Bleaching of Pulp From Indigenous Raw Materials

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The Pulping Process in M/s. Seshasayee Paper & Boards Ltd., Erode—the Bleaching in particular—is described in detail. Apart from Bamboo, hardwoods like Dandup, Dattle, Rubber wood, Bluegum, Eucalyptus and Alberia were used for making pulp. Results of the trials on these hardwoods in Laboratory as well as in plant scale were furnished. Their experience on alkali extraction before hypochlorite and the effect of sulphidity on bleaching of the pulp obtained from continuous PANDIA Digesters were discussed in detail.

Introduction :

Modern pulp bleaching techniques have evolved over the past forty years. Continuous multi-stage bleaching superseded batch bleaching about twenty-five years ago, but only within the past ten years there has been some semblance of agreement on the most desirable process for a particular problem.

What do we mean by pulp bleaching and why do we wish to bleach? Broadly, bleaching may be defined as the process of "improving" the color or brightness of a pulp. Color is a more subtle characteristic and may mainly concern us if it is unpleasant or not normally associated with paper. Thus, we may wish to "bleach" to accomplish any or all of the following:

1. Change color or hue, perhaps without a great change in brightness.
2. Increase brightness to provide more pleasing appearance or to accept multi-color printing while retaining the proper balance of colors.
3. Remove or stabilize those constituents which tend to change color or revert in brightness on exposure to light or heat.
4. To effect a change or improvement in pulp properties demanded by the end use, such as strength, opacity, bulk, softness, absorbency, etc.

What causes color in pulp ?

The color in wood or other pulps is a function of the type of raw material and the pulping process used. Whereas the cellulose and hemicellulose constituents are colorless, (for example, cotton fibre) there are many colored or potentially color-producing constituents in the non-cellulosic fractions of many plants. Lignin, which is a methylated phenyl propane type structure, has a number of reactive groupings which may be colorless in the wood but which readily condense when released during pulping or in the presence of digestion liquors into highly colored compounds. The pulping liquors dissolve lignin and wood sugars and carry them away; however, there will always be a portion still combined with the fibre which must either be removed during bleaching or decolorized in situ.

How to correct the Color :

Regardless of the source of the pulp—that is, whether it is a groundwood, chemi-groundwood, semi-chemical or chemical type pulp from wood, bamboo or an agricultural fibre such as bagasse, Straw, bleaching will be accomplished by one of the following means:

1. Altering of the chromophoric groups in the lignin, hemi-cellulose or extraneous substances present, either by oxidation or reduction.
2. Complete removal of the color-producing compounds, such as lignin, by chemical modification, degradation and ultimate solution.
3. Removal of non-cellulosic carbohydrates, pentosans, etc. by alkaline extraction.

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4. Combinations of the above, where the bulk of the undesirable material is removed and the remainder decolorized.

It is interesting to note the effect of such processes on yield. If the brightness improvement is achieved by merely alteration of the chromophoric groups, through oxidation or reduction, it follows that the potential color-producing substance still remains in the paper where it contributes to the yield. Thus, bleaching losses by these means are relatively minor, (less than 2%) being confined principally to the nearly water-soluble low molecular weight carbohydrate fraction. However, one would also expect that these reactions might be reversible and that aging, particularly in the presence of heat, light and a moist atmosphere, might cause reversion or loss of the color and brightness again. The bleaching of groundwood with hydrosulfite or peroxide is an example. Where the groundwood is to be used in newsprint, for example, this is not particularly serious, as the newspaper has served its purpose within a few days after being printed. However, bond, book, writing and printing grade papers—the so-called "cultural paper"—require permanent whiteness which can only be achieved by removal of the color-producing material.

Lignin is the principal offender, representing 20 to 28% of the raw material, 50 to 90% of this is removed during digestion and the balance during bleaching with a corresponding loss in yield; however the resulting pulp, if properly prepared, will then be very stable to further color change.

"Bleaching" is not a proper term to cover all aspects of brightness improvement. In the case of the chemical pulps, we prefer to think of bleaching as a continuation of the digestion process and call these subsequent treatments "Pulp Purification" rather than bleaching. For example, chlorination and caustic extraction stages are certainly not bleaching in the usual sense of the term and, in fact, often very little brightness improvement is achieved. On the other hand, treatments with hypochlorite or peroxide are indeed bleaching.

We might now consider further the practical significance of these observations as they relate to the bleaching of indigenous raw materials.

Indigenous raw-materials:

Until it was proved in the early twenties by the efforts of pioneers like Mr. Raitt, that bamboo can yield a pulp that is satisfactory for making paper, no suitable raw material was explored in the country for establishment of this industry on a large-scale Unfortunately, this raw material is available only to a limited extent in our country, in somewhat inaccessible areas after domestic demands are met with. In some areas, a scarcity has occurred for a temporary period because bamboos have flowered necessitating clear felling of all standing clumps and then waiting for a few years before growth takes place again from the seeds. In view of the limited long fibre resources in the country, any major expansion of the industry must be based on short fibred raw materials or a combination of long and short fibred raw materials. A comprehensive survey of the potential resources of long as well as short fibred cellulosic materials especially hard woods for maintaining production, has been indicated. Processes that give higher yields of pulp have also to be investigated for immediate application, to our growing Pulp and Paper industry.

Our mill complemented with a rapid continuous digester has provision for cooking bamboo and bagasse besides hard woods and we have been trying pulping of hard woods to obtain various grades of pulp. In addition to bamboo and bagasse the following raw materials were found to yield pulp of good strength and bleaching properties when used in admixture with bamboo and also economical to use due to their equally good yield.

		Botanical name.
1.	Dadup.	... Erythrina Suberoza.
2.	Wattle.	... Acacia Arabica.
3.	Rubberwood.	.. Pararubber Hevea-Brazeleanes.
4.	Bluegum.	... Eucalyptus globulus.
5.	Eucalyptus.	... Hybrid.
6.	Albesia	... Albecia Lebec.

Process :

Chipping of bamboo and hard woods is carried out in two Summer Veneer chippers and a KMW Chipper, and classified in a vibrating screen and oversize chips are recycled through a Jeffrey re-chipper. The chips fed to our continuous digester has the following chip-size distribution.

Retained	2″ mesh	—	13.0%	
	1″ ”	—	16.0%	
	½″ ”	—	52.0%	rest fines and dust.
	¼″ ”	—	16.0%	
	⅛″ ”	—	2.0%	

Cooking operation is done in our rapid Pandia continuous digester, at 140 psi with a cooking time of 32 mts. for bamboo and wood. For bagasse, the cooking pressure is maintained at 70 lbs. psi with a cooking time of 15 mts. Cooked pulp is continuously blown through the discharger to a 30 m^3 blow tank, and continuously washed in Dorr-Oliver Washers equipped with three 8″ × 10′ filters.

Screening of the pulp is done through a battery of three primary Trimbey screens with one secondary screen for handling the rejects from the primary screens. The accepted pulp from screens is passed through a set of centricleaners, to the thickener for thickening and storage. Recently, a tailing screen was also added to recover the tailings and process it back in the digester.

Bleaching :

We have summarised below the bleaching plant set up in the mills and results of our working, which may be of interest in this Seminar.

Bleaching consists of chlorination in the first stage followed by alkaline hypochlorite oxidation in the second stage and third stages. A fourth stage provision has been made for bleaching to higher degree brightness, when required for special quality papers.

Equipment for bleaching :

Chlorine Mixer : Pulp chlorination is done in the Dorr-Oliver chlorine mixer before it is introduced into the chlorination tower. The chlorine mixer is a rubberlined vessel with twin rubber lined paddles run at 1000 rpm. Pulp at 3% consistency is passed through the mixer with the introduction of chlorine gas in the pulp stream just before the mixer. Chlorine is introduced as a gas only and not as water-gas emulsion. We have made a few trial with chlorine gas emulsifier with no better performance. We shall continue our trials with an independent water boster pump and Pensault's mixer.

We have successfully used indigenous soap stone tiles and special cement for the chlorine tower lining. More than 55% to 60% of the total chlorine consumed by the pulp, is by chlorination in this 12′ × 35′ chlorination tower, provided with two circulators one near the inlet point and the other just below the outlet point, to produce a thorough mixing of the pulp in this pump-through tower.

Pulp is washed over three 8′ × 10′ Dorr-Oliver vacuum filters and discharged through a conveyor screw into the bleached stock chest. Heater mixers are provided between the second and third bleaching stages.

Hypochlorite bleaching in this four stage bleaching system is carried out in the two downflow hypochlorite towers, 13.5′ × 28′ height equipped with dilution nozzles and circulators at the bottom. Bleaching is done at a consistency of 10%.

Trials on Hard-wood Pulping : —

Laboratory trials were made on cooking the chips from indigenous hard wood (ie.) dadup, Wattle, Albesia and Rubber wood and bleaching the resultant pulp to assess the suitability of these materials for plant scale use.

The trials were carried in the lab. autoclave at 20% alkali as NaOH on the O.D. wt. of the raw-material at 100 lbs. psi. 1:4 bath ratio and cooking time of 3 hrs. The results obtained are tabulated below.

	Dadup.	Wattle.	Albesia.	Rubber-wood.
Yield % ...	52	57.4	50-52	55.2
KlNo. ...	22-23	21	18-19	20.5
Initial freeness ...	16.9	16.0	17.9	16.7
Physical Strength				
At 45°SR.				
Tear Factor ...	38	44	41.8	40 2
Burst factor ...	63	67.8	50.5	71.4
Breaking length ...	5300	5418	7373	5086
Double folds ...	54	78	317	247
At 55°SR.				
Tear Factor ...	42	44.5	42.8	45.6
Burst Factor ...	52	66.7	46.5	56.1
Breaking length ...	5500	5379	7250	5361
Folds ...	56	118	190	301
Chlorine demand	13-14%	12-13%	8-9%	10%
Brightness (PV) ...	75	75	71	70-72

It was noticed that under suitable cooking conditions, hard woods, viz. Erythrina Suberoza, Acacia Arabica and Albecia gave pulps of adequate physical properties in terms of strength and bleachability for production of normal grades writing and printing papers in admixture with about 40 to 50% of other long fibered pulps. Only in the case of Acacia, the unbleached pulp was found to be comparatively darker and consuming more chlorine to attain the same degree of bleaching.

Rubber Wood (Hevea Brasiliensis):

Is available in appreciably abundant quantities in Kerala. This wood is being presently used in packaging industries and there has been no other suitable use yet found for this abundantly available material from clear-felled rubber plantations before the replantation work commences, since this has not been considered as a good fuel on account of its fast burning and smoky characteristics. Our Mill made some laboratory and plant scale trials on the utilisation of rubber wood for pulping and it was found that rubber wood is likely to provide no technical difficulties in pulping and a pulp of acceptable quality can be made either by cooking rubber wood exclusively or in admixture with bamboo.

It has a specific gravity of 0.55 and fibre characteristics were noticed to be similar to other hard woods with its average fibre length of 1.55 mm., fibre diameter of 22 microns, and cell wall thickness of 2.8 microns.

We have to mention here that the mill did experience a difficulty in processing this material on account of latex entering the pulp system and causing web breaks in the presses and calender of the Paper Machine. This difficulty is being now gradually overcome by better debarking at the felling site and cleaning the surface free of latex extrusions before despatch to the mill.

Rubber wood chips were cooked on a plant scale and the characteristics and suitability of the pulp were studied. A resume of the results of these plant scale trials on pluping of rubber wood. is given below:—

	Bamboo	Bagasse.	Rubber-wood.
Cooking.			
Alkali as Na OH ...	20%	10%	18%
Pressure-lbs. psi. ...	140	70	140
Cooking time. Mts. ...	30	16	25
K. No. ...	16-18	12-14	18-20
B. Liqr. Tw at 700°C. ...	14	6-7.5	12-12.5
Residual alkali ...	15-16 gpl	—	13.3 gpl.
Initial freeness. ...	17-20	30-35	19,5
Bleaching:			
Chlorine demand ...	14%	10-11%	14-15%
Brightness ...	75-78 PV.	70-72 PV.	75 PV.
Strength Characteristics.			
40°SR.			
Burst Factor ...	28.5	30.6	38.5
Tear Factor ...	61.1	61.8	52.6
Breaking length ...	4414	4628	4837
Folds ...	27	54	15
50°SR. ...			
Burst Factor ...	35.2	39.5	39.5
Tear Faetor ...	56.1	43 7	49.5
Breaking length ...	5140	5264	4212
Folds ...	24	18	57
60°SR.			
Burst Factor ...	30.1	35	35.7
Tear Factor ...	56.1	53.4	47.2
Breaking Length ...	4678	4029	4198
Folds ...	22	9	21
Fibre length: Mean ...	2.3 mm.	1.5 mm.	1.37 mm.
Max ...	3.0 mm.	2.2 mm.	2.00 mm.
Min	0.9 mm.	0.5 mm.	0.84 mm.

It would not be out of place in the context of discussions on bleaching of pulp from indigenous raw materials, to mention something about our experience on alkali extraction in pulp purification and bleaching. We have tried at varying concentrations and percentages extraction as specified in conventional practices for chlorinated pulps, but the results obtained were varied both in relation to improvement in strength characteristics as well as economics.

Addition of caustic in hypochlorite stages (Hot alkaline oxidation) as a buffering agent has also been tried to have the bleaching carried out at a pH of 8 to 8.5.

It has been our experience that 2½% addition of alkali for extraction after chlorination, does not give an accepted shade or reduction in chlorine consumption, one would normally expect. Shade variation was still there though reversion was much less. When the extraction dosage was increased to say 4½% to 6%, variation was less and chlorine consumption also became less by only one per cent. However, there was no specific increase in strength characteristics though the reversion problem was practically overcome. The advantages obtained this way, did not justify the increase in cost to an extent of about 40 Rs./tonne of pulp. Hence this was discontinued.

Another observation noted during these trials, was that the K. No. of chlorinated pulp was of the order (12-13) and when only pure caustic extraction was done; this K. No. could be brought down to (8 or 9). On the other hand, when hot alkaline extraction was done (i.e.) Hypochlorite and 2% caustic was added, the K.No. could be brought down to 5 and sometimes even lower.

Hence, we feel, that in our pulp obtained by cooking in a rapid Continuous Digester, there are certain compounds, like colouring matters that are left back which need oxidation more than extraction. Alkali added as a buffer in the first stage along with hypochlorite gives the desired result, in the form of better brightness in C.H.H. sequence and reduces the reversion of brightness of the final bleached pulp. There is evidence that the material which consumes chlorine and reduces permanganate number is largely something other than lignin and that this material is not rendered soluble by chlorination. Subsequent alkali extraction produces a dark coloured effluent but still does not reduce the permanganate demand as much as would be expected. Hence, the C.H.H. sequence with buffer caustic in hypochlorite stage to keep bleaching done at a pH of 8 to 8.5, was selected for our particular set up.

After we switch over to stationary digesters cooking in future, and if pulp properties undergo any change, we shall further continue to try and adopt a suitable sequence, economical and suitable to us.

The plant is equipped with a continuous hypochlorite preparation plant. Milk of lime enters the lime cooler at 70°C. This cooler is provided with a main evaporation chamber under vacuum reducing the temperature of the milk of lime from 70°C to 45°C. Vacuum is maintained at 27″ Hg. The slurry is stored at 10% concentration and afterwards it is diluted to 3½%. Subsequently, the temperature falls to about 40°C. This slurry is processed through Door-clones, where the grits are separated. The accepted slurry is capable of passing through a 250 mesh screen before being pumped to the reactor and then on to the storage tank. Practically. no settling is required as the bleach liquor contains very little sludge. This purified liquor is pumped up from here at a concentration of 30 g/l.

Bleaching of Semi-chemical and Mechanical pulps:

With increased cost of production, we, Pulp and Paper Technologists cannot but think of producing very soon high yield pulps by semi-chemical and mechanical pulping methods to reduce the losses the industry is undergoing at present.

Bleaching of semi-chemical pulp obtained from Hard wood and also Raffinator Mechanical pulp to an acceptable shade of brightness and mixing up with highly bleached chemical pulp to produce a sort of cheaper printing paper, will become popular very soon. When this will enable to find a better use for the Raffinator mechanical pulp, it also will go a long way to satisfy the demand for a cheaper rate of writing and printing papers in our country.

In this case, neither a real high brightness nor the great permanence is required. A brightness of 60 to 65 G.E. is adequate for printing purposes and 65 to 70 G.E. for speciality publication purposes. In such cases, any bleaching process which removes lignin is not desirable as it reduces the yield. This eliminates chlorine and chlorine dioxide as bleaching agents, as these are specific reactants for dissolving lignin. Therefore, hydrosulphites of zinc or sodium or peroxide bleaching are considered as suitable bleaching agents. Hypochlorite can also be used occasionally.

The Effect of sulphidity on bleaching of pulp in our Mills:

We have tried to cook our chips with a liquor containing practically nil sulphidity for about three months duration. We found that K. No of pulp was always higher than 20 and we have to use as high as 18% total chlorine to bleach our pulp to a required degree of brightness. Even then, we found there is lot of variation in the pulp and the quality was now and then below standard. Later, we tried to vary the sulphidity from 18% to 25%. We found that we could get much softer pulp, which could be bleached without much shade variation at 12½ to 13% total chlorine consumption. The optimum sulphidity, which gave us the desired results, was found to be 20 to 21%. At present, we are trying to maintain our sulphidity more or less at this level.

Improved methods of bleaching and economics:

Kraft bleach plants have a common need for higher brightness pulp with better brightness stability. Multi-stage bleaching systems using one chlorine-dioxide bleaching stage can consistently produce pulp above 85°PV. Hypochlorite bleaching increases the carboxyl content of the pulp probably by oxidation of carboxyl group chlorine dioxide bleaching decreases the carboxyl content by removal of lignin associated carboxyl groups from the pulp, thereby reduces reversion characteristics of the pulp.

In view of the increase in cost of sodium sulphate on which the entire name of sulphate process has come to stay, increased consideration is being given to the manufacture of chlorine dioxide by reacting sulphuric acid with sodium Chlorate and sodium chloride (Rapson's R_2 process) in a generator resulting in production of sodium sulphate, chlorine dioxide and chlorine. As long as the cost of salt cake was in the order of Rs. 400/- per tonne at mill site, the economics of running a chlorine dioxide generator in a pulp mill was not convincing. But to-day the situation is different. The cost of salt cake as is received in any mill is somewhere of the order of Rs. 800/- and even at this price, sometimes it is not available. As such, chlorine dioxide which was so far considered as a costly bleaching agents, can be thought of being manufactured in the mill itself along with sodium sulphate as a by-product. Of course, the problem of obtaining sulphur and sulphuric acid will be a major hurdle to be crossed over in view of import restrictions. But chlorine dioxide bleaching by this process with its consequent advantages of chemical balance in sulphate mills, deserves further deep study by all the pulp and paper technicians.

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