Pulping-Mechanical to Dissolving Grade

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Pulp is a product that is derived from bamboo wood and other cellulosic plant materials by mechanical or chemical treatments and is optionally followed by bleaching and other purifications depending upon its end uses. Pulping therefore means the separation of cellulose fibres from various raw materials viz., bamboo, wood, etc. by removal of other impurities. The major objectives of all pulping processes are to liberate the fibres from the raw material.

In mechanical pulping, the wood is ground and the pulp is washed. In this process, we are trying to retain as much of other constituents besides cellulose in the wood as we can retain. At the other extreme end of pulping is the manufacture of dissolving grade pulp wherein we mainly aim at retaining the alphacellulose and removing to the extent possible the other constituents of the bamboo and wood to the limits prescribed by the users of the pulp towards making staple fibre or continuous rayon filament In semi-chemical and semi-mechanical pulping, yarn. in addition to the physical softening of the interfibre bonds, a mild chemical dissolution of the middle lamella is achieved. In other words, this pulping process tries to overcome some of the draw backs of both the chemical and mechanical pulping. The chief draw back of the chemical pulping methods is ofcourse the comparatively low yield. Mechanical pulping gives mainly quantitative yield, but causes rupture of the fibre walls and give pulps which contain substances of little value for many purposes and do not fulfill quality requirements for many grades of paper except for newsprint for which it is used mainly. The dissolution of some of these unwanted chemicals are achieved in semi-chemical pulping. In this paper, an attempt is made to cover the whole range of pulping from mechanical pulping which is at one end of broad spectrum, to Filament grade pulping which is at the other end.

As the pulp industry is developing and adjusting to the necessities of times, various processes of pulping have come into vogue, depending on situations and needs of the industry quite a few of them have come to stay becoming standard processes of pulp making. To mention a few of them, as follows :

- 1. Mechanical pulping
- 2. Thermo-mechanical pulping
- 3. Semi-chemical and chemi-mechanical pulping

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- 4. Neutral sulphite semi-chemical pulping
- 5. Cold soda pulping
- 6. Chemical pulping
 - (a) Soda process
 - (b) Sulfite process
 - (c) Kraft or sulfite process
 - (d) Polysulphide pulping.
- 7. Prehydrohyed kraft process for dissolving grade pulp manufacture for
 - (a) Making of staple fibre
 - (b) Continuous rayon filament.

The salient features of all these pulping processes, which cover a wide spectrum are discussed in this paper, although dissolving grade pulping is dwelt at some length.

The first step in all the pulping processes is the preparation of the bamboo, wood and other similar raw materials. In case of wood, bark must be removed from the wood, as it is a source of dark colour and dark fibres in the wood. The bamboo and wood must then be reduced to units small enough so that the cooking liquor can penetrate to the maximum extent and uniformly in a reasonable time. This is done by cutting to the chips which have the preferred dimension.

Mechanical pulp (ground wood) is produced by pressing the debarked logs against a grinding wheel in presence of water. The yield of pulp is over 90%. It is used primarily for newsprint without much bleaching.

THERMO-MECHANICAL PULPING (TMP)

One of the main draw backs of ground wood pulp as pointed out earlier, is the difficulty of separating fibres without damage to the fibrewalls especially in the case of hardwoods with their high content of vessel elements with thin walls. Ground wood pulp of hardwoods therefore gives low strength papers and so TMP requires long fibred soft woods. In order to overcome this difficulty the thermo-mechanical pulping process was developed, which used mechanical forces for fiberising the chips that have been softened with the aid of water and high temperature.

In thermo-mechanical pulping disc refiners of various types are mainly used, and the pulp produced from disc refiner, consists of less damaged fibres than that of ground wood pulp. Further, the thermo mechanical pulping takes cognisance of the fact

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that it is beneficial for both the pulp qualities and energy consumption to soften the inter fibre bonds in the wood. This is achieved by thermal softening together with swelling in water. High temperature disc refining is used in Asplund process and high temperature steam expansion in the Mason process.

Each TMP system now in use employes the same basic technology : chips are conditioned with thermal energy prior to refining to produce a long fibered pulp freer of rejects and with bonding properties superior to conventional stone or refiner ground wood pulp. Chips are then conveyed to a pressurised refiner, cyclones and second stage refiner. A comparison of the properties of the thermo-mechanical pulp and the ground wood pulp is given in Table 1.

CHEMI-MECHANICAL PULPING

In semi-chemical pulping, in addition to the physical softening of the interfibre bonds, a mild chemical dissolution of the substances of the middle lamella is achieved. Semi chemical pulping is thus a two stage process that requires a mild chemical treatment followed by a mechanical treatment to separate the fibres. Chemi-mechanical pulping is similar, but consists of a still milder treatment by chemical followed by more drastic mechanical action.

The chemical pulping stage can be conducted with any known pulping reagent and many have been shown to serve the purpose. The first and most important is acid sulfite and there is now a minor use of soda and kraft liquor, the other pulping regents. However, the major portion of the semi chemical pulps and a part of the chemi mechanical pulps are made with sodium sulfite buffered with sodium carbonate or bicarbonate or kraft green liquor. Buffering to a pH range of 7 to 9 is particular to NSSC pulping. This controls the corrosions as well as the pulping rate which is naturally slower in this range than under strongly acid or alkaline range.

The semi-chemical processes are most readily characterised by their yields of pulp, which are taken at 85 to 95% for chemi-mechanical pulps and 65 to 85% for the semi-chemical pulps as claimed by McGovern in the hand book of pulp and paper technology edited by Britt.

The semi chemical pulps vary in brightness from 25 to 65%, depending on wood species, process, degree of pulping and final pH value in working. The brightest pulps are made with sodium sulfite or sodium bisulfite slightly on the acid side. The darkest pulps are made under alkaline conditions. The chemi-mechanical pulps tend to be brighter than the corresponding semi chemical pulps although the NSSC pulps increase in brightness with decrease in yield within their defined yield range. Semi-chemical pulps can be and are bleached by the conventional multistage methods depending on the brightness required.

The bright semi-chemical pulps are used to a smaller extend, though unbleached, in newsprint and other paper grades, having minimum brightness requirement. They are also used for corrugating boards, tubes, cores, containers etc.

COLD CAUSTIC PULPING

Cold caustic pulping is a classic example of semichemical pulping and has found wide spread application. This requires no pressure equipment but still involves essential chemical treatment prior to mechanical fiberizing.

In this process, the chips from the silo are conveyed to fractionator by means of blowers, where they are reduced to matchstick size. After this these small chips are fed into soaking bin wherein they are soaked in NaOH for about 2 to 3 hours, the dosage of NaoH being 4% on the basis of B.D. weight of the chips. After soaking the chips are extracted by a set of extraction screws from where soaked chips are pumped to the Head Box. In the head box it is diluted by means of spent liquor and thickned in thickners. After thickner, the washed chips are refined in a two stage refining process to 25-30°SR. The refined pulp after storing in chest is washed and screened and sent to paper machine. This pulp is used in fluting medium and coarse varieties of paper. The results of this pulp evaluation are given in Table II.

CHEMICAL PULPING

Chemical pulping of wood may be defined as a process in which the fibre cementing material, viz. lignin is dissolved by reasonably specific reagents and the individual fibers are liberated.

Chemical pulping is always a compromise. Although lignin is largely concentrated in the middle lamella, its distribution throughout the secondary wall makes it difficult to remove quantitatively. On the other hand, the low molecular weight carbohydrates are rather easily soluble in pulping. Process conditions and chemicals used in chemical pulping attack even the resistant cellulose.

The common commercial pulping-reagents in use today in rendering lignin soluble are—

- (a) Sodium sulfite plus sodium carbonate
- (b) Sulfurous acid plus a bisulfite (both are known as sulfite process)
- (c) Sodium hydroxide plus sodium sulfide (known as sulfate process or kraft process)

SULFITE PROCESS

In sulfite process the delignification is achieved by converting the lignin into a water soluble lignosulfonic acids and then washing them off.

The sulfite cooking acid is a solution of sulfur dioxide and a bisulfite as stated earlier. The latter may be an alkali or an alkaline earth, but usually for economic reasons it is calcium or magnessium. The sulfite cooking cycle is divided into three main parts-the penetration period, the cooking period and

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recovery period. Time must be allowed for the chemical to penetrate the chips completely. The temperature of the digester is then raised slowly over a period of 4 hrs. to 110° C, at which level the cooking becomes significant. Penetration becomes rapid from 80° C on. Following the penetration period the temperature is raised to a maximum usually between 135° C and 145° C. The pressure is allowed to rise until it reaches about 80 lbs after which it is maintained constant by relievers gas, when the cook reaches the proper stage and at about the end of the cooking, pressure is reduced to 30 lbs during a period of about 1.5 hrs. At the end it is blown into a pit.

Sulfite pulp as discharged from the digester has a greyish white colour. Yields of pulp on the basis of dry wood are 46-48%.

The pulp is of medium strength and very versatile in its paper making qualities.

It is mixed with ground wood to make newsprint; it will also make soft papers such as napkins and the various sanitary tissues; and also it can produce excellent bond papers.

SODA AND KRAFT PULPING

Although the soda process was the first historically and although it is still in use, it has never reached the prominence of either sulfite or kraft, because of the superiority of the latter, in yield and strength of pulp, and ease of cooking and ease of further bleaching. The pulping involves cooking of the chips with NaOH as 20-22% Na₂O, at a pressure of 80 to 110 lbs/sq. in. for a period of 4 to 6 hours.

In kraft pulping, the cooking liquor differs from the soda liquor primarily in its sodium sulfide content. The presence of sodium sulfide results in more efficient delignification during the cooking, with less Carbohydrate degradation resulting in pulps of high strength and easy bleachability. The basic theory of kraft pulping is discussed under dissolving grade pulping.

Kraft pulp is brown in colour the familiar brown of grocery bags. It is the strongest pulp made from wood and other plant materials. Probably the largest use for kraft pulp is in the paper board field for manufacture of corrugated or solid fiber cartons.

DISSOLVING GRADE PULPING

Dissolving grade pulps are highly purified form of cellulose, containing mainly alpha cellulose and are used in the manufacture of rayon, cellophane, methyl cellulose, ethyl cellulose, nitro cellulose and other cellulose derivatives.

Pulp to be used for rayon manufacture has an alpha cellulose content of above 90%. A high percentage of pentosans and other hemicelluloses are objectionable in rayon grade pulps, because these materials cause troubles in filtration and also affect their reactivities to-words Xanthation in the viscose making process.

The problem of characterisation of the rayon grade pulp is complicated because the processing properties of dissolving pulps depend on the physical state as well as on the chemical composition. In addition to chemical analysis, a considerable number of rayon grade pulp producers also control some of the processing properties of the pulp by simulating the operations of the viscose plant in a small scale.

The normal specifications of dissolving pulps of various grades are presented in Table III.

It should be stated here that there are evidences to show that resin is apparently not harmful upto 0.45% to 0.70% and may even increase the transparency of the viscose.

Now let us review the processes of manufacture of dissolving grade pulps. This can be made either by sulfite process or by prehydrolysed kraft process.

SULFITE PROCESS

In sulfite process, the cooking is same as in the case of paper grade pulping but the bleaching of this sulfite pulp is different for dissolving grade pulp is different in the sense that either a cold alkali or hot extraction stage is prominent and in this stage the removal of hemicelluloses are accomplished.

PREHYDROLYSED KRAFT PROCESS

The first stage of the treatment in the cooking process is known as pre-hydrolysis. This can be defined as breaking or weakening of the chemical and physical association of the non-alpha cellulose components of wood with native resistant cellulose. It also serves to render hemicelluloses more susceptible to ultimate removal by alkali. In this stage some of the original pentosans are made watersoluble and extracted; some are hydrolysed to simple structural unit that respond to second extraction, some retain the resistivity and appear in the final pulp.

This prehydrolysis can be achieved in a number of ways. This is done mostly by adding small amounts of mineral acid like sulphuric acid (to hydrolyse the glylosidic bonds linking cellulose components with non cellulosic ones). This is known as APS process (Acid prehydrolysed sulfate). Other methods of prehydrolysis are by water and steam. In these cases, the organic acids, mostly acetic acid is liberated first during the reaction, and this acts as catalyst for further reactions. The efficiency of this water and steam catalysed prehydrolysis depends mostly on the acetyl content of the wood. This process is known as WPS sequence (water prehydrolysis sulphate).

It should be emphasized here that the prehydrolysis is of relatively little benefit, and may even be harmful, when the pretreated wood is cooked by, sulfite process, as is evident by the investigations of Correns and his group. Therefore the prehydrolysis is applied normally when high alpha-pulps are prepared by sulphate process.

It is also pertinent to point out here some of the undesirable side effects of prehydrolysis. The pre-

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hydrolysis stage is known to lead to lignin condensation which on severe conditions may be so extensive that the delignification ability of the kraft cook is impaired. It may also be pointed out here that similar reasons exclude even fairly mild prehydrolysis is prior to sulfite cooks which are more sensitive to precondensation of the lignin. When the delignification of the kraft cook is delayed by too severe prehydrolysis, reasonable chlorine numbers can be achieved only by increasing the temperature or chemical charges of the kraft cooking stage and that will lead to increased degradation of cellulose. Therefore in arriving at the process conditions for prehydrolysis stage are must be taken to find a balance between the maximum removal of pentosans and minimum condensation of lignin.

SULFATE COOKING STAGE

The prehydrolysed chips are then subjected to cooking with cooking liquor comprising mainly of NaOH and Na₂S.

In the initial stages of the cook, it is chiefly the carbohydrates are dissolved. The rate of delignification increases only after most of the pentosans and hemicelluloses have been dissolved. Lignin is dissolved much more rapidly due to the effect of sulfur compounds.

The effect of sulfur components has been a subject of a number of investigations. Klasson has demonstrated that the sulfur content of the cooking liquor gradually decreased during the sulfate cook and it was shown that the kraft black liquors contained organically bound sulfur, which has been estimated to be 2% of the lignin.

During the sulfate cook, lignin in the solid phase first takes up sulfur. The hydroxyl groups in the substituted benzyl alcohol groups are replaced with mercaptan groupings. Mercaptans, are however not stable in the alkaline solutions and are converted partly into sulfide groups by reacting with hydroxyl groups from either the same or another molecule. Another part is dehydrogenated, probably by disproportionation reaction to disulfide compounds. Besides these sulfidisation reactions, an hydrolytic splitting of lignin by alkali takes place. In this manner free phenolic hydroxyl groups are formed and the lignin becomes soluble in alkali. Furthermore, disulfide compounds are split under the influence of alkali into the corresponding mercaptans and sulfonic acids, which are again not stable. The hydrogen sulfide which is then split off, from the acid can react again with more lignin. The mercaptans in turn react further, being converted into sulfide and disulfide. Thus by means of sulfidisation a condensation sensitive group is blacked and the polymerisation of undissolved lignin is reduced or prevented keeping the lignin in a more soluble form. The polymerisation of the lignin in a sulfide free alkali cook probably explains the marked decrease in the rate of solution of lignin as the cook proceeds. Such a condensation is very possibly the reason for the fact that lignin

remaining in the wood in a sulfide free alkaline cook is more difficult to bleach.

The purpose of bleaching operations is to impart the desired final characieristics of the pulp. The viscosity control and the brightness are the main criteria in bleaching process. The carbohydrate removal, carried out mainly in the alkali extraction stage, improves the quality of the dissolving grade pulps. Deresination or pitch removal occurs mainly in the alkali stages and is important in obtaining a high brightness. Viscosity adjustment or depolymerisation of the remaining carbohydrates is mainly carried out in the oxidative stages(mostly hypochlorite) and is desired for dissolving pulps to achieve an uniform viscosity level of production, for a pulp with uniform D.P. distribution will result in better yarn strength.

BLEACHING

CHLORINATION

This comprises the first stage of most bleaching sequences. Chlorine reacts rapidly and smoothly with the noncarbohydrate fraction of the chemical pulps, viz. lignin to form partially water soluble material known as 'chloro-lignin'. The chlorinated phenolic material becomes easily removable by the action of alkali and oxidants like hypochlorite and chlorine-dioxide in the subsequent bleaching stages.

The chlorine charge in this stage is determined on the basis of Roe chlorine number or permanganate number of the unbleached pulp. For Eucalyptus pulp, the chlorine charge is given by the equation. % chlorine charge = 0.357 × P.NO.

The chlorination stage is carried out at low pulp consistencies of 3-4%, for about 45 minutes to 1 hr. at atmospheric temperature.

When chlorine gas is disolved in water, reversible hydrolysis occurs according to the following equilibrium

$$\begin{array}{rcl} \mathrm{Cl}_2 + \mathrm{H2O} &\rightleftharpoons & \mathrm{HOCI} &+ & \mathrm{HCI} \\ & & & 1 & & 1 \\ & & & H^+ + \mathrm{OCI}^- & & H^+ + \mathrm{CI}^- \end{array}$$

The proportion of chlorine, hypochlorous acid and hypochlorite ion in solution depends on pH. Below a pH of 2.0 molecular chlorine is present substantially as chlorine. That is why the pH of the chlorination stage is about 2.0.

Because of the highly acidic nature of the medium, in this stage of bleaching, most of the metallic impurities contributing to the ash content of the pulp are converted into their corresponding water soluble chlorides and are removed.

ALKALI EXTRACTION STAGE OF BLEACHING

In this stage of bleaching, most of the "Chlorolignin" which are partially soluble in alkali are rendered water soluble by alkali and removed.

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The normal alkali dosage is given by the equation: % alkali charge=% Cl_2 charge×0.5+0.5

In alkali extraction stage, in addition to "chlorolignin' removal and hemicellulose dissolution, a considerable deresination of the pulp also takes place. This is in principle a saponification of the ester components of the resin, a disolution of the fatty acids and resin acids in the form of sodium salts (soaps) and a micellar solubilisation of more or less hydrophobic constituents of the resins. Non-ionic surfactants of the type-nonyl phenol, condensed with ethylene oxide have been found to be the most effective. The mechanism of the micellar solubilisation can be explained as follows :

The surface active agents form-micellar particles with a considerable degree of orientation, the hydrophilic parts of the molecule turned outwards into the solution and the hydrophobic parts into the interior of the micells, enclosing the non-polar constituents of the resin and the hydrophilic parts subsequently reacts with alkaline solution.

In alkaline purification the cellulose normally undergoes endwise degradation called "peeling reaction". This reaction will be facilitated by the presence of a carbonyl group in the C-2 or C-3. Application of excessive chloine or hypochlorite would create such reactive centres in the cellulose molecules and make it much more susceptible for alkaline degration in the alkali extraction stage. This, therefore, necessitates a careful control of bleaching in the chlorination and hypochlorite treatment which usually precede the alkaline extraction stages.

HYPOCHLORITE TREATMENT

Hypochlorite treatment is one of the most important stages in any bleaching sequence for the production of dissolving pulp. Because of its ability to alter the viscosity of the pulps as per the needs, uppochlorite bleaching enjoys aiqn euun place. In the bleaching of dissolving grade pulping, sodium hypochlorite is used and not calcium hypochlorite which is only for paper grade pulps.

The rate and extent of hypochlorite bleaching reaction depends on the nature of the pulp, temperature, pH, bleaching time, ratio of hypochlorite to pulp etc. Pulps that still retain a lot of lignin at the start of the hypochlorite stage and consumemore hypochlorite before degradation proceeds very far, than pulps that have been more highly purified by previous treatment. Therefore, great care must be taken to control properly the hypochlorite stages near the end of a bleaching sequence.

Normal hypochlorite bleaching temperatures range from 30° C to 60° C.

pH is the most important factor in hypochlorite bleaching. Hypochlorite reacts with the pulp to form organic acids and carbon dioxide and also the substitution reactions of lignin which will liberate HCl. These together will result in the lowering of the pH of the system and this is not desirable as this will damage the pulp.

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The hypochlorite reaction at pH 7–8 causes the following damaging reactions to cellulose :

- (1) Oxidation of the primary alcoholic group at C6 to a aldehydic group and then to a carboxylic acid group.
- (2) Oxidation of the secondary alcoholic groups on C2 and C3 to ketonic groupings which on further contact with oxygen results in ring cleavage.
- (3) In extreme cases Cl and C2 carbon atoms may be cleavaged with the formation of aldehydic and carboxylic groups.

This is because at these pHs we have a significant fraction of hypochlorous acid. If one compares the oxidation potential, it will be seen that HOCl is the most powerful oxidising agent and hypochlorite is the least one.

Form of chlorine	Oxidation potential
OC1-	+ 0.94
Cl ₂	+ 1.35
HÕCI	+ 1.50

Several investigators have reported, that hypochlorite oxidation of cellulose at high pH favours the formation of relatively stable carboxyl groups while at low pHs. Unstable carboxyl groups are formed. This degrades the pulp in the alkaline extraction stage and also results in colour reversion. Therefore, the pH of the hypochlorite stage is normally controlled at desired range by adding enough caustic at the start of the reaction to maintain the desired final pH, by neutralising the acids formed during the course of the reaction.

The hypo dosage is determined after extensive pilot plant trials.

CLO₂ BLEACHING

The advent of ClO_2 as a bleaching agent was in the production of pulps of high brightness and strength. This bleaching agent is an unique one in the sense that it preferentially attacks lignin and has very little effect on carbohydrates except under conditions of high pH.

EFFECT OF pH

In common with many bleaching agents, the chlorine dioxide reacts with water and under the conditions most effective for pulp bleaching, forming chlorate and chlorite ions.

The pH affects these reactions as follows :

 $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_3^- + \text{ClO}_2^- + \text{H}_2\text{O}^-$

This reaction is faster at higher pH.

In the presence of pulp the same reaction occursexcept that oxidising equivalent made available by a reduction of a mole of ClO_2 to chlorite ion is taken up by the pulp, instead of by oxidising another mole of ClO_2 to chlorate ion.

TABLE-I

		NEWS GRADE		MAGAZINE GRADE	
		IMP	GWD	TMP	GWD
Freeness	ml.	110	90	65	60
Breaking length	m.	3500	2500	3800	2800
Tear index	$Mn M^2/g$.	8.3	3.5	7.3	3.7
Burst index, KPa	m^2/g .	2.4	1.3	1.6	2.5
Shives (someville)	%	0.2	0.2	0.1	0.2
Bauer McNett	70				
± 28 mesh	mesh	42	14	33	14
28-48	"	. 13	22	14	18
48-100	"	11	17	14	16
100-200	,,	8	14	7	14
_200	**	26	33	32	38
Specific energy	Kwh/t	2000	1400	2200	1700
40 G/M ² Newsprint					
Pulp basis		TMP	GWD		
GWD	%		73		
TMP	Ž				
Chemical pulp	ĺ,		27		
Caliper	mm	0.066	0.061		
Roughness	ts ml/min	. 79	75		
Porosity (bend sten)	ml/min.	280	350		
Oil absorbency	ts g/m^2	14	18		
Tear MD	mN	150	150		
CD		180	200		
Brightness (IDSO)	%	60	60		
Opacity (ISP)	%	92	90.5		

COMPARISON OF MECHANICAL PULPS

From reference 5

TABLE-III

Properties	i	Dissolving pulp for rayon continuous filaments	Dissolving pulp for tyre Cord Yarn	Dissolving pulp for polynosic fibres
Alpha Cellulose Beta cellulose Gamma cellulose Pentosans Ash SiO ₂ Ca + Mg Fe Cu Mn	ppm ppm ppm ppm ppm ppm	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
Resin (alcohol-benzene solubility) Copper number Degree of polymerisation Brightness, G.E Moisture content Sheet substance Sheet thickness Sheet apparent density	% % g/m² mm g/cc	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

From reference 3

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TABLE---II

EVALUATION OF COLD SODA PULPS FROM MYSORE GUM

SI. No.	Size of chips	Freeness I CSF ml.	Breaking length	Burst factor	Tear factor
1.	Long	250	730	3.0	17.0
	-	200	1480	5.4	18.1
		150	1590	7.2	19.7
		100	2000	10.5	24.4
2.	Medium	250	1290	8.1	25.0
		200	1730	8.7	25.3
		150	1930	11.1	27.9
		100	2540	11.0	27.4
3.	Short	250	1900	8.0	22.7
		150	2200	9.0	26.1
		100	2440	10.5	25.7

 $ClO_2 + pulp \rightarrow ClO_3^- + Oxidised pulp$

As the pH rises above 7, this reaction becomes increasingly vigorous and the cellulose is attacked as well as the lignin. This is shown by the lowered viscosity and greater solubility in hot alkali of the pulp as the pH increases.

Chlorine dioxide reacts with pulp to form chloride ions and the bleached pulp.

 $ClO_2 + pulp \rightarrow Cl^- + oxidised pulp - (3)$

Reaction (3) is independent of pH and does not degrade the pulp.

Therefore the pH of the chlorine dioxide bleaching is maintained at 4.5-6.0 for obtaining the best results.

TEMPERATURE

High temperatures of the order of 70-80°C are favoured for getting best results.

CONSISTENCY AND TIME

 ClO_2 bleaching at a consistency of 10 to 12% for a period of 3 hours are found to give best results.

SULPHUR-DI-OXIDE

After the last stage of bleaching treatment with SO_2 water is carried out. This has two fold effects.

(1) It is an excellent antichlore and will remove all the residual chlorine. (2) It removes the metal ions like Fe/+++ Mg++ Al+++ in the form of sulphtes. This is because the polyvalent ions listed above have a tendency to be fixated on the pulp. However, this tendency is pH dependent as carboxyl groups of the pulp (cellulose) are effective only in the carboxylate form. Carboxyl groups of this type have 3.5-3.8 and therefore Ka of a p at pH 3.0, the usual pH of sulphur dioxide treated pulp, only 10% of it should be in the carboxylate anion form. With 90% of the cellulose in COOH form, the polyvalent metal ions will come out into solution as sulphtes. After this bleaching sequence the pulp is subjected to centricleaning to remove sand and heavier particles.

Thus the normal bleaching sequences for a prehydrolysed kraft dissolving grade pulp is C-E-H E D(H) SO₂. The second stage of hypo becomes necessary only when the viscosity is not properly controlled in the first hypo stage of bleaching.

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