Colour Reversion - Consideration of Practical Aspects towards its Control and Prevention

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ABSTRACT

At high brightness levels, the colour reversion is observed to be acute in Calcium hypo chlorite bleached pulps than Dioxide Bleached pulps. The influenece of Acidity is profoundly seen. Selection of dyes appears to have a major role in colour stability. Direct dyes even though have lesser colour reversion, they tend to decrease the initial brightness and visual efficiency of the paper. Optical brightening agents have no significant role in mitigating the colour reversion. The method of bleaching sequence and the nature of the dyes and effect of acidity appear to have the most direct impact on the colour reversion.

INTRODUCTION

The yellowing or brightness reversion of papers upon exposure to heat or light is a major quality concern for paper makers in the case of printing and writing papers. Various research laboratories are pursuing an effective and economically feasible solution to this problem. Practical studies are very scarce in this area even though a lot of fundamental research work has been carried out by various researchers. It has been frequently emphasized that thermo-induced reversion and photo-induced reversion are the major factors. Permacence refers to the retention of significant use properties, particularly folding endurance and colour over prolonged periods (1). Paper is said to have good permanence if it retains its original properties of brightness, strength and flexibility over along period of time (2). Permanence with special reference to colour stability is disucussed in this paper. Even though the determination of Post Colour Number is currently used, still due to many drawbacks it is not considered as a standard method and there is no other standard methods (3) available to determine the extent of colour reversion absolutely. In the present context, the authors have attempted to study the practical aspects of colour reversion under various heat irradiation conditions such as direct sunlight and direct heat and extreme heat. Published papers suggest that practical, real time measurements are possible only through the use of accelerated aging test (4).

The yellowing of newsprint which contains mechanical pulps, which are rich in lignin content has been studied by various researchers. It is not meaningful to talk on colour reversion in the case of newsprint where the basic yellowness itself is very high due to the presence of very high lignin content (5). Therefore the present study attempts to discuss the practical considerations of colour reversion of the tinted white papers made out of chemical pulps available in the common market. To illustrate, we have shown in Table 1 some paper samples undergoing rapid colour reversion.

When the subject of colour reversion is discussed it is to be borne in mind that, it mainly implies brightness drop and fading of the colour or the predominant bleu or the visible shade with a short period of time during storage. Brightness drop normally indicates the the brightness stability of pulps, which is again dictated by the raw material structure and the method of bleaching employed. Therefore the influencing factors can be broadly classified into two major parts viz. 1) Bleaching method 2) Pulp/Stock Preparation for paper making which includes the addition of additives like dyes, alum and optical brightening agents.

EXPERIMENTAL

Samples

Hand made sheets were prepared in Standard British

Sheet Former after disintegrating the pulps in the Standard Tappi Disintegrator. Pulp pads were prepared in the Buchener Funnel through Filter paper. Machine made samples were cut intó 12.5 x 10cm dimensions for the experiments.

Preparation and Testing

The samples of pulp pads or hand made sheets or machine made paper samples were initially air dried and the initial required optical properties (Brightness, Yellowness, CIE colour values) were measured and the end properties were measured after the required mode of exposure Viz. (Day light shade for 3 days/ Direct sun light for 7 hrs/ at 105°C, in Hot air oven for 4 hours/ at 160°C for 15 minutes in a closed hot plate) whatever is applicable. For exposing to day light in shade or direct sun light, the samples were clipped to a board and kept flat in an area free from dust and dirt. The measurement was made on the exposed side of the sample.

The Post Colour Number (PCN) was calculated using the Kubelka -Munk relationship, [K/S=[1-R∞)2/ 2R∞], where R∞refers to the relative reflectance at 457 nm measured in a reflectance Electro photometer. (K/s) was measured before and after the exposure to determine the PCN. The comparison studies were carried out in the same manner for all the samples. Yellowness was calculated with the following empirical formula. [(Reflectance in Red Filter-Reflectance in Blue Filter) x 100 /(Reflectance in Green filter)]

Measurements

All the reflectance measurements needed for calculating the PCN, brightness, yellowness, and CIE colour values, were made in the Elrepho 2000 Brightness Tester which is calibrated against standard barium sulphate.

RESULTS AND DISCUSSION

Influence of pulps

When the subject of colour reversion is discussed it is imposible to ignore one of the most important aspects which is the basic brightness and yellowness of the pulps used for the paper making. Findings that are practically applicable for a paper making system were analyzed. Pulps of different raw materials which were bleached with different bleaching chemicals were studied. These pulps by virtue of their chemical structure, varied in the initial brightness and yellowness levels. For these studies, hardwood eucalyptus pulp bleached to a final brightness of 82-84% with calcium hypochlorite and 85% with chlorine dioxide and wood pulp, bleached with chlorine dioxide and Bagasse pulp bleached to 85% with Calcium hypo were taken.

Brightness pads made out of these pulps were exposed to various heat conditions. The brightness after the exposure was measured. The brightness drop is depicted in Fig. 1 at various exposure conditions. Hardwood eucalyptus pulps have more yellowness than bagasse pulps even though they are bleached with calcium hypo. This results in a high brightness reversion in the case of hardwood pulps compared to bagasse pulps. However, when we compare the hypo-bleached pulps with dioxide bleached pulps there is remarkable reduction in colour reversion as indicated by the very low PCN. (Table 1).

This means that, the method of bleaching plays a crucial role in the colour reversion. Paper made with hardwood hypo pulp and hardwood dioxide pulp, under identical conditons show significantly different reversion tendency. This is to be attributed to the fact that during hypochlorite bleaching of pulps, carbonyl groups are turned in C-2 and C-3 carbon atoms of glucose moiety which is due to the oxidation of secondary hydroxyl group of the C-2 and C-3 carbon to keto group. In chlorine dioxide bleaching it does not generate carbonyl groups in the C-2 and C-3 of the glucose moiety. Hence the colour reversion in the chlorine dioxide pulps is comparatively less when

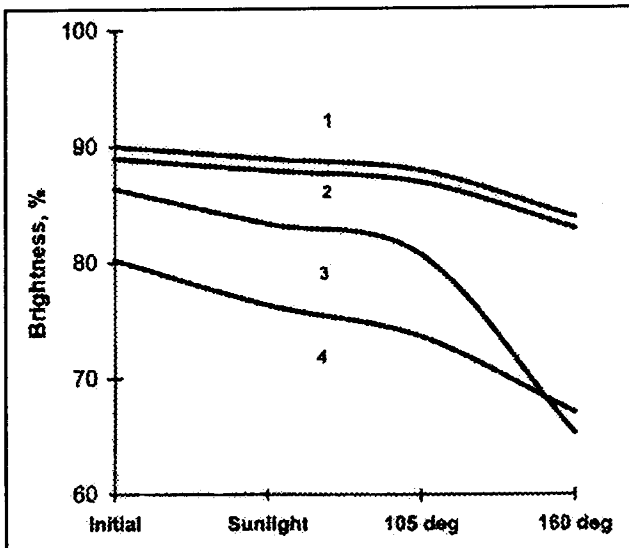

Fig. 1 Brightness drop of different pulps

1. Soft Wood Dioxide Pulp
2. Hard Wood Dioxide Pulp
3. Bagasse Hypo Pulp
4. Wood Hypo Pulp

Table 1. Colour reversion in some papers

Sample	CIE Colour values												
	Brightness, %		Brightness drop on exposure	Yellowness, %		Yellowness increase on exposure	Before exposure			After exposure		
	Initial	Final		Initial	Final		L*	a*	b*	L*	a*	b*
Printing paper	82.0	77.5	4.5	-7.4	+6.6	14.0	89.3	+1.1	-4.0	91.7	-0.1	+3
High bright printing paper	85.9	81.4	4.5	-11.6	+0.9	12.5	89.5	0.2	-4.4	91.8	+0.3	+1

The samples were exposed to day light in shade for 72 hours
L* Luminosity,
a* Positive Value indicates Red and Negative Values indicates Green
b* Positive Value indicated Yellow and Negative Value indicated Blue

compared to hypo bleached pulps.

In bagasse pulping, we start with unbleached pulp of low kappa number and hence the quantity of hypo needed is very less, since the attack of hypo on lignin and attack on glucose moiety are competitive reactions and with the former being faster of the two, most of the hypo is utilized for the delignification and hence the formation of C-2 and C-3 carbonyl groups are kept to a maximum in the case of bagasse pulp with conventional bleaching of calcium hypo but with ClO_2 it is even less.

Therefore in practice we find bagasse hypo bleached pulps to be less susceptible for colour reversion than wood hypo bleached pulps. However, when we go for high brightness, the problem becomes more acute. The understanding of the susceptibility of various pulps towards colour reversion helps us to decide the furnish apportioning during stock preparation. When we come to the discussion of practical considerations the reversion of brightness in the base pulps results in increase in the yellowness, which directly affects the shade stability of the final finished paper. The very high PCN in wood pulp results in quick fading of paper. So in the context of colour reversion two important factors are observed. (1) Bagasse pulps have comparatively better colour stability than wood pulps 2) Dioxide bleached pulps are superior to the traditional hypo bleached pulps.

Poor brightness stability has been shown to be directly related to the high extractives content. Hardwood pulps have been found to be more stable when a high degree of chlorine dioxide substitution is used in the bleaching. A decrease in the extractives content is associated with this increase in brightness stability (5). However it has been reported that chlorine dioxide substitution has little impact on brightness stability of soft wood pulps (6).

Effect of acidity on the brightness reversion in pulps

In many parts of India, at the present context of paper manufacturing, acid sizing of paper is still followed except in one or two mills where alkaline paper making is restricted to one or two machines. Acid sizing has shown to be one of the primary factors governing the permanency of the paper, which is to be traced to general acid catalyzed hydrolysis β-O-4 ether linkage in cellulose moiety in turn in the reduction of degree of polymerization. Acid hydrolysis is one chemical reaction that results in the loss of over all paper permanency and this is due to residual acidity present in the paper. Not withstanding this, It has long been recognized that the papermaker's alum contributes sulphate ions to the process in addition to the desired aluminum ions. In the aqueous system the sulphate and aluminum ions are free to react with available protons to produce weak acids, also when excess alum adheres to the pulp, it undergoes hydrolysis which results in alumina ions contributing to colour reversion.

Normally paper premanence includes the commonly

Table 2. Effect of acidity on the brightness

Exposure condition	Brightness, %			
	Low acidity		High acidity	
	Wood pulp	Bagasse pulp	Wood pulp	Bagasse pulp
Intial	80.2	86.4	80.2	86.4
Direct heat sunlight (7hrs)	76.3	83.4	73.3	81.1
Direct heat, 105°C (4 Hrs)	73.6	80.7	73.0	79.0
Direct heat, 105°C (15 min)	67.1	65.3	59.0	59.8

Table 3. PCN of different pulps

Pulp	PCN at 105°C	PCN at 160°C
Wood Hypo bleached pulp	2.0	5.0
Bagasse Hypo bleached pulp	1.0	5.0
Wood Dioxide bleached pulp	0.3	1.0

accepted measure such as colour reversion, the general loss of brightness and whiteness and the retention of original strength (6). Even in acid paper making the degree of acidity also plays an important role in the brightness stability. To explore this, the effect of pH was studied with reference to the brightness drop yellowness increase with respect to chemical pulps obtained from calcium hypochlorite bleaching at different exposure conditions. The results are shown in Table 2.

It can be seen that high acidity accelerates the brightness drop in all the exposure conditions. This is further proved from PCN as given in Table 3.

This is the reason why alkaline papermaking is more attractive in the colour stability of the finished paper. It is also noted in the above studies that even though bagasse hypo pulps show less reversion tendency at milder conditions, it is almost similar to wood hypo pulp at aggressive exposure conditions which indicates that hypo bleaching is distinctly inferior to dioxide bleaching because of the formation of C-2 and C-3 carbonyl, groups. Dioxide bleached pulps even at drastic conditions do not suffer brightness loss as we see in hypo pulps.

The extent of shade reversion of paper as noted earlier depends upon the brightness reversion characteristics of pulps used. Studies were made on fine papers containing hypo bleached pulps and dioxide

Table 4. PCN and Acidity

Pulp	PCN at Low acidity 105°C for 4 hours/ 160°C for 15 min	PCN at High acidity 160°C for 4 hours/ 105°C for 15 min
Wood Hypo Pulp	2.3/2.7	5.6/11.9
Bagasse Hypo Pulp	1.2/1.7	8.1/12.4

Table 5. Effect of heat irradiation on papers made with hypo pulps & dioxide pulps

Particulars	Fine paper with hypo pulp	Fine paper with dioxide pulp
Initial brightness	83	87
Final brightness	78	84
PCN	1.2	0.6

bleached pulps. The PCN and brightness drop are also shown in the Table 5.

In the foregoing results we observed that even in the case of dioxide bleaching, it is still possible that there could be minimum reversion of brightness but is singnificantly low when compared to hypo bleached pulps.

Colourants and their interaction with shade

The term colour reversion takes its true meaning when colour is imparted to the virgin pulp by the application of colourants or dyes. The reversion denotes the fading of the imparted colour towards the original yellowness, which had been present, before the addition of colourants in the bleached virgin pulp.

Table 6. Acidity and Colour reversion of pulps

Particular	Hardwood Hypo Bleached pulp			Bagasse Hypo Bleached pulp		
	L*	a*	b*	L*	a*	B*
Low acidity, before exposure	94.6	-0.1	+7.4	95.4	-0.5	+4.2
Low acidity, after exposure	93.2	0.2	+8.1	94.4	0.0	+5.0
High acidity, before exposure	94.8	-0.4	+7.4	95.3	-0.6	+4.3
High acidity, after exposure	93.0	+0.2	+8.9	94.4	0.0	+5.8

Table 7. Effect of exposure on brightness and yellowness with basic and direct dyes

Description	Initial Brightness %	Final Brightness %	Drop in Brightness points	Initial Yellowness %	Final Yellowness %	Increase in Yellowness % points
Basic dye at low acidity	82.0	81.4	0.6	-12.8	+3.5	16.3
Basic dye at high acidity	80.6	80.3	0.3	-8.6	+5.2	13.8
Direct dye at low acidity	80.6	78.6	2.0	-11.2	-5.6	6.6
Direct dye at high acidity	79.6	78.2	1.4	-10.8	-3.7	7.1

Practical aspects have been considered towards this issue. In order to study this, the changes that happen in the CIE colour values were observed and the factors that mostly affect this were also studied. Since, the colourants are more susceptible to aggressive heat radiation, the samples were exposed to milder conditions like normal day light shade and to direct sunlight. Unlike the case with original pulp samples, extreme heat like 105°C and 160°C destroys the colourant completely and it is not possible to come to logical conclusions. Therefore after the preparation, the respective sheets or pads or paper samples were exposed to day light shade or direct sunlight what ever applicable.

Effect of acidity on the colour values of virgin pulps

Since the visual perception of a shade is actually based on the CIE colour values as a first case the change in the L, a, b values of the virgin pulps were studied at the high acidity and low acidity. The results are shown in Table 6. It can be observed that the colour of the virgin pulps denoted by a* and b* are not much affected by the acidity. The L value drops by 1.5 points. Though we do not observe a large reduction in the colour values, the visual appeal and the shade substantially alters resulting in a new visual perception. Therefore, any alteration in the basic shade of pulp is undersirable for mitigating the shade reversion mechanism. Further, it is also cobserved that the reversion mechanism always works in the direction of yellowness increase only, in other words, the 'B' value goes on incresing towards the positive side which changes the Total Colour perception dramatically.

Shade reversion and the addition of dyes

When dyes are added for tinting for getting a shade as desired by the customers, it is most desirable that the shade obtained at the time of production should not change and it is widely known that the human eye is capable of identifying even subtle differences in the shade. Therefore paper production should be carried out in such a manner that there will be minimum colour reversion. For this, the present studies focused on the selection of dyes as the most important factor.

Table 8. Colour reversion on exposure with basic and direct dyes

Description	Initial colour			Final colour		
	L*	a*	b*	L*	a*	b*
Basic dye at low acidity	87.0	+3.5	-7.5	93.0	0.0	+2.7
Basic dye at high acidity	87.0	+2.4	-5.2	92.0	-0.1	+2.5
Direct dye at low acidity	86.0	+3.4	-6.7	88.0	+1.1	-2.9
Direct dye at high acidity	86.0	+3.3	-6.7	88.0	+1.2	-2.5

Laboratory sheets were prepared with a combination of bagasse hypo pulp and wood hypo pulp with basic dyes and direct dyes that are common in the industry at a very low acidity and a high acidity. The sheets were exposed to the day light for 7 hours. The brightness and yellowness values at various modes are shown in Table 7.

To confirm the role of acidity, another study was conducted with only the direct dye at various levels of increasing acidity. The hand sheets were prepared at various acidity levels starting from 2 ppm to 260 ppm and the dried sheets were exposed to day light shade for 72 hrs. The results are shown in Fig. 2. The effect on colour values is shown in Table 8. It appears that the shade is not much altered by the degree of acidity.

It is interesting to note that after the exposure, the colour values indicate a singificant increase in the 'L' value. This clearly shows that the on exposure, the dye in its original form is physically removed or modified into a different form. In other words the absorption coefficient decreases, which starts the 'Fading' . It is reported that when a dye is added to paper, it filters off some shade that otherwise would have been reflected (9). In contrast, the 'L' value incraese when a dyestuff is removed from the paper during the exposure.

It can be seen that the blue becomes yellow and red becomes green which clearly indicates the removal of dye. As it is known, yellow is the complimentary colour to blue in the colour spectrum. Brightness is measured in the blue region. Therefore, any change in the yellow region drastically affects the visual apparance/shade and brightness of the substrate and vice versa.

Even though there is no appreciable change in the colour by changing acidity both in basic dyes and acid dyes, we see a marked improvement in colour stability with direct dyes compared to basic dyes. Therefore, it is emphasized that the most appropriate dyes should be used. When it comes to appropriateness of selection, we observe that among the two classes, direct dye suffers significantly less reversion when compared to basic dye.

Our studies conducted on machine made papers produced under alkaline conditions but with basic dyes showed similar trend of colour reversion observed with papers made under acidic conditions. This underscores the need of dye selection. Changing to alkaline medium without changing the nature of the dye does not appear to be a good solution to prevent the colour reversion. Incidentally, it is also observed that, direct dyes even though have superior colour stability over basic dyes, they tend to reduce the intiial brightness of the pulps or the 'L' value of the paper. About 2 points brightness reduction is observed (Table 7) and 1 point reduction in the 'L' value (Table 8). Further, in our experiments we have observed that the consumption of direct dyes to achieve a given shade is more than the basic dyes, since basic

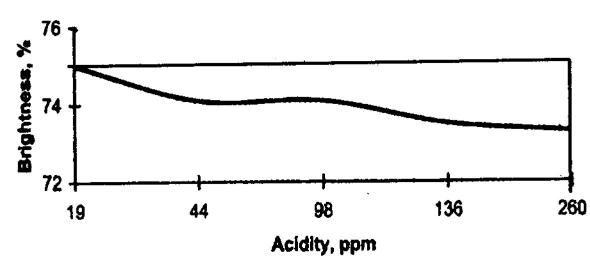

Fig. 2 Effect of acidity on birghtness with direct dye

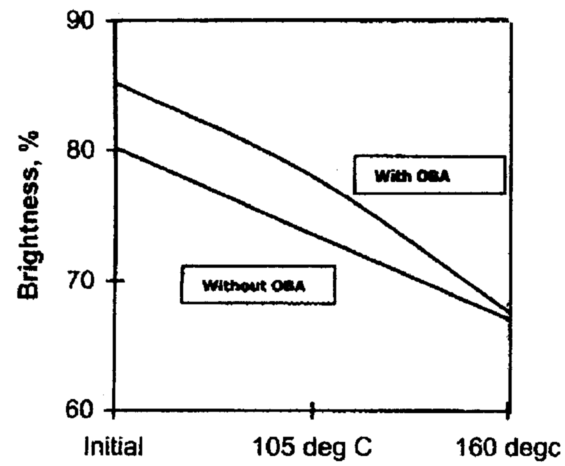

Fig. 3 Effect of OBA in low acidity in bagasse pulp

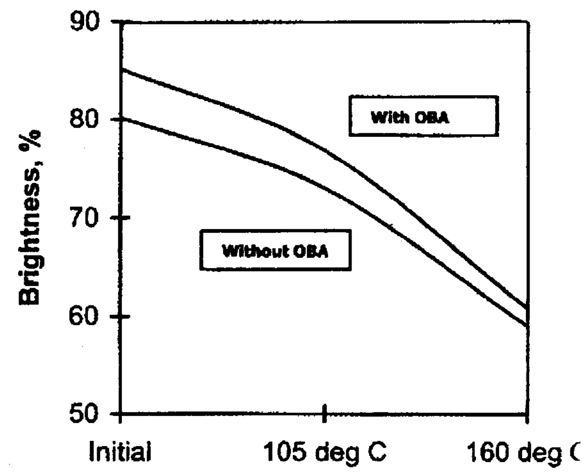

Fig. 4 Effect of OBA in high acidity in bagasse pulp

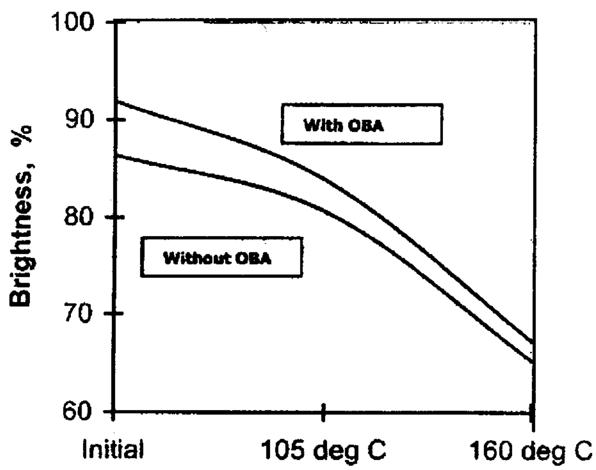

Fig. 5 Effect of OBA in low acidity in wood pulp

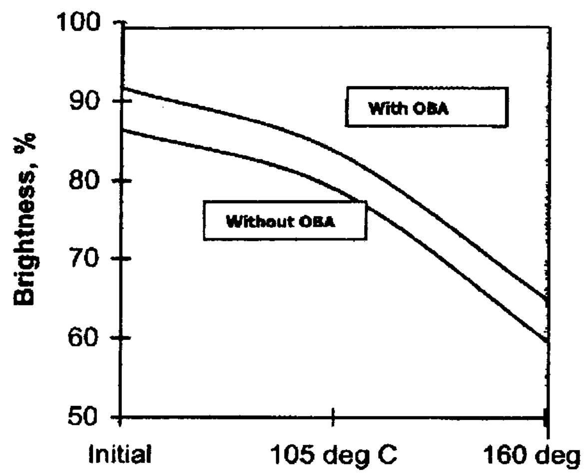

Fig. 6 Effect of OBA in high acidity in wood pulp

dyes possess much more Tintorial value as they produce more intense colour when compared to the direct dyes. However, as it is seen here basic dyes have very poor lightfastness which leads to shade reversion.

Influence of optical whitening agents on the colour stability

Usage of Optical Brightening Agents (OBA) dring the paper making has become a common practice not only to take care of the variations occur in the brightness of the virgin pulps but also to improve the visual appeal of the paper. The added OBA decreases the overall yellowness, which in turn improves the visual appeal (10). Hand sheets from Hypo bleached wood and bagasse pulps were made with and without OBA in low acidity and high acidity. The effect on brightness and yellowness was studied at 105°C and 180°C. Figs. 3-6 show the effect of optical brightening agents on virgin pulps at low and high acidity levels.

The brightness reversion, under heat irradiation, and under similar conditions, appears to be not affected favourably with the addition of OBA. The end point is almost the same for the pulps with OBA and with out OBA for hardwood and bagasse hypo pulps.

CONCLUSION

Acidity of the paper making system plays very important role in the brightness reversion of virgin pulps. Chlorine dioxide bleached pulps are more stubborn than the traditional hypo bleached pulp with respect to brightness reversion or yellowness increase. Bagasse pulps have relatively lesser tendency towards colour reversion when compared to wood pulp. However under drastic conditions the effect in the case of bagasse and wood hypo pulp. Alkaline paper making system is congenial for colour stability. However, direct dyes rather than basic dyes are more stable. Direct dyes reduce the initial brightness. The role of OBA is not profoundly affecting the colour stability. The combination of alkaline paper making with direct dyes with dioxide bleached pulps seem to be ideal for improving the colour stability during the production of the paper. However, the colour reversion can never be completely subjugated but the foregoing practiced observations help to improve the colour stability

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REFERENCES

1. American Paper and Pulp Association, **the Dictionary of Paper**, New York, (1965).
2. Rose, G.R. Alkaline Paper Making, **Anthology of Published Papers**, p. 374, (1987, 1992).
3. Bailey, A.L., **Tappi J.**, Vol. 76, 9 p. 175 (1993).
4. Rose, G.R., Alkaline Paper making, **Anthology of Published Papers** P. 374, (1987-1992).
5. Andrady, A.L., and Searle, N.D., **Tappi J.**, Vol. 78 No. 5, P. 131-132 (1995).
6. Reeve, D.W., **Pulp Bleaching-Prinicipels and Practice** ed. Carton W.Dense & Douglas W. Reeve, P. 279 (1996).
7. Reeve, D.W., **Pulp Bleaching-Prinicipals and Practice** ed. Carton W.Dense & Douglas W. Reeve, P. 279 (1996).
8. Crouse, B.W., and Wimer D.G., **Tappi J.**, Vol. 74, No. 7 P. 155, (1991).
9. Vekoba Rao, G., Maheswari, H.K., **Tappi J.**, Vol. 62, No. 1 . 87, (1979).
10. Mark Holmberg, Paper Making Chemistry, Ed. Leo Neimo, Pub. by Finnish Paper Engineer's Association & **Tappi J.**, P. 306 (1999).