

Some Aspects of Wood pulp Bleaching

J. S. CHAWLA and

A. N. SHARMA

The main purpose of bleaching is the production of a white pulp of stable colour at an economic cost.

The carbohydrate portion of wood mainly consists of cellulose and is largely associated with impurities like lignin and other non-cellulosic polysaccharides in addition to the other minor constituents such as inorganic substances, tannis, resins, colouring substances and sterols etc.

These carbohydrate portion of wood pulp i.e. (cellulose & hemicellulose) obviously do not contribute the colour, because they are inherently white. Neither are they easily transformed to coloured compounds by usual chemical treatment.

The lignin part of pulp probably represents the principal site of the colour, due to the presence of certain chromophoric groups. Since lignin contains a large number of phenolic groups, in both etherified and free form. The assumption may be made that various oxidative processes might convert a part of them to coloured quinon like substances. These processes could perhaps occur in part in the living wood and may also take place during the pulping operations. Whatever the chemical nature of the coloured groups

associated with lignin, they probably represent not one, several structures and are present in small amounts in comparison with the bulk of lignin, which contribute to the colour of the pulp.

Besides, extraneous constituents of wood also contribute to the colour of certain pulps, especially in ground wood pulps, the leuco-anthocyanins in certain wood species and spruce wood have been considered as potential colour forming substances, since they are easily oxidised to strong coloured compounds.

A minor colouring effect may be due to the resinous components of wood, namely, fats, resin acids and sterols. Heavy metal ions, such as ferric and cupric ions may form coloured complexes with phenolic elements in pulps and thus deepen the colour and tannin may exert a similar effect. Occasionally, the presence of finely divided bark or humic acids absorbed on the pulp from mill water, can darken the colour. It is probable that the extractives do have some effect on the colour and bleachability of the pulp although specific proven examples have not yet been recorded in the literature.

There are many colourless extractives retained by the pulp, such as reactive polyphenols, will consume bleaching chemicals thereby reducing efficiency of bleaching operations. In addition, many polyphenols will react on contact with steel equipment to give the

well known blue black ferric reaction. The use of stainless steel equipment in several Australian mills using pale coloured eucalyptus and their derivatives undoubtedly reduces the type of colour formation.

Many pulps appear darker when suspended in an alkaline solution this is probably due to ionisation of alkali by some phenolic or enolizable groups associated with the chromophor.

With the increasing trend of using mixture of hard woods the processes of bleaching also require adjustment accordingly.

The removal of lignin and the other colouring matter can be achieved by various chemical treatments such as oxidation and reduction. The principal bleaching and purifying agents are chlorine, chlorine dioxide and hypochlorite. Other bleaching agents used in smaller quantities are hydrogen peroxide and chlorites. The dark brown colour of sulphate pulp may also be due to sulphur containing lignin products formed during the cooking either by extensive condensation or by degradation. Discolouring substances are also formed partly by humification of the carbohydrate constituents.

The bleaching process consists in converting lignin compounds into water soluble products. This process may be carried out as gently as possible so that the carbohydrate is not attacked, otherwise the strength of the pulp for pap-

Dr. J. S. Chawla, Scientist, and A. N. Sharma, Senior Scientific Assistant, Regional Research Laboratory, Jammu-Tawi, J & K.

er would decrease; while the rayon pulp would show irregular decrease in viscosity and in alpha-cellulose content. Therefore, residual lignin and other colouring matter has to be removed by such a bleaching process which does not damage the cellulose.

Investigations carried out by several workers on the acidic chlorination of chemical pulp show clearly that substitution is the predominant reaction during the initial phase of chlorination. The substitution proceeds very rapidly and is completed in about 15 minutes.

Chlorine consumption is entirely due to oxidation. Methoxyl groups are gradually split off during the course of chlorination. In the first stage of chlorination the substitution and not the oxidation reaction is the decisive factor in the dissolution of lignin. It is almost certain that the initial rapid substitution reaction takes place at the aromatic nuclei of the phenyl-propane units that form the lignin micro-molecule. In order that the following oxidative stages may be most effective, it is necessary to remove as much of the chlorinated lignin as possible. Since these material themselves can be oxidised and will be consumed by "Oxidative bleaching agents".

Most of the materials are relatively soluble in warm alkali solutions which has led to the use of one or more alkaline extraction stages. In a multi-stage bleach sequence viscosity data have consistently shown that this alkaline-extraction has not effect on pulp strength i.e. there is no noticeable cellulose degradation. Sodium hydroxide is used exclusively to maintain alkalinity in this stage. Other alkalies, sodium carbonate, meta silicates, sulphides have been used in experimental trials. Calcium hydroxide has been found to be ineffective because of the precipitation of chlorinated lignins, which are themselves highly coloured and very difficult to bleach. More recently extractions with ammonia

have been tried with better brightness values. It has been reported that a mole of ammonia is less expensive than a mole of soda, moreover, extraction with ammonia could be carried out at high consistency with a potential advantages of short reaction and economy of heat. Recovery and reuse of the ammonia may also be possible.

Bleaching with chlorine dioxide has special properties as a delignifying agent for wood which makes it possible to obtain very high yields of lignin free products. For this reason chlorine dioxide was early proposed as a bleaching agent. The technical application of this agent began only very recently, however, when its commercial preparation became possible. Chlorites have the same reaction as chlorine dioxide. Bleaching with chlorine dioxide can be carried out in acid, alkaline or neutral solutions. The entire oxidising power of the chlorine-dioxide is utilised in the acid bleach.

Only one fifth of the potential oxidising power is used in the alkaline medium. Chlorine dioxide does not react with alcohols or carbohydrates, and acts very slowly on even so reactive an aldehyde as formaldehyde. Due to the high cost of these bleaching agents, they can be used only for completing the bleaching. Sulphur dioxide, sodium sulphide, zinc or sodium-hydrosulphite, used as a reducing agents, at pH7 or lower, to destroy traces of peroxide at the end of bleach, reduce ferric ion to colourless ferrous form, and generally improve pulp brightness.

It has been known that pulps bleached to high brightness by using several hypochlorite stages are less stable than those bleached with chlorine dioxide or peroxide. The amount of yellowing reaches a maximum when the hypochlorite bleaching is performed near neutral and a large excess of chlorine used. Apparently, the pulps containing large quantities of hemicellulose are more susceptible to colour reversion

because of the high accessibility of these polysaccharides to the oxidant. It has been shown that colour reversion can be minimized through the elimination of carbonyl groups by reduction with sodium borohydride and, to much lesser extent, by oxidation with chlorous acid to carboxyl groups. The carbonyl groups responsible for brightness reversion can be associated with hemicellulose as well as cellulose. Carbonyl groups, as such, are not involved in colour reversion as the brightness stability of the boro-hydride reduced oxycellulose indicates, nor as the shortening of the cellulose molecules accompanying the oxidation with hypochlorite.

When wood pulp is bleached with hypochlorite the pH should be kept as high as possible and the quantity of active chlorine low to minimize the colour reversion, hot-alkali solubility and loss of strength of the pulp. Although the first two detrimental effects can be largely corrected by the Borohydride treatment, this is by no means an economically feasible methods at the present.

Now a days, for bleached kraft pulp there seems to be a trend towards higher brightness and brightness stability, this has been achieved by using peroxide in a final chlorine dioxide stage. The improvement in brightness is obtained at the expense of a loss in viscosity of the pulp and consequently some strength. One way of compensating of this would be to reduce the drop in viscosity obtained in the delignification by adding chlorine dioxide to the chlorine. An attempt to elucidate the mechanism for the stabilisation in viscosity caused by this addition is made. It is postulated that chlorine dioxide and/or the chlorite formed oxidise aldehyde group at the position in glucose residue (formed through oxidation by chlorine). Thus preventing hydrolysis during the chlorination and cleaves of the chain during the following alkaline extraction stage. Some recent investigation indicates that chlorine

is an excellent delignification agent with some draw backs such as impairing deresinification and lowering the viscosity of the pulp. Mixtures of chlorine dioxide and chlorine of varying composition are considered to be very useful bleaching agent. Six stage process CEHEDP, sequence can consistently give 90 oven-dry brightness, two brightness point higher than is obtained in multi-stage processes that do not include a peroxide, bleaching stage. Pulps bleached in the CEHEDP sequence loses about one brightness point when subjected to the oven-dry reversion test, (air-dried

hand sheet dried for one hour at 105°C in an air circulated oven).

For an equivalent oven dry brightness performance, the chemical costs for six stage bleaching process CEHEDP are shown to be competitive with processes using two chlorine dioxide stages.

Pulps of different brightness or whiteness may be obtained by varying (1) amount of chemical added, (2) sequence of stages, (3) number of stages. The sequence of operation of the various stages will of course, depend on the type of un-bleached pulp, the quality of the bleached pulp, the

brightness or whiteness desired, and the economics of the process.

REFERENCE

1. Libby, C. E., "Pulp & Paper Technology", New York, McGraw Hills 1962 Vol. 1.
2. Rydholm, S. A. "Pulping Processes", New York, Inter Science 1965.
3. Rapson, W. H., & Anderson, C. B. R. Paper Trade Journal. July 5, 1965.
4. Leibergott, N. and Yorston, F. G., Paper presented at the International Bleaching Conference held in May 1-4, 1967, by Tappi.

Bombay-1.