STUDIES ON
ENVIRONMENTALLY COMPATIBLE PULPING AND BLEACHING OF BAGASSE

A DISSERTATION

submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF ENGINEERING
in
PULP AND PAPER

by

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"I dedicate this report to my
beloved parents, wife, son and
all those well wishers who always
inspired, encouraged and stood by me
at many a difficult occasions during the
entire course of my Master of Engineering."

DECLARATION

I hereby declare that the work which is being presented in the thesis paper entitled "Studies on Environmentally Compatible Pulping and Bleaching of Bagasse" submitted to University of Roorkee, in partial fulfillment of the requirements for the award of degree of Master of Engineering in Pulp and Paper Technology from Institute of Paper Technology, Saharanpur, is an authentic record of my own work carried out during the period from June 1995 to December 1995, under the guidance of **Dr. J.S. Upadhyaya**, Reader at Institute of Paper Technology, Saharanpur and **Dr. S.K. Kapoor**, Scientist E-II at Central Pulp and Paper Research Institute, Saharnpur.

The matter presented in this report has not been submitted by me for the award of any other degree.

Dinesh Chand Mohta

Date : 4th Jan. 1996
Place: Saharanpur

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

Bagasse is an important raw material resource for pulp and papermaking in India. It has all the requisite properties to replace the conventional raw material like bamboo and wood for economical manufacturing of high grade of paper.

Conventionally, bagasse is being cooked with soda to a reasonable Kappa number ranging between 20-24. The addition of a small fraction (0.05-0.1% on o.d. basis) of AQ has helped reduce the Kappa number of the pulp significantly (sometimes it is reduced by 40-50% of kappa number of soda pulps). The brown stock washed pulp is normally being bleached with elemental chlorine. The chloride ions generated from chlorine reacts with lignin and appear in bleach plant effluent as "original chlorine" resulting in increased pollution load to the stream.

Considering environmental impact of chlorine, it is imperative to restrict the use of it to maximum possible extent in the bleaching process. As the amount of chlorine is directly related to the kappa number of the pulp to be bleached, the first and foremost need is to look back into the cooking process and explore the possible remedial solution for reducing the kappa number of the pulp as minimum as possible. As the delignification has its own limitations, the most suitable eco-friendly way of achieving the kappa number could be pre-bleaching of pulp with molecular oxygen. The pre-bleaching of brown stock pulp in the presence of caustic soda has the advantages of low bleach chemicals consumption and higher bleaching efficiency in later stages.

Modification of bleaching process is generally the least expensive and simplest means of reducing environmental load of bleach plants. The replacement of chlorine by chlorine dioxide (D/C ratio as 70/30) has helped reduce the color and toxicity of bleach plant effluent significantly.

The development of chlorine free bleaching employing oxygen, hydrogen peroxides and ozone has reduced the AOX generation to nil and the effluent so generated may be utilised for burning in chemical recovery for generation of steam.

In this experimental work it has been planned to study the various pulping and bleaching techniques for bagasse, a promising future raw material for countries like India, compatible to environment.

1. INTRODUCTION

Environmental protection is a dominant issue now a days and new governmental regulations and pressure from the society are forcing industries to take drastic changes in the way chemical pulps are being produced and bleached. Chemical pulping process is the most widely used process for papermaking. The organic chlorine compounds formed during the bleaching of chemical pulp have perhaps attracted most attention in recent years earlier measures taken by the pulp industry to solve the chlorine problem have focused on improving effluent treatment methods, i.e. measures external to the process. Today the emphasis of research in this area has shifted more towards improving the processes. The efficient and more selective pulping processes reduce the amount of lignin going with the pulp to bleach plants. Also the amount of chlorine required for bleaching is being reduced by the use of bleaching chemicals like chlorine dioxide, oxygen, hydrogen peroxide and ozone with an ultimate aim of completely chlorine free bleaching.

The environmental loading is very less caused by final bleaching as compared to that of earlier bleaching stages. Thus, the often proposed reduction in final pulp brightness will do little to reduce the amount of chlorinated compounds discharged with the effluents. The aim of researchers working in this particular field is to overcome the chlorine problems associated with bleaching by modifying cooking stage by various means or the subsequent chlorine free residual delignification stages such as oxygen-ozone etc. in order to minimise the amount of lignin going for chlorine bleaching. (1-3)

1.1 Objective of the Present Studies

Environmental regulations on industrial emission, particularly the emission of sulfur compounds, together with the need of more effective utilisation of raw materials have contributed to the intense work done in recent years for the development of cooking methods which will give similar pulp qualities and preferably higher yields than the kraft method without the addition of sulfur compounds. One such method might be old soda process, if only the yield and pulp quality could be improved. Many different additives have been used to improve the yield and quality of soda pulp. Among the additives, anthraqinone (AQ) has given quite encouraging results. It appears that AQ is still the most cost effective sulfur free accelerator for alkaline pulping, albeit of limited applications. The soda-AQ process does offer a direct advantage of eliminating air pollution associated with kraft process.

The suitablity of bagasse as a papermaking raw material has been studied extensively. Even as early as in the 1950's, the chemical compositions - fiber dimensions, need of depithing, pulping characterstics and bleachability were studied. These studies revealed that bagasse, if properly depithed , is easier to pulp than wood and the resulting pulp is easier to bleach giving a good quality short fiber pulp. More studies have been concentrated on the bleachability of the bagasse pulp with various bleach sequences. There is a dire need for developing processes which is compatible with environment but produces a good quality market pulp.

2. PULPING, BLEACHING AND ENVIRONMENT

More than the eliminating the use of chlorine gas, there is clear trend to avoid the use of any chlorine compound in the bleaching of pulp, so as to reduce the quantity of chlorinated organics going in the effluent discharges. Consequently, pulp mills are being upgraded for improving the effluent treatment facilities and introducing process modifications to meet new chlorinated organics discharge limits. Fig. 1 gives environmental impact of chlorine and chlorine containing compounds. (37,38)

The conventional CEHH bleaching process produces AOX to the tune of 3-4 kg per ton of pulp, while elemental chlorine free (ECF) processes discharge 0.1-1.0 Kg per ton of pulp, depending on the technical status of the mill. Important techniques to reach the low AOX levels (below 0.2 Kg per ton of pulp) are oxygen delignification/pre-bleaching and AOX minimised chlorine dioxide, TCF techniques give no detectable AOX values below 0.1 Kg per ton of pulp.

The kappa number of the pulp to be bleached is directly related to the generation of AOX in bleach plants. So the efforts are on to keep the kappa number of the pulp as minimum as possible. The extended delignification, RDH, superbatch processes and use of anthraquinone during cooking has reduced to the kappa number of the pulp considerably. Moreover the pulp to be bleached should have minimum carry over of black liquor. An efficient brown stock washing system has the potential of reducing the dioxin and toxicity level by 10-15% while AOX may be reduced by 15-20%. Because there is no such pulping process which can remove all the lignin without seriously degrading the carbohydrate fraction, thereby affecting both strength and yield. Hence the remaining lignin is to be removed by employing dif-

ferent chemicals (Chlorine, Chlorine dioxide, oxygen, hypochlorite, hydrogen peroxide, ozone, sodium hydrosulfite etc.) in bleaching. (1-12, 30, 32)

Modification of bleaching process is generally the least costly and simplest means of reducing environmental load of bleach plants. The growing concerns about Chlorinated Organic Compounds have resulted in a decreased use of chlorine in the first stage. It is being replaced by more and more chlorine dioxide and hypochlorite in the later stages are also rapidly being eliminated in favour of chlorine dioxide. In principle, there are three ways in which chlorine dioxide may be used in the first stage.

- In mixtures with chlorine
- In a sequential order with the chlorine dioxide usually preceding the chlorine treatment
- As a total replacement of chlorine

When a moderate amount of chlorine dioxide is applied in a sequential ClO_2/Cl_2 treatment, most of the chlorine dioxide is consumed prior to the addition of chlorine. As a consequence, little chlorine dioxide may remain to exert its protective influence on the carbohydrates in the ensuing chlorination phase of the treatment, as compared to the case when chlorine dioxide and chlorine are mixed. The sequential addition of chlorine dioxide and chlorine is preferred when delignification is the prime consideration.

The use of chlorine dioxide in the first stage decreases the color of the bleach plant effluent. This effect becomes more pronounced with an increase in the proportion of chlorine dioxide used in this stage. The addition of chlorine dioxide in the first stage also helps reduce the toxicity of the effluent.

Therefore the environmental regulations has made the use of chlorine dioxide a must and more over it is economical too, even if total replacement of chlorine by chlorine dioxide is done. (12)

Moreover, the addition of Hydrogen peroxide or Oxygen or both is reported to have further cut down the stream consumption of chlorine dioxide. The TOCl formation has also been reduced due to oxidative extraction.

The formation of chlorinated compounds have been decreased by pre-bleaching the pulp with oxygen. By employing oxygen pre-bleaching the kappa number of the pulp can be reduced by 40-50% without affecting much the viscosity of pulp and thereby decreasing the consumption of bleaching chemicals in the following stages. (13-16)

The pretreatment of pulp with xylanase and use of other enzymes for bleaching too has reduced the consumption of chlorinated chemicals in the later stages and thereby re formation of chlorinated organic compounds. This process has a great potential in India. To use the commercial enzymes, it is important to assess and optimise the process under Indian conditions with the pulps produced form different raw materials. This process has been implemented at different places all over the world for reducing the pollution load of effluents and of course to obtain a pulp of higher brightness without any adverse effect on pulp properties and yield. The use of Pulpzyme HA may reduce the chlorine consumption by 30-35% and TOCl content by 30% in the extraction stage effluent. (18-24)

The development of chlorine free bleaching employing oxygen, hydrogen peroxides and ozone constitute milestones in bleaching technology. Now the efforts are on to commercializes the use of chlorine free sequences involving Oxygen, Ozone and Hydrogen

peroxides so that the AOX generation is reduced to nil and the effluent is used for burning in chemical recovery and generating energy. (13, 31)

The other possible way of reducing the environmental load of bleach plants could be to reduce the fresh water intake by closing the plant. The technological modifications and some in plant measures have made it possible to recycle the effluent at different levels. Now a days a completely closed bleach plant is a result of the introduction of counter current washing and replacement of chlorine and Hypo with chlorine dioxide in a conventional system. And later the emergence of total chlorine free bleaching the zero effluent discharge is a reality now. (26-29, 33, 34, 36

2.1 OXYGEN PRE-BLEACHING OF PULPS (3, 4, 6-12)

Due to environmental concerns oxygen pre-bleaching has played an important role in reducing the consumption of chemicals in the following stages of bleaching. It is a continuation of delignification process with oxygen in presence of an optimum dose of alkali. In bleaching, Oxygen has resulted in significant environmental benefits, such as substantial reduction in color, COD, and formation of chloro-organics. The use of oxygen, alone or in combination with hydrogen peroxide in reinforcing alkaline extraction, "activating" the lignin retained in the fibres towards subsequent treatment with chlorine dioxide, consequently, requiring less chlorine dioxide in the following stage. Thus, substantial reduction in the generation of chloro-organics and/or savings in chemical costs can be realised.

Every related benefits include recovery of heat from the burning of the material removed from the pulp in the oxygen stage, lower refining energy equipments of oxygen bleached pulps

and the fact that the manufacture of oxygen requires only about one eighth of the energy required to make a chemically equivalent amount of chlorine.

Moreover is the development of the less expensive medium consistency technologies, and, of course, the increasing concern about the formation of chlorinated organic, particularly of potential toxicants such as polychlorinated dibenzodioxins and dibenzofurans, by chlorine and chlorine-based bleaching agents have lead to oxygen delignification and bleaching capacity world wide.

Two key obstacles that must be overcome in using oxygen to bleach pulp are its tendency to attack carbohydrate as well as lignin and difficulty in getting it to the reaction site within the fiber wall. Among the factors governing selectivity in oxygen bleaching, one of the most important is the transition metal ion content of the pulp, since these ions catalyze the generation of harmful radical species, copper and manganese, all of which have this effect. One approach to dealing with the problem is to remove the metals by acid washing prior to the oxygen stage. Another is to add compounds to the pulp that inhibit carbohydrate degradation. These compounds are called carbohydrate protectors. The protector of greatest commercial importance is the magnesium ion.

It is normally applied at levels as low as 0.05-0.1% (as Mg^{+2}, o.d. pulp basis). It is believed to function by precipitating as magnesium hydroxide, which adsorbs the metal ions, making them unavailable for catalysis of peroxide decomposition.

The stoichiometry of oxygen bleaching is such that, for each unit of kappa number reduction, about 0.1-0.13% NaOH (o.d. pulp basis) and a similar amount of oxygen are required. In high con-

sistency system, alkali consumptions in this range are realized in practice. Medium consistency systems tend to consume slightly more alkali, because its concentration is lower at a given charge in these systems. Oxygen consumptions are usually somewhat higher than theoretical because of losses due to reactor venting or entrainment with the pulp.

The presence of alkali plays an active role in delignification. Moreover it also neutralises the organic acids formed during delignification. So if alkali charge is low, it becomes very difficult to dissolve the degraded lignin and reaction between oxygen and lignin would slow down. And the degraded dissolved lignin would be adsorbed on the surface of the fiber surface resulting in the higher consumption of chemicals in the later stages. On the other hand if higher alkali is charged, although the delignification is enhanced but carbohydrates are also badly damaged. Therefore an optimum dose of 2-3% of alkali is charged. The higher oxygen pressure is required in order to increase the delignification rate because oxygen has a lower solubility in alkali. It has been observed that the pulp yields have insignificant changes at the sufficient oxygen gas and delignification rate can be controlled in the range of 40-45% at an oxygen pressure of 5 Kg/cm^2.

3. STUDIES ON PULPING AND BLEACHING OF BAGASSE

Bagasse is an important source of raw material for pulp and paper making in countries like India where sugar cane is produced in plenty. In India it is being used abundantly in the industry as in the present day context there is an acute shortage of raw materials like wood and bamboo. Hence there is a strong need for more quantitative understanding of the role of different process variables in determining pulping rate, which can result higher yield and more uniform quality of pulp. More over from the point of view of environmental concerns and increasing competition and customer's awareness has forced the manufacturers to adopt a process which is environmentally compatible and gives a product which has higher brightness and strength.

There is not much literature available on bagasse which can give an idea as to what process for pulping and bleaching is best suited as far as its impact on environment is concerned. Hence it was planned to carry out a detailed study on the development of a process to manufacture a pulp of high quality and causing least environmental load.

Normally soda pulping is the technique for pulp and paper making from bagasse. Corrugating medium, boards and packaging paper are produced from high yield unbleached bagasse. Bleached bagasse pulp are extensively employed as a major furnish for fine quality writing, printing and other grades of paper. The process used are mechano-chemical, semi-chemical, neutral sulfite and chemical (soda or sulfate processes with or without Anthra-quinone. Quite a few industries have also used lime or lime-soda processes.

Soda-Anthraquinone, a non sulfur pulping process of fibrous materials involves soda cooking in presence of small amount of Anthraquinone or its derivatives, which has marked catalytic effect on alkali delignification reaction. This results in improved yield with less rejects without affecting any quality of pulp. Even though the effect of anthraquinone on pulping of hardwood and softwoods are extensively reported in literature, the information on non wood raw material in particular is not abundantly available.

In the next phase of the project it was planned to study the various possibilities, schemes of bleaching sequences which use elemental chlorine, chlorine containing compounds and total chlorine free chemicals for bleaching of soda and soda-AQ pulps from bagasse. Prior to regular bleaching of bagasse pulps pre-bleaching with oxygen was also planned so as to reduce the Kappa number of the pulp as much as possible before normal bleaching. Following bleaching sequences were to be studied-

- Conventional bleaching sequence CEH
- Sequential Chlorination in first stage by replacing 70% of the total chlorine by chlorine dioxide i.e. C/DEHD
- Elemental chlorine free bleaching sequence i.e. DED
- Total chlorine free bleaching $OE_{o+p}P$

4. EXPERIMENTAL

4.1 Raw Material Preparation

The whole bagasse was procured from M/s Century Pulp and Paper, Lalkua and M/s Shiva Paper Mills, Rampur. The dry and wet depithing of bagasse was done at the recently installed depithing plant at Institute of Paper Technology, Saharanpur. The physical composition of moist and wet depithed bagasse were determined as per Tappi UM-3.

4.2 Soda Pulping of Bagasse

The depithed bagasse (1500 gms od basis) was pulped in a 0.02 m^3 litre rotary type laboratory electrically heated digester using 12% sodium hydroxide (an optimum charge of the cooking chemical was taken from the literature) as Na_2O as cooking chemical on oven dry bagasse basis. The other process conditions were maintained as stated in Table 2.

4.3 Soda-AQ pulping of Bagasse

The depithed bagasse(1500 gm oven dry basis) was pulped in the 0.02 m^3 laboratory electrically heated digester with 12% sodium hydroxide charge as Na_2O and a dose of 0.1% AQ on od bagasse basis (the charge of chemicals are reported to be optimum in literature). Rest of the process conditions are same as maintained during soda cooking.

4.4 Washing of cooked bagasse

The soda and soda-AQ cooked bagasse pulps are washed separately on a laboratory flat washing system having double fold cloth (300 mesh) placed on the wire mesh. The liquor is squeezed from the pulps and the filtrates are collected for various chemical tests. Now the pulps are washed thoroughly with fresh water on a buckner funnel under suction. The washing is continued until the filtrates are colourless and the pulp pads are slush dry.

4.5 Screening

The pulp is disintegrated for five minutes in water and screened over a laboratory vibration screen of 0.15 mm slots. The screened pulp is dewatered and stored at 4°C. The screened rejects are collected and dried in the oven at 105 2°C.

4.6 Oxygen Delignification/Pre-Bleaching

The soda and Soda-AQ pulps were oxygen delignified/pre-bleached in the 0.02 m^3 laboratory digester fitted with lids incorporating valves to introduce oxygen into the vessel. Pulp samples (100gm oven dry basis) were mixed with magnesium carbonate (1%, pulp basis), sodium hydroxide (2.5%, pulp basis) and water to give pulp concentration of 10%. The mixtures were placed in the digester which were pressurised with oxygen (a boost of 5 Kg/Cm^2 to the initial pressure of digester at 55-55°C) and heated at 110-115°C for 60 minutes while time to temperature was 30 min.

4.7 Bleaching of Pulps

The initial chlorine, chlorine dioxide/chlorine and chlorine dioxide stages were done in plastic bags as per the conditions mentioned in Table . In chlorine dioxide/chlorine bleaching, the chlorine dioxide and chlorine was maintained at an optimum (as per literature) dose of 70 and 30% respectively of the total chlorine charge to the first stage. Also the chlorine dioxide was added 30 seconds ahead of the chlorine. Unless otherwise mentioned in the tables the active chlorine multiple was 0.18 (the active chlorine multiple is the quantity of chlorine and/or chlorine dioxide (as active chlorine) applied to the pulp in the first stage of the bleaching sequence, expressed as a percentage on a pulp basis, divided by the Kappa number of the pulp). The chlorine and chlorine dioxide solutions had a molecular content of 5.6 and 3.0 gpl. There was no adjustment of the pH. The amount of residual bleaching chemical was determined and in nearly all the instances it was found not detectable. If there was a residual it was less than 0.2% (active chlorine on a pulp basis).

The E-stage bleaching was done at 10% concentration in plastic bags. The plastic bags were placed in water bath for controlling the temperature.

The E_{o+p} stage was done at 10% pulp concentration in a laboratory rotary type digester and the conditions were maintained as given in Table 7 unless otherwise mentioned. The amount of alkali and hydrogen peroxide charged were 1.5% and 0.5% respectively and now the vessel was pressurised to 5 Kg/cm^2.

The final stage bleaching with hypo, chlorine dioxide and hydrogen peroxide as the case was, were done in plastic bags and the process conditions were maintained as given in Table 6 and

7. The pH in the D stage of C/DEHD and two stages of DEDED was adjusted by sulfuric acid or sodium hydroxide at the beginning so that a final pH of 3.5-4.0 was maintained. In case of final P-stage bleaching of $OE_{o-p}P$, pH was adjusted by Sodium Hydroxide. The amounts of residual bleaching chemicals after each stage of bleaching in final stages varied from nondetectable to 0.2% (active chlorine on a pulp basis) with most of the filtrates having no residual chemicals.

The amount of the chemicals charged in each stage of bleaching is given in Table 8.

The pulp was washed thoroughly with fresh water on a Buckner funnel under suction after each stage of bleaching and it was continued till the water became clear and the pad was slush dry.

4.8 Chemical Tests

The pH, total solids, suspended solids, dissolved solids, COD (chemical oxygen demand) were determined for black liquor of soda and Soda AQ pulps and combined bleach effluents of each sequence. This may also please be noted that no effluent was recycled else where for washing or dilution.

Chemical Oxygen Demand (COD) of different bleaching effluents were measured by using COD reactor from Hach Company, USA according to ASTM.

The color of the bleaching effluents were determined by using spectrophotometer from Hach Company, USA according to ASTM.

4.9 Pulp Properties

The Kappa number of the screened pulps were determined according to TAPPI standard method T-236-os-76.

The SCAN C15:62 method was used for determining the CED intrinsic viscosity of oxygen prebleached soda and soda-AQ pulps by using capillary tube viscometer (Sweden Made) at 25°C.

The breaking lengths of Oxygen prebleached soda and soda-AQ pulps were determined by using Pulmac Zero-Span instrument.

The papermaking properties of the bleached pulps were evaluated as follows. The pulps were beaten in a stainless steel PFI mill under standard conditions as per ISO DP 5264 method i.e.

Beating Pressure	- 17.7 N/cm
Relative Speed	- 6.0 m/s
Beating Consistency	- 10% on weight basis
CSF measurement	- ISO DP 5267

Handsheets ,made as per ISO DP 5269 and dried on plates in standard conditions, were conditioned at 27 1°C and 65 5% relative humidity, and tested according to ISO standards for the following and the results quoted on an oven dry grammage-

Tensile Index	- ISO 1924
Tear Index	- ISO 1974
Burst Index	- ISO 2758

5. RESULTS AND DISCUSSION

5.1 Fiber Characterisation and Depithing of Bagasse

Composite samples of whole bagasse was prepared and moist and wet depithing was done. The samples of bagasse was procured from two North Indian mills. The results of the two bagasse samples analysed as per Tappi Um-3 for their physical composition indicated the content of fiber as 67% and 69%. The rest of the amount contained pith and epidermal cells and water solubles. The results of the analysis are conforming the general physical composition of bagasse available from different sources.

The whole bagasse was depithed in moist and wet depither which removed almost 80% of the total pith present in the whole bagasse. The wet depithed bagasse after drying was again analysed for useful fibers and pith fractions and gave the following results-

Useful fibres	79.7%
Pith	13.6%
Water solubles	6.7%

The above data also resembles the data obtained from the two mills from where the bagasse was procured.

5.2 Pulping of bagasse

The conventional soda pulping and Soda-AQ pulping of bagasse was done in a rotary digester with 12% (an optimum dose as is available from literature) sodium hydroxide as Na_2O in either case while a 0.1% (optimum dose as available from literature) of Anthraquinone was charged for Soda-AQ pulping. The rest of the conditions for two types of cooking were maintained same. The results are shown in Table 3 for the conventional and Soda-AQ cooks. Under the same alkali charge , the soda-AQ pulp gave much lower kappa number as compared to conventional soda cook (13.3 vs 21.5). However the soda-AQ cook also resulted in much lower yield than the conventional soda cook (51.4% vs 53.6%) while the screened yield was slightly lower than the soda cook (49.3% vs 50.1%). The viscosities of the unbleached pulps are almost same in either of the cases (900 cu.cm/g vs 860 cu.cm/g).

5.3 Oxygen Bleaching of Bagasse Pulps

The soda and soda-AQ pulps were oxygen prebleached so as to enhance the delignification and thus reducing the Kappa number. The amount of sodium hydroxide used to treat the soda and soda-AQ pulps was 2.5 % on pulp basis. The other process conditions and results of oxygen pre-bleaching for soda and soda-AQ pulps are given in Table 4 and 5 respectively. It can be seen from the results that the pulps respond very well to oxygen bleaching and about half of the remaining lignin can be removed easily. The delignification levels off at Kappa numbers 11.8 and 6.8 for soda and soda-AQ pulps respectively. This conforms to the general rule that about 40-45% of the remaining lignin (Kappa number 11.8 vs 21.5 for soda pulp while 6.8 vs 13.3 for soda-AQ pulp) can be removed before the strength properties of the pulps are seriously affected. The viscosities of the oxygen bleached pulps were

[illegible]

measured as this property can be indicative of fibre damage if the value is below a threshold level. The values of the viscosities (820 vs 900 cu.cm/g for soda pulp while 790 vs 860 cu.cm/g) for oxygen bleached soda and soda-AQ pulps show that there is slight loss of viscosities as compared to the corresponding unbleached pulps.

The pulp evaluation data for the unbleached pulp and the oxygen bleached pulps were determined. A measure of possible fibre damage in a pulp can be obtained form a plot of the tear index versus the tensile index. This was done for the pulps and it can be seen from Fig.2 that the oxygen bleached pulps have slightly lower tear values at a given tensile than the unbleached pulps. This also confirms that there has been some fibre weakening during oxygen delignification. The yield losses for the two types of pulps during oxygen bleaching have been very marginal.

5.4 Bleaching Studies

The one of the objectives of this study is to develope an environmentally compatible bleaching in order to achieve the brightness of the pulps at the prerequisite level with good strength properties and causing less environmental problems. The targeted ISO brightness for soda and soda-AQ pulps was 80-85%. In view of this, the pulps were bleached by employing the following sequences -

(i) Conventional bleaching technique employing CEH sequence
(ii) Sequential chlorination and final stage bleaching with Chlorine dioxide
(iii) Elemental chlorine free bleaching employing DED sequence
(iv) Total chlorine free bleaching

The soda and soda-AQ pulps were also pre bleached with oxygen and later bleached separately by employing CEH, C/DEHD and DED sequences.

The process conditions and the dose of chemicals in various stages of bleaching sequences are given in Tables 6, 7 and 8. The active chlorine multiple of 0.18 was kept in the first stage of either of the bleaching sequences. The soda-AQ pulp requires less chemical as compared to soda pulp because of its lower Kappa number. The consumption of the bleaching chemicals was further reduced for the oxygen delignified pulps because the lignin content was reduced to almost half the amount in original pulps.

In the conventional bleaching involving CEH sequence, the consumption of the chlorine drastically reduces as the kappa number of the pulp decreases. In case of the soda pulp it is highest at 54 Kg/Ton of pulp while it is only 17 Kg/Ton of pulp in case of oxygen bleached soda-AQ pulp. The brightness achieved at the end of the final bleaching in each case is almost same except a slightly lower value for the soda pulp.

In the sequential chlorination, as noted from the literature an optimum ratio of 70 to 30 was maintained for chlorine dioxide and chlorine. The substitution of chlorine with chlorine dioxide had a very large effect on the total environmental load of this bleaching sequence. As shown in the Table 8, the bleaching chemical requirement went down with the decrease in Kappa number. The Table 11 and 12 shows that environmental load is at lower level when compared to the corresponding CEH sequence. It is also notable from the table that it is lowest for the soda-AQ oxygen prebleached pulp because of its having the lowest kappa number and the substitution of chlorine in first stage and of course

final stage bleaching with chlorine dioxide decreased the environmental load considerably. More over it had the highest brightness with comparable strength properties.

In the next stage of bleaching studies the 100% substitution of chlorine with chlorine dioxide was done and a ACM of 0.18 was maintained in the first stage of DED sequence. The total replacement of chlorine further reduced the environmental load very significantly. In comparison to C/DEHD the environmental load of DED sequence is very low, as is evident from Table 11 and 12.

Bagasse pulps can be bleached efficiently with oxygen and peroxide. It has produced considerable insight over the chlorine free bleaching of bagasse. It has been frequently stated that for achieving TCF brightness levels, the kappa number of the brown stock pulp to be bleached must be reduced to lowest possible levels. This is the reason soda-AQ pulps has the higher final brightness as compared to soda pulps (76.5 vs 73.6% ISO). However the brightness of TCF bleached pulps are lower than those of pulps bleached with chlorine or chlorine containing compounds. The possible reason for this seems to be not doing the chelation of pulp prior to extraction and hydrogen peroxide treatment. More over the use of normal fresh water containing high level of minerals too led to lower brightness as a substantial amount of peroxide and oxygen might have been consumed by these metal ions.

5.5 AOX Values of Bleach Plant Effluents

The AOX levels in the filtrates from bleaching the pulps are given in Table 13. The quantities of AOX in filtrates from the first two stages of each bleaching sequence and for the whole sequence were calculated by using a formula devised by Germgard for

the estimation of chlorinated organics formed during bleaching of pulps from the quantities of chlorine, chlorine dioxide and hypochlorite consumed in the various bleaching stages. The equation is as follows-

$$AOX = 0.1(Cl_2 + 0.2ClO_2 + 0.6H)$$

Where AOX is the amount of adsorbable organic halide expressed as Kg/t of pulp.

Cl_2 is the total amount of molecular chlorine used in the bleaching sequence expressed as Kg/t of pulp.

ClO_2 is the total amount of chlorine dioxide expressed as Kg of active chlorine/t of pulp.

The factor of 0.1 can vary with the type of pulp but this value is used in most of the cases.

In these calculations the quantities of applied chemicals were used, as the residuals were usually very small.

The results show that the AOX generated in CEH sequences is higher than C/DEHD and DED bleaching sequences. The DED sequence produces the least AOX. The AOX value is highest (4.8 Kg/t of pulp) from the CEH bleaching of soda pulp while it is least for (0.4 Kg/t of pulp) for soda-AQ oxygen pre-bleached pulp. Hence it can be concluded from these values that the kappa number of the pulp and the amount of chlorine were the main contributors to the generation of AOX.

Now from the bleaching of Soda and soda-AQ pulps we see that the amount of AOX generated goes down as the chlorine is replaced by chlorine dioxide in first and following stages of bleaching.

In fact the majority of AOX is generated during the first two stages of any bleaching sequence involving the use of chlorine or its related compounds. However in the later stages, as the pulps contain very low amount of lignin left, hence most of the chemical is used in brightening only.

The oxygen pre-bleaching too reduced the generation of AOX significantly. The amount of the chemicals used in the subsequent stages was reduced as the kappa numbers of the pulps to be bleached were reduced by almost half of their initial values after oxygen pre-bleaching.

Fig. 3 clearly indicates how the amount of AOX generated ((CE)/(C/DE)/(DE)) decreases with the reduction in Kappa number and the amount of chlorine being used.

5.6 Physical Properties of Pulps

The bleached pulps were beaten in a PFI mill so as to give a CSF value in the range of 310 ± 20 (= 40-45 °SR). As per the initial CSF values of pulps, a total of 700 revolutions were given to a 30 gm OD pulp at 10% consistency in the PFI mill.

The 60 gm/m² gsm hand sheets were prepared on the British sheet former with recycling of water, so as to retain fines within the sheet. The hand sheets conditioned at 27 ± 1°C and 65 ± 5% RH were tested for tear, burst and tensile indices. The values are given in table 8 and 9 for Soda, Soda-AQ and Soda- O_2 and Soda-AQ-O_2 pulps bleached with different sequences.

The results show that the DED bleached pulps have shown the higher strength values amongst all the four sequences used for bleaching. The higher strength of the DED bleached pulps is a

result of chlorine dioxide being more selective in attacking lignin. At a pH of 3.5-4.0, the rate of removal of lignin by chlorine dioxide is much higher than its attacking carbohydrate. Due to this reason the pulp has shown higher strength values. The strength properties of C/DEHD bleached pulps are comparable to that of corresponding DED bleached pulps. The sequential chlorination with chlorine dioxide preceding the chlorine in the first stage seems to have protected the carbohydrates from degradation due to its selectivity towards lignin. Moreover the last stage bleaching with chlorine dioxide also helped the cellulose maintain its strength.

Further, chlorine, hypo and oxygen being more prone towards attacking the cellulose, the lower strength of CEHH and $OE_{o-p}P$ bleached pulps is probably due to this reason.

It was also observed from the Table 8 that the strength of Soda-AQ pulp is lower than that of the Soda pulp. This is probably due to higher retention of hemicelluloses in soda-AQ pulps which seem to be protected by AQ during delignification.

The strength of Soda and Soda-AQ pulps are higher than the soda-O_2 and Soda-AQ-O_2 pulps respectively for each bleaching sequence. The reason for the same seems to be the degradation of cellulose during oxygen bleaching.

6. SUMMARY AND CONCLUSIONS

6.1 SUMMARY

It is possible to produce bagasse pulp of low kappa number (half the kappa number of soda pulp) by introducing a small fraction (0.1%) of anthraquinone during cooking of bagasse.

Bagasse pulps were easily delignified under oxygen bleaching conditions and the response was excellent. The Kappa number of the soda and Soda-AQ pulps were reduced to 11.8 and 6.8 respectively which is almost half of their initial values. The bleaching chemicals consumption in the following stages decrease sharply which not only saves the money but also reduces the environmental load significantly. The equivalent chlorine consumption in CEH, C/DEHD and DED bleaching sequences with respect to decrease in kappa number, is reduced from 54 Kg/ton to 29 Kg/ton of pulp in case of soda pulp and 33 Kg/ton to 17 Kg/ton of pulp in case of soda-AQ pulp. And this has resulted in a decreased load of pollution. The COD from a high of 123 Kg/ton to 36 Kg/ton and Colour from a high of 247 Kg/ton to 58 Kg/ton are also reduced in case of bleaching with chlorine and chlorine containing compounds.

The bagasse pulps showed a very good response to elemental chlorine free bleaching. The oxygen prebleached soda-AQ pulps can be bleached to above 85% ISO brightness by using ECF bleaching.

The chelation is must for TCF bleaching of bagasse pulps. In absence of it there was a drop in the brightness of pulp. More over the higher content of minerals in the fresh water used for dilution at various stages also significantly affected the final brightness of the TCF bleached bagasse pulps.

The ECF bleaching yields a pulp of higher strength than the bleaching with chlorine and oxygen. The cellulose is directly exposed to chlorine and oxygen which weaken it. However the use of chlorine dioxide protects the carbohydrate due to its higher selectivity of attacking the lignin first.

The environmental load of the bleaching process is related to the amount and type of chemicals used for bleaching. However the amount of chemicals is related to the degree of delignification. Oxygen prebleached soda-AQ pulp produced the least environmental load when bleached in the later stages with DED sequence except a slight loss of strength properties. Practically there willbe no pollution load from the $OE^{o+p}P$ sequence as the effluent generated is free from chlorine ions and hence can be recycled to chemical recovery plant.

The Germgard equation over estimated the amount of AOX formed during bleaching bagasse pulps with modern bleaching sequences. In fact, the pulp after CE or C/DE or DE stages contains very low amount of lignin hence in the last stages most of the bleaching chemical is used for brightening only.

6.2 Conclusion

From the above studies it can be stated that pulps cooked by modified techniques and followed by oxygen pre-bleaching, the Kappa number of the pulps entering to the bleach plants can be reduced considerably. In today's context the need for such modification has been emphasised in the literature with increasing awareness towards cleaner environment, the modified techniques for reducing the kappa number are likely to become usual practice and therefore bleaching chemicals demand can also be reduced further. In countries like India where bleach

chemicals like ozone will take a long time before they are utilised, due to much higher installation costs, the oxygen pre-bleaching can be exploited in which digester itself can be utilised as a reactor. The black liquor so generated after washing can be burnt in the boilers after concentration.

Bagasse which is an important raw material resource for pulp and paper making in India, can be successfully used with its least impact on environment. The bagasse pulp can be bleached with DED sequence to almost 85% ISO brightness level by using even a very less amount of chlorine dioxide (7 Kg/t of pulp as such) as has been obtained for bagasse pulp after oxygen pre-bleaching.

The values of strength properties of the pulps have shown that the bagasse bleached pulp is suitable for manufacturing high quality cultural grades of paper. However for better runnability conditions on paper machine and physical properties, the bagasse pulp may be substantially blended with a longer fibred pulp (10-15%).

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ANNEXURE

TABLE 1: COMPOSITION OF WHOLE WET BAGASSE

S.NO.	INGREDIENT	VALUE
1.	Pith, %	Appox.29.0
2.	Useful fiber, %	46.3
3.	Moisture, %	43.1
4.	Sugar, %	3.5
5.	Ash, %	1.3
6.	Silica, %	0.28
7.	Pentosan, %	19.74
8.	Lignin, %	19.63
9.	Holo Cellulose, %	77.60

TABLE 2: PROCESS CONDITIONS FOR SODA AND SODA- AQ COOKING OF DEPITHED BAGASSE

S.No.	PARTICULARS	SODA	SODA-AQ
1.	Alkali charge, % NaOH as Na_2O on o.d. bagasse	12	12
2.	AQ Dosage, % on o.d. Bagasse	-	0.1
3.	Bath Ratio	1:5	1:5
4.	Cooking Temperature, °C	165	165
5.	Time to 100°C Temperature, min.	30	30
6.	Time to Maximum Temperature, min.	60	60
7.	Time at Maximum Temperature, min	60	60

TABLE 3: RESULTS OF SODA AND SODA-AQ PULPING

PARTICULARS/PULP	SODA	SODA-AQ
Yield, %	53.6	51.4
Screen Yield, %	50.1	49.3
Screen rejects, %	3.5	2.1
Pulp Kappa No.	21.5	13.3
Pulp viscosity,cu.cm/gm	900.0	860.0

TABLE 4: CONDITIONS OF OXYGEN PRE BLEACHING OF SODA AND SODA-AQ BAGASSE PULP

CONDITIONS	
Alkali Charge, %	2.5
$MgSO_4$ Charged, %	1.0
Consistency, %	10.0
Oxygen Dosage, Kg/cm^2	5.0
Temperature at which oxygen is charged, °C	50-55
Max. Temperature, °C	115.0
Time to temperature, min.	30.0
Time at Max. Temperature, min.	60.0

TABLE 5: RESULTS OF OXYGEN PRE-BLEACHING

PARAMETERS/PULP	SODA	SODA-AQ
Yield Loss,%	1.7	1.2
Pulp Kappa Number	11.8	6.8
Pulp Viscosity, Cu.cm/gm	820.0	790.0
Brightness, % ISO	45.0	49.9
Breaking Length, Km (Zero Span)	9.0	8.9

TABLE 6: CONDITIONS FOR BLEACHING OF PULP AT DIFFERENT STAGES WITH CHLORINE OR CHLORINE COMPOUNDS

STAGE	C	C/D	E	H	D
CONSISTENCY, %	3.0	3-5	8.0	8.0	5.0-8.0
TEMPERATURE, ° C	30-35	70	60	40	70
TIME, min.	30-60	70	60	120	120-180
pH	3.0	4.0	10.0-10.5	10.5-11.0	4.0-4.5
FINAL pH	-	3.0	9.5	9.0-9.5	3.0

TABLE 7: CONDITIONS FOR BLEACHING OF PULP AT DIFFERENT STAGES WITH OXYGEN AND HYDROGEN PEROXIDE

STAGE	O	E_{O+P}	P
NaOH, % on o.d. pulp	2.5	1.5	-
$MgSO_4$,% on o.d. pulp	0.5	0.5	-
H_2O_2, % on o.d. pulp	-	0.5	1.5
Sodium Silicate,% on o.d Pulp	-	-	1.0
Oxygen pressure, Kg/cm^2	5	5	-
Consistency, %	10	10	10
Temperature, °C	115	105	70
Time to temperature, min.	30	15	-
Time at Temperature, min.	60	60	90
pH	-	-	10.5

TABLE 8: CHEMICAL DOSAGES FOR BLEACHING OF BAGASSE PULP

DETAIL/PULP	SODA	SODA-AQ	SODA-OXYGEN	SODA-AQ-OXYGEN
Kappa Number	21.5	13.3	11.8	6.8
CEH Sequence				
C-Stage,% active Cl	3.9	2.4	2.1	1.2
E-Stage, %	2.3	1.5	1.4	0.9
H-Stage,% active Cl	1.5	0.9	0.8	0.5
CE-Kappa Number	4.1	2.8	2.4	1.7
C/DEHD Sequence				
C/D-Stage C,% act. Cl	1.2	0.7	0.6	0.4
(30C 70D) D,% act. Cl	2.7	1.7	1.5	0.8
E-Satge, %	2.3	1.5	1.4	0.9
H-Stage, % active Cl	1.1	0.7	0.6	0.4
D-Stage, % as ClO_2	0.20	0.15	0.11	0.07
(C/D)E-Kappa Number	4.6	3.1	2.8	1.9
DED Sequence				
D-Stage, % as ClO_2	1.5	0.9	0.8	0.5
E-Stage, %	2.3	1.5	1.4	0.9
D-Stage, % as ClO_2	0.6	0.4	0.3	0.2
DE-Kappa Number	4.7	3.0	3.0	1.9

TABLE 9: STRENGTH PROPERTIES OF BAGASSE PULP BLEACHED WITH VARIOUS SEQUENCES

PULP	BLEACHING SEQUENCE	CSF	TEAR INDEX ($mN.m^2/g$)	TENSILE INDEX ($N.m/g$)	BURST INDEX ($KPa.m^2/g$)
SODA	CEH	320	3.30	52.5	2.70
	C/DEHD	315	3.70	57.0	3.20
	DED	305	3.95	58.0	3.30
	$OE_{o+p}P$	320	3.60	52.5	2.95
SODA-AQ	CEH	310	3.10	53.0	2.75
	C/DEHD	300	3.70	57.5	3.20
	DED	300	3.80	58.0	3.30
	$OE_{o+p}P$	320	3.60	51.0	2.95

TABLE 10: STRENGTH PROPERTIES OF BAGASSE PULP PRE BLEACHED WITH OXYGEN AND FOLLOWED BY VARIOUS SEQUENCES

PULP	BLEACHING SEQUENCE	CSF	TEAR INDEX ($mN.m^2/g$)	TENSILE INDEX ($N.m/g$)	BURST INDEX ($KPa.m^2/g$)
SODA	CEH	315	3.10	50.0	2.50
	C/DEHD	300	3.35	55.5	3.10
	DED	320	3.45	53.5	2.90
SODA-AQ	CEH	330	3.50	51.0	2.50
	C/DEHD	320	3.60	53.0	3.00
	DED	300	3.65	55.5	3.15

TABLE 11: COMPARISON OF EFFLUENT CHARACTERISTICS OF VARIOUS BLEACHING SEQUENCES FOR SODA AND SODA-AQ BAGASSE PULPS

PULP	PARAMETERS/BLEACHING SEQUENCE	CEH	C/DEHD	DED	$OE_{o+p}P$
SODA	pH	8.4	8.3	8.0	9.2
	Total Solids,Kg/t	191	186	183	242
	Suspended Solids,Kg/t	43	43	39	68
	Dissolved Solids, Kg/t	148	143	144	174
	COD, Kg/t	123	72	56	160
	Color, Kg/t	247	114	58	239
SODA-AQ	pH	8.8	8.3	8.3	9.1
	Total Solids,Kg/t	127	130	134	155
	Suspended Solids,Kg/t	26	34	36	48
	Dissolved Solids, Kg/t	101	96	98	107
	COD, Kg/t	79	39	32	113
	Color, Kg/t	117	44	41	119

TABLE 12: COMPARISON OF EFFLUENT CHARACTERISTICS OF BLEACHING SEQUENCES OF OXYGEN PREBLEACHED BAGASSE PULPS

PULP	PARAMETERS/BLEACHING SEQUENCE	CEH	C/DEHD	DED
SODA	pH	8.6	8.5	8.3
	Total Solids,Kg/t	155	158	144
	Suspended Solids,Kg/t	45	39	36
	Dissolved Solids, Kg/t	1110	119	108
	COD, Kg/t	65	28	19
	Color, Kg/t	78	35	16
SODA-AQ	pH	8.4	8.8	8.3
	Total Solids,Kg/t	121	117	110
	Suspended Solids,Kg/t	33	34	26
	Dissolved Solids, Kg/t	88	83	84
	COD, Kg/t	32	10	9
	Color, Kg/t	46	25	9

TABLE 13: BRIGHTNESS AND AOX LEVEL OF BLEACHING OF DIFFERENT PULPS

PULP BLEACHING SEQUENCE	BRIGHTNESS ISO %	AOX FROM (CE/(C/DE) (DE), Kg/T	TOTAL AOX Kg/T
SODA PULP			
CEH	81.3	3.9	4.8
C/DEHD	82.2	1.7	2.5
DED	81.9	0.8	1.1
$OE_{O+P}P$	73.6	-	-
SODA-AQ PULP			
CEH	82.7	2.4	3.3
C/DEHD	81.6	1.0	1.5
DED	82.1	0.5	0.7
$OE_{O+P}P$	76.5	-	-
SODA-O_2 PULP			
CEH	82.0	2.1	2.6
C/DEHD	82.5	0.9	1.3
DED	83.6	0.4	0.6
SODA-AQ-O_2 PULP			
CEH	83.1	1.2	1.5
C/DEHD	82.8	0.6	0.8
DED	84.4	0.3	0.4

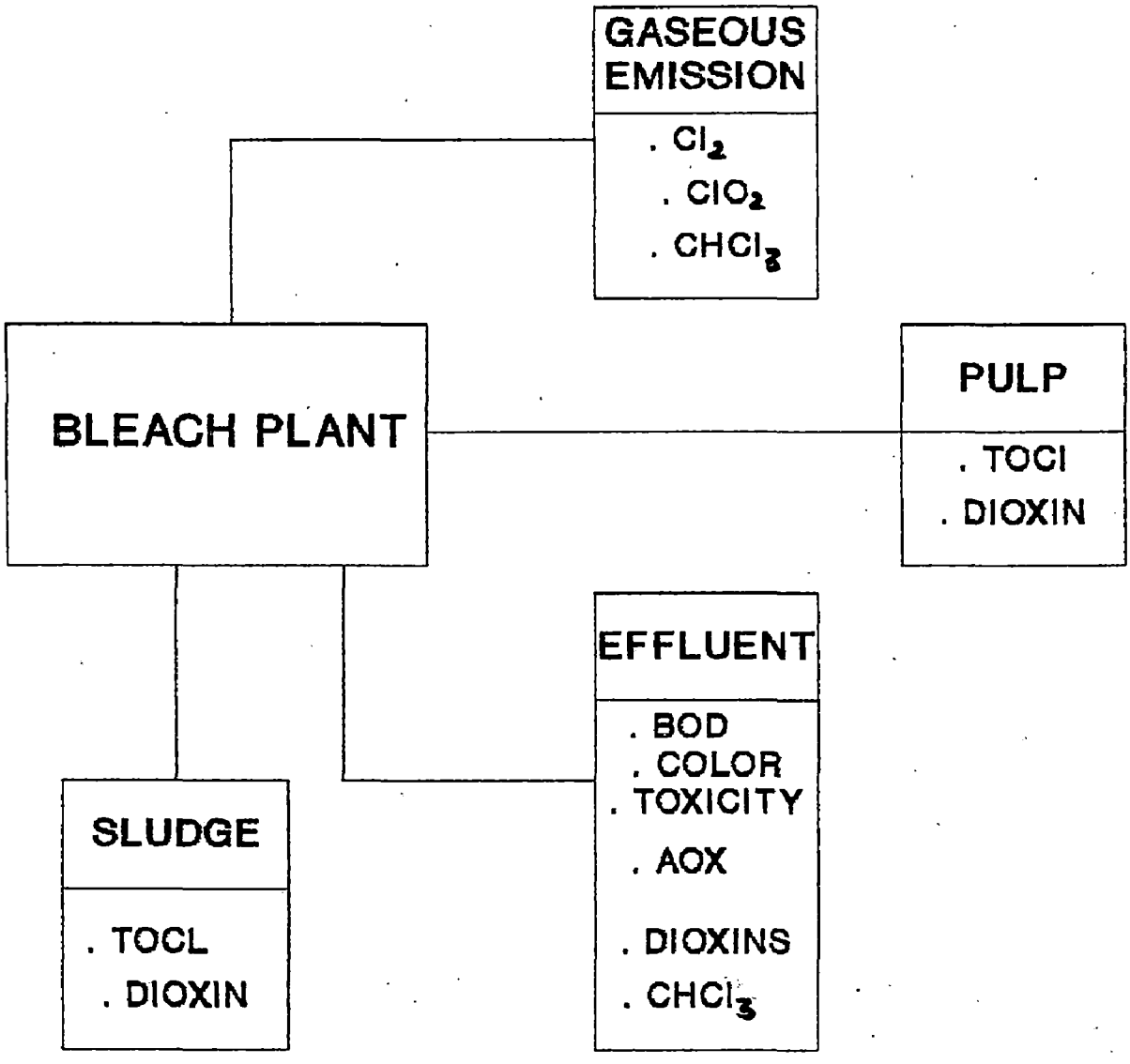

FIG. 1 : ENVIRONMENTAL IMPACT OF BLEACHING WITH CHLORINE AND CHLORINE CONTAINING COMPOUNDSS

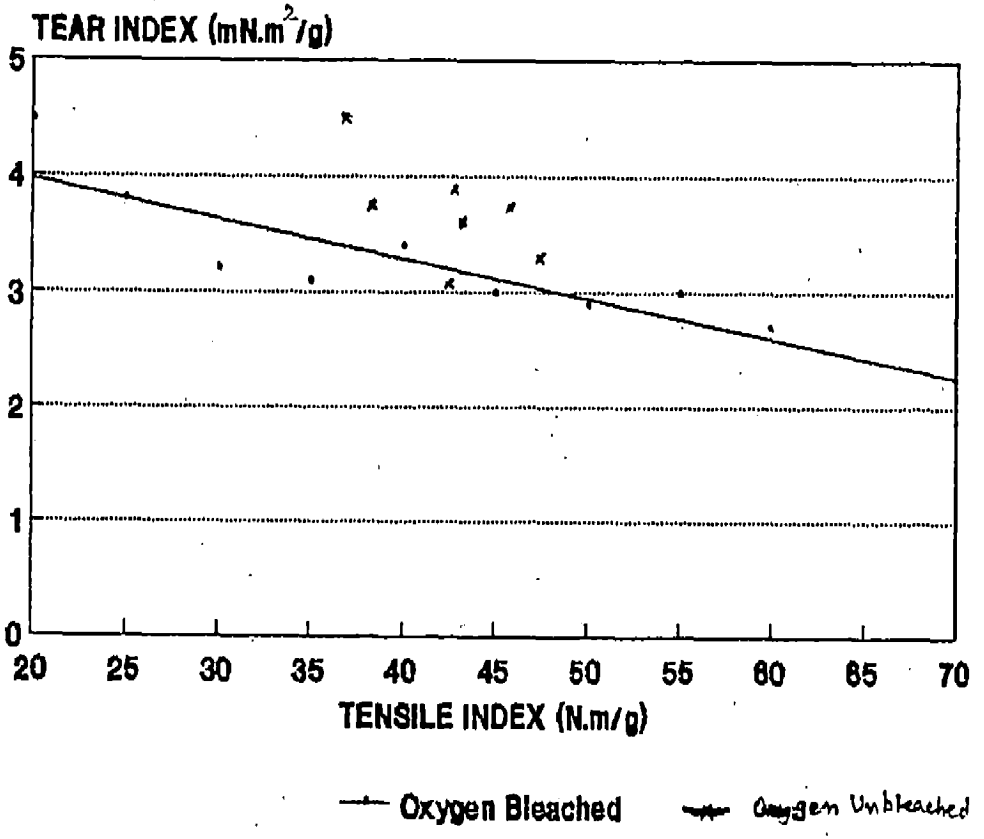

FIG. 2 : TEAR INDEX vs TENSILE INDEX FOR SODA UNBLEACHED AND OXYGEN BLEACHED PULP

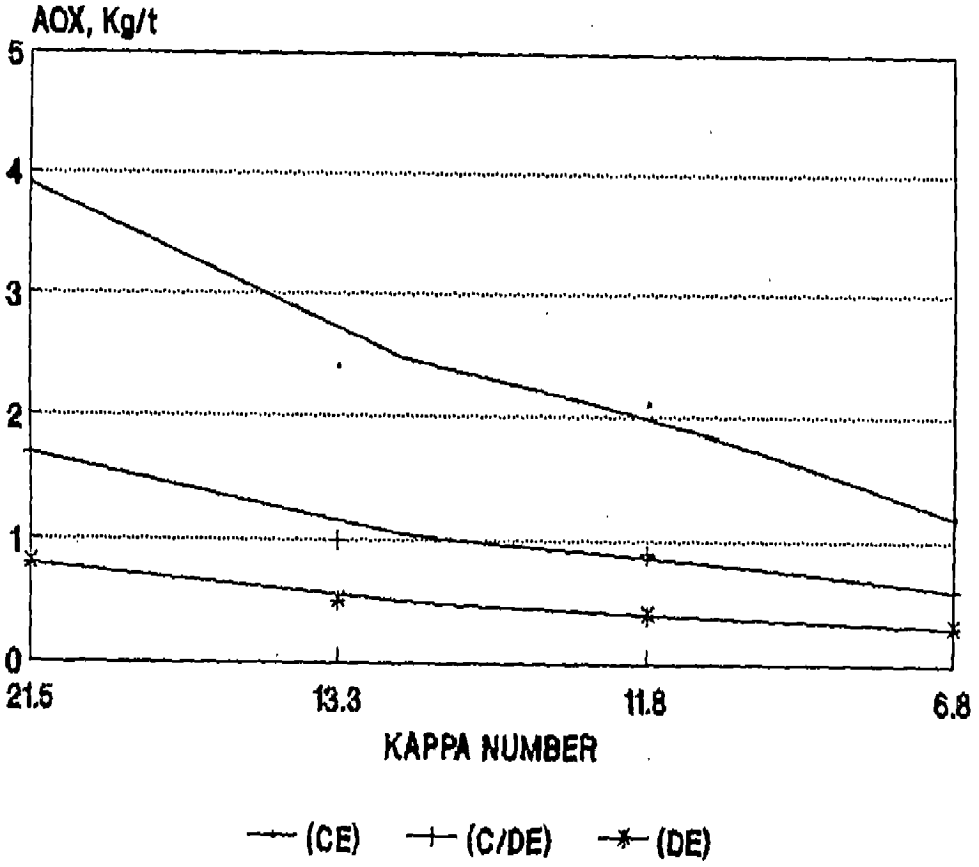

FIG. 3 : AOX IN FIRST STAGE vs KAPPA NUMBER

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