inspite of large colloidal release and high potential of precipitation of soluble substances the stability of colloids generated is good.

(iv) The impact of **Cashew nut** is detrimental and has the highest potential for precipitation of colloidal pitch particles, as well as soluble / dissolved substances as shown by high aggregation index and precipitation index.

(v) **Acaccia** on the other also shows detrimental impact due to high release of colloids, which are not colloidally stable and sensitive to electrostatic destabilization.

CONCLUSION

✓ The studies conducted has helped in understanding the colloidal behavior of pitch components present in most native form in different wood species.

✓ Among the five species the order of merit in terms of release of colloidal pitch, its colloidal stability and precipitation index for all the wood species is **Bamboo > Vaneer Waste > Eucalyptus > Cashew nut > Accacia.**

✓ In the forthcoming publication, the modification of colloidal pitch particles during pulping and bleaching stages for all the five species will be presented.

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