INFLUENCE OF FINAL BLEACHING STAGE ON ECF BRIGHTNESS DEVELOPMENT, REFINEABILITY AND PULP PROPERTIES

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ABSTRACT

The use of chlorine dioxide in the final bleach stage of a multi-stage bleaching has helped mills to produce high brightness and optically balanced pulps, enabling paper makers to produce very high brightness and whiteness paper products, necessitating the use of as little Optical Brightening Agents (OBA) as possible. Since bleaching is oxidative chemistry related, pulps have a tendency to revert when bleached to very high brightness. Therefore, the chemical used in the final stages of bleaching to reach a given brightness target is critical. In this paper, the chemistry of chlorine dioxide and hydrogen peroxide, two predominant chemicals used in final bleaching stages, is reviewed and two distinct final bleaching stages, DD and DP are compared with respect to their ability to produce not only very bright and optically balanced pulps but pulps with low brightness reversion. Comparison is also made between DD and DP stages in terms of refineability and final pulp properties

In ECF bleaching of pulps, the norm for final bleaching is a chlorine dioxide stage. However, in some bleach plants, particularly the ones that bleach hardwood pulp, hydrogen peroxide is also used as a stand alone final stage in place of a D-stage. Some bleach plants use hydrogen peroxide as a polishing step (after final D-bleaching) in high density storage chests, prior to delivering pulp to the paper machines.

Extended cooking to lower Kappa numbers is practiced by many South American mills to manage bleach chemical use and reduce cost. Hardwood pulps as compared to softwood pulps have less free phenolic groups in their residual lignin; extended cooking and oxygen delignification further decreases the availability of free phenolic structures in their residual lignin before bleaching. Kumar et al (1996) contended that extended cooking and oxygen delignification of hardwood pulps make them difficult to bleach to high brightness even with high stages of bleaching because of high concentration of non-phenolic structure in their residual lignin. Gellerstedt et al (2000) and George et al (2000), as against McDonough et al (1999), argued that the decreased amounts of free phenolic groups in the residual O4 linkages adversely affected the bleaching of softwood pulps too (Lachanel et al (1999) and Daniel et al (2004).

One of the objectives of multi-stage bleaching is to eliminate chromophoric groups from pulp. According to Littia et al (2005), the chromophoric structures in alkaline pulps is to a large extent depends on the cooking conditions and are formed during cooking (Voiron et al 2005). Since the raw materials used in pulping are colorless, the dark brown color of Kraft pulps should have come from cooking. The largest known pulp chromophores come from the lignin (Gierer 1970) and to a small extent from the decomposition of carbohydrates (Forskahl et al 1976). The bleachability of fully bleached pulp artificially enriched in lignin during pulping (CL) was compared against the bleachability of a pulp enriched in precipitated lignin (PL) and a semi-bleached pulp (BKP) of same Kappa number. According to Voiron et al (2005), PL was easily removed and is unlikely to contribute to bleachability

problems whereas CL, probably recondensed on carbohydrates, was found to be the origin of bleachability problems.

In extended cooked pulps, particularly in hardwoods, the residual lignin contains fairly a large amount of lignin-carbohydrate (LCC) linkages, of which hexenuronic acids (HexAs) are part of (Parthasarathy 2005). The increased LCC linkages and condensed lignin structures in residual lignin necessitates stronger delignification conditions. This results in decreased free phenolic groups in pulps and increased chances of oxidation of cellulose, both of which can contribute to decreased pulp bleachability as well as brightness reversion of pulps (Kumar et al., 1996 and Parthasarathy, et al., 1996).

Chirat and Lachanel (2002) discounted the role of LCC and the chromophores from cellulose degradation as contributing to the bleachability of the pulps. They argued that the chromophores present on the carbohydrate matrix were found degraded easily by the bleaching chemicals to make them innocuous and should not interfere with the bleaching process or with the degradation of other chromophores which must be located in the lignin macromolecule.

While chromophores in cellulose may not play a role in the bleachability of pulps or in brightness development, the oxidation of cellulose and in particular, the presence of carbonyl groups does play a major role in brightness reversion of pulps both under monochromatic and light induced (polychromatic) radiation (Andrady and Parthasarathy 1991)

One of the consequences of bleaching pulps to very high brightness ($\geq$90%ISO) is that brightness reversion become prominent. The mechanisms of brightness reversion are fairly complex and involve a great many reactions of both cellulose (Eiras et al., 2005) and residual lignin (mostly chromophoric groups) (Lachenal 2005).

With the increase in pulp brightness, the chances of oxidation of cellulose increase and the tendency for the pulp to revert become more pronounced. Cellulose can be oxidized during bleaching, giving rise to carbonyl and carboxyl groups (Eiras 2005). The oxidations lead to the deduction of cellulose molecular weight resulting in new water-insoluble aromatic structures including certain chromophoric groups (Daniel et al., 2004).

Bleaching is an oxidative process and uses chemicals like oxygen, ozone, hydrogen peroxide and chlorine dioxide. Among the bleaching chemicals, chlorine dioxide is a very specific oxidant and prefers to react with residual lignin rather than cellulose. However, certain decomposition and disproportionation products of ClO_2 like ClO^- and Cl^- is indiscriminate oxidants and attacks both lignin and carbohydrates in pulp. The attack on lignin by these radicals does result in the generation of quinones whereas the attack on carbohydrates does not result in the oxidation of either C2 or C3 in the cellulose molecule to carbonyl groups but the oxidation of C6 to hexenuronic acid (Stewart and Smelstorius 1968 and Miyazaki 1971).

Hydrogen peroxide is used as reinforcement in the oxidative extraction of pulps but also as a stand alone bleaching chemical. Its decomposition products are the hydroxyl and hydro peroxyl anions which react mostly with lignin structures and hydroxyl radicals which are strong electrophiles and indiscriminate oxidant reacting with both residual lignin structures and carbohydrates. The reactions of the hydroxyl radicals with the carbohydrates mainly results in the oxidation of C2 and C3 carbons in cellulose and hemicelluloses to result in carbonyl groups. Andrady and Parthasarathy (1991) attributed the presence of excessive carbonyl groups in cellulose structures for the yellowing (brightness reversion) of hydrogen peroxide bleached TMP under monochromatic radiation.

In the bleaching of pulps, Arrhenius rate law dictates the elimination of chromophores (Teder and Tormund 1980, Desprez et al., 1994). Therefore, the rate is dictated by the concentration of

chromophores (measured by the light absorbent coefficient of pulp through Kubelka-Munk equation) and the concentration of active specie(s) involved in the bleaching reaction. The principal active specie in chlorine dioxide bleaching is "ClO_2" (Teder and Tormund 1980) and in hydrogen peroxide bleaching, the "perhydroxyl" anion (Lachanel et al., 1994, 2005). For an efficient removal of chromophores, particularly when pulps have to be bleached to very high brightness, conditions need to be conducive for maximum concentration of these active specie(s). This avoids the side reactions of those species not taking part in the bleaching process (a waste of chemical) or those that may be involved in reactions that adversely affect the final pulp properties. Since the rate equation is also dependent upon the chromophoric groups' concentration, the extent of removal of lignin in the preceding stages is critical too, leaving as low a residual lignin in pulp as possible.

Mellander, Dahl and Norden (2005) advocated that the bleaching response of conventional chlorine dioxide delignified (D_o) and bleached pulps differ from D_{HT} and $A_{HT}D$ delignified and bleached pulps. While the final P-treatment helped the brightness stability of D_o pulps, neither a final D-bleaching nor P-bleaching made any difference to the brightness stability of D_{HT} and $A_{HT}D$ delignified and bleached pulps. Actually, a final D-Stage provided the pulps a shade higher brightness than peroxide treatment.

According to Finar (1956) the fastness of color developed using a particular dye is dictated by the extent of changes in quinone (color) to quinhydroxy (colorless) structure. According to Lachanel and Chirat (2004 and 2005) the residual lignin in unbleached pulps had different quinone concentration and that the pulps which were more difficult to bleach were richer in quinone structures. These were also more colored, with a more pronounced reddish hue given by the presence of large concentration of quinone groups. However, according to Andrady and Parthasarathy (1992), both the unbleached and bleached TMP have shown a strong reddish hue, despite having much less condensed lignin structures and higher concentration of carbonyl structures. It is theorized by Lachanel and Chirat (2005) that since quinones are not easily degraded by ClO_2, pulp bleachability would be related to the amount of quinone groups and by proxy by tracking the value of a* in the L*a*b* space.

Brightness reversion is a complex phenomenon and can be initiated by light and/or thermal radiation. Also, the extent of brightness reversion depends not only on the intensity of the light or heat but also on the ambient moisture content (relative humidity). Since market pulps are shipped to different destinations, they do experience cyclical changes in both heat and relative humidity during transshipment which changes the brightness of pulp at delivery points. Therefore it is important that for market pulps not only the final brightness but the brightness stability is critical. The heat relative humidity changes also bring about profound changes in the pulp properties including their refineability and strength development.

In this paper, we have used chromacity values to track the efficacy of ECF bleaching with DD and DP stages and to measure the brightness reversion of pulps under different humidity conditions. The objective is to verify the assertion by Lachanel and Chirat (2005) that H_2O_2 is better than ClO_2 in reducing the quinone (color) structures to quinhydroxy (colorless) structures. This implies that bleach plants with final P-stage are better suited to produce high brightness pulps than D-stage. Even if this could be true, more importantly, it is not the brightness but the brightness stability of the pulp will dictate the efficiency of the bleaching process to very high brightness (> 92 % ISO).

It is inferred that to compare the efficiency of a bleaching process, particularly the efficacy of providing very high brightness and brightness stability, it is important to have a unified measurement. In this study we have used the chromacity measurements to track the efficiency of bleaching of pulps to very high brightness.

Color Index and Chromacity Values

Brightness is a measurement of pulp's ability to reflect light in only a very narrow blue band of the spectrum. On the other hand, whiteness is a measurement of a pulp's ability to reflect light across the entire color spectrum. Color is defined by value, hue, and chroma (Judd and Wyscezi 1975). Brightness is a measure of reflectance of blue light at 457 nm (Popson and Malthouse 1990) and is a function of its lightness or whiteness (L*), since the chromacity of these substrates are rather low. For white and near-white pulp or paper, brightness is a single optical measurement. However, when pulps are bleached to very high brightness, a* (red-green) and b* (blue-yellow) numbers do change in the L*a*b* Hunter space. They have to be tracked so as to understand what influence they will have on the "Chromacity Value". The* and b* values have to be optically balanced to minimize the "Grayness" of the pulp or sheet. "The "grayness" influences the extent to which OBAs are needed to further brighten the papers. TAPPI's TAPPI T 524 om-94 sets the criteria for white or near-white paper, having L*$\geq$ 84.0 and a chromacity value of $(\sqrt{(a*^2 + b*^2)})^2 \leq 10.0$. This specification of L*a*b* is not adequate to define pulps bleached to very high brightness.

In this study, a deviation to T 524 om-94 is applied to define the efficiency of a given bleaching chemical or process; bleached pulp having L $\geq$100.0 and chromacity values of $(\sqrt{(a*^2 + b*^2)})^2 \leq 5.0$ at a minimum brightness of 90% ISO is considered as pure white or near-pure white pulp suitable for use in premium grade papers (Exhibit 1). In addition, the pulps should have optimum "x" and "y" values of 0.3 and 0.3, respectively, when plotted in the CIE chromatic diagram at wavelength coordinates of 450 nm, 550 nm and 610 nm.)

A unified measurement called "Chromacity" defines the changes in color on the Hunter's color space and an extension of the "Chromacity" measurement is "Color Index (CI)" which takes into account the difference in the lightness, darkness, and the chromatic differences between the sample and the standard. Both the measurement of chromacity and color index is used in this study to track the efficacy of a particular bleaching sequence. The Color Index (CI) is calculated as follows:

Color Index $=\sqrt{(\Delta L*^2 + \Delta a*^2 + \Delta b*^2)}$……. **(1)**
Where,
$\Delta L* =$ **Delta of whiteness before and after aging**
$\Delta a* =$ **Delta of a* before and after aging**
$\Delta b* =$ **Delta of a* before and after aging**

METHODS AND MATERIALS

The pulp used in the study was an extended cooked and oxygen delignified mill eucalyptus pulp. The pre-O2 properties of pulp used in this study are provided in Table 1.

TABLE 1: Pre-O_2 Delignified Pulp Properties

Oxygen Delignified Eucalyptus Kraft Pulp	
Brightness, % ISO	47.6
Kappa No.	12.5
Viscosity, cP	31.0
HexA´s, mmol/kg	69.5
COD, kg O2/t	7.6

Pulp bleaching was carried out in Quantum Mixer/Reactor model Mark V, equipped with a haste alloy bowl.

o Two different chlorine dioxide delignifications were compared – (1) conventional chlorine dioxide delignification (D_O), and (2) Hot chlorine dioxide delignification (D_{HT}).
o Chlorine dioxide used in the delignification and bleaching was a pure chlorine dioxide with less than 0.1 grams of chlorine per 10 grams of chlorine dioxide and was prepared by the acidification sodium chlorite (simulating industrial R8 and R10 ClO_2)

The following conditions were employed:

- Three pH (4.0, 6.5 and 9.0) and two temperature conditions (70oC and 90oC) were used for the final chlorine dioxide (D2) bleaching stage. The stage conditions were listed elsewhere (Parthasarathy and Brooks 2006 and Coledette 2006).

o Three pH (9.0, 10.0 and 11.0) and two temperature conditions (70oC and 90oC) were used for the final peroxide (D2) bleaching stage. The stages conditions were detailed elsewhere (Parthasarathy and Brooks 2006 and Coledette 2006).

All bleaching experiments were run in duplicate and the samples analyses were run in triplicates to get a minimum of six data points to meet the statistical requirements of population size to calculate the standard error of the standard deviation of the mean.

The methods and materials for conventional chlorine dioxide delignification (D0), hot chlorine dioxide delignification (D_{HT}), peroxide reinforced oxidative extraction (EP) and bleaching with chlorine dioxide (D) and peroxide (P) are detailed elsewhere (Parthasarathy and Brooks 2006 and Coledette et al 2006).

Effluent load was measured on mixed samples comprised of equal parts of filtrates from each bleaching stage of the sequence. For example, for the sequence D-EP-D the equivalent to 9 m^3/BDMT of filtrate was collected for each one of the stages comprising a 27 m^3/BDMT of effluent.

Pulp Kappa number, Brightness and Viscosity and physical properties were measured by TAPPI Standards and SCAN methods. Brightness reversion was tested under two different aging conditions, wet (60ºC, 7 days, 90% RH) and dry (105ºC, 4 hours, 0% RH) following TAPPI Useful Method for the dry test (Modified) and Finnish Pulp and Paper Institute's (KCL) Suggested Method for the wet reversion test (Modified). For the wet reversion test, the original KCL procedure calls for subjecting the pulp sheets at 100% RH at 100ºC for one hour. In this study, the procedure was modified and the exposure time prolonged to 7 days at lower humidity levels (90% RH) and lower temperature (60ºC) to simulate the conditions that the market pulps would be subjected to when shipped overseas. HexAs in pulp was measured by the procedure established by Vuorinen et al., (1996). The "selectivity" of the bleaching process is the ration of Δ Kappa number (% Kappa number drop) to Δ Viscosity (% Viscosity Loss). Bleaching yield was calculated using the formula,

Bleach Yield Shrinkage (Loss) % =
$$0.0812*TOC \ (Kg \ of \ C/BDT) +1.913 \quad (1)$$

TOC is measured in Kg of C in BDT of pulp. Yield shrinkage is calculated as an average of triplicate samples, correcting the standard error to the standard deviation of the average (Standard Methods for the Examination of Water and Wastewater 1995). Pulp OX was measured by the standard PTS-RH: 012/90. The AOX in effluent was measured by SCAN standard SCAN: P69-94. Effluent COD and Color were measured by CPPA standard methods H: 3 and H: 5 respectively.

RESULTS AND DISCUSSION

Brightness for the conventionally delignified (Do) and D_{HT} delignified and DP and DD bleached pulps at three different pH conditions and two bleaching stage temperatures are detailed elsewhere (Parthasarathy and Brooks 2006 and Coledette et al., 2006).

It is observed that increasing final D-stage temperature from 70 to 90 °C has no significant impact on bleaching chemical consumption and bleachability but decreases bleach yield slightly and also lowers the dry/wet brightness reversion. Final D-stage temperature has no significant impact on pulp viscosity. Increasing final D-stage pH increases bleaching chemical costs for a given brightness, a result that can be explained by the higher demand of NaOH to reach the higher pH values. The excess alkali applied result in decreased yield and organically bound chlorine through dissolution of low molecular weight hemicelluloses and chlorinated lignin but increases pulp brightness stability through stabilization of residual hexenuronic acids against acid hydrolysis and through removal of organically bound chlorine. Increasing pH above 6.5 has a dramatic effect on pulp viscosity, a result that can be explained by the hypochlorous acid, a strong and indiscriminate oxidant of cellulose. Also, the chlorine dioxide bleaching at pH values above 4 tend to leave significant ClO_2 residuals at the end of bleaching. Therefore, the choice between high or low temperature and pH in the final D-stage is driven by bleaching cost and pulp quality issues. Lower numbers will decrease bleaching costs whereas higher numbers will improve brightness stability, decrease chlorinated organics and penalize viscosity. Similar observations and conclusions are drawn for D_{HT}(EP)DD sequence too.

The stage-by-stage bleaching results with the D(EP)DP sequence are listed elsewhere (Parthasarathy and Brooks 2006 and Coledette et al., 2006).. It is observed that increasing final P-stage temperature from 70 to 90 °C has no significant impact on bleaching chemical consumption and bleachability but decreases the bleach yield though slightly but again decreases the dry/wet brightness reversion. Final P-stage temperature has a slight negative impact on pulp viscosity. Increasing final P-stage pH increases bleaching chemical costs for a given brightness, a result that can be explained by the higher demand of NaOH to reach the higher pH values. The excess alkali applied result in alkaline hydrolysis of carbohydrates particularly hemicelluloses resulting in increased pulp shrinkage. However, such a hydrolysis lowers the organically bound chlorine and increases viscosity because of the dissolution of low molecular weight hemicelluloses and chlorinated lignin. Again pulp brightness and brightness stability is increased through stabilization of residual hexenuronic acids against acid hydrolysis. Therefore, the choice between high or low temperature and pH in the final P-stage is driven by bleaching cost and pulp quality issues. Lower numbers will decrease bleaching costs whereas higher numbers will improve brightness stability and decrease organically bound chlorine. The D_{HT}(EP)DP sequence follows similarly that of Do(EP)DP bleaching. Increasing final P-stage temperature from 70 to 90 °C has no significant impact on bleaching chemical consumption and bleachability. However, final pH showed significant impact on bleaching yield and dry/wet brightness reversion. Increasing final P-stage pH increases the bleaching chemical costs to bleach brightness and improve brightness stability but has no significant impact on pulp viscosity.

Final D-stage pH and temperature showed no significant effect on L*a*b* color coordinates for both D(EP)DD and D_{HT}(EP)DD sequences before or after dry/wet reversion tests. It was concluded that the final D-stage should be run at the temperature of 70ºC and pH 9.0 for both D(EP)DD and D_{HT}(EP)DD sequences. Although the pH of 9.0 results in higher bleaching cost it is necessary to maintain pulp brightness stability and minimize organically bound chlorine. It was observed that the final P-stage should be run at the temperature of 70 ºC and pH 9 for both D(EP)DP and D_{HT}(EP)DP sequences. The pH of 9.0 results in lower bleaching cost and does not penalize dry/wet brightness stability and organically bound chlorine significantly.

Tables 2 and 3 list the reverted brightness values of the pulps subjected to two different thermal degradation conditions, wet (60ºC, 7 days, 90% RH) and dry (105ºC, 4 hours, 0% RH). The chromacity values for the bleached pulps are provided in Tables 4 and 5 and the brightness and whiteness values of pulps in Table 6.

As the data in Tables 2 and 3 shows, the final brightness of DD and DP bleached pulps is dictated by the first delignification stage, whether it is a Do or D_{HT}. In general, D_{HT} delignified pulps have higher brightness than Do delignified pulps but at lower (~-10%) bleach chemical consumption. Again, DD bleached pulps had a small but statistically significant increase in brightness over DP bleaching (Table 6).

The pulp brightness to whiteness is a straight line relationship (Figure 1).
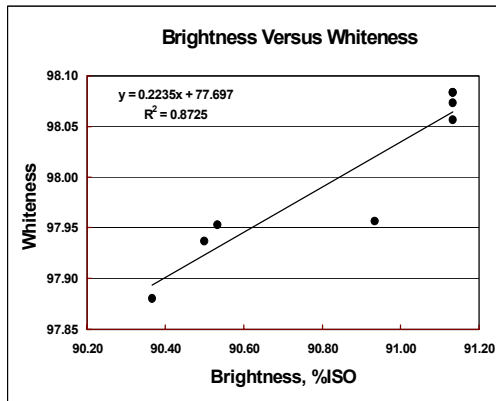
Figure 1: Relationship between Brightness and Whiteness of DD or DP Bleached Pulps.

Increasing the final (D or P) stage temperature from 70°C to 90°C also did not improve either the brightness or whiteness for both Do and D_{HT} delignified pulps. Increasing the final stage temperature though may result in higher brightness, can also initiate cellulose hydrolysis resulting in yield loss. But, the data in this study does not support such an assertion. The other concern is bleaching pulps at high pH and temperature with hydrogen peroxide may result in alkali darkening of pulps and hence lower final brightness (Kutney, and Evans1985 and Zeronian and Inglesby, 1995). Again, such a concern is also unfounded since the brightness, whiteness and the b* (blue-green) values for P- bleaching did not change as the temperature and pH is increased.

Increasing final P-stage pH increases bleaching chemical costs for a given brightness because of the higher demand of NaOH to reach the final pH values. The excess alkali applied result in decreased yield and organically bound chlorine but increased viscosity through dissolution of low molecular weight hemicelluloses and chlorinated lignin. The pulp brightness stability also increases through stabilization of residual hexenuronic acids against acid hydrolysis. Therefore, the choice between high or low temperature and pH in the final P-stage is driven by bleaching cost and pulp quality issues. Lower numbers will decrease bleaching costs whereas higher numbers will improve brightness stability and decrease organically bound chlorine.

While the pulps can be bleached to greater than 91% ISO brightness, the whiteness value was always under 98%. For "pure" white pulp, the whiteness value should be equal to 100. However, since the L* (whiteness) values of both DD and DP bleached pulps are below 100%, they can be categorized only as "near pure" white pulps. Again, the DD bleaching resulted in a small but statistically significant higher whiteness value at comparable brightness than the DP bleached pulps.

It is tempting to infer from the difficulty in bleaching pulps to greater than 100% whiteness to the presence of certain chromophoric groups (Lachanel 2005). These groups may be resistant to bleaching introducing red hue to the pulps thereby suppressing brightness development and increasing reversion. However, the negative a* (green-red) values measured before and after aging (Tables 2 and 3) suggest otherwise. The after reversion

"a*" values for DD bleached pulps were slightly higher than that of DP bleached pulps but measured to be statistically insignificant. The negative a* value of pulps is an indication that bleached pulps have a strong "green" hue than reddishness. Under monochromatic light radiation, the absorbency of quinones is maximum at near infra-red and red spectrum (Andrady 2006). Therefore, the negative a* value and statistically insignificant difference in a* values between P and D bleached pulps is indicative of the fact that quinone structures in the DD bleached pulps may not be any more higher than that of DP bleached pulps, as suggested by Lachanel and Chirat (2005) and again quinone groups unto themselves may not be a factor in the brightness or whiteness development of DD or DP bleached pulp as well as in influencing brightness reversion. This is clearly established from the negative a* values (which indicates more greenish than reddish hue in pulp). This inference is different than the conclusion reached by Lachanel and Chirat (2004 and 2005) that D-bleached pulps have more quinone structures over P-bleached pulps and would be less bright. The data presented in Tables 2 to 6 supports such an inference. However, to make an irrefutable conclusion more data is needed.

The efficacy of DD and DP bleaching can be conclusively judged only after monitoring the brightness reversion upon aging. This would show which bleaching process provides better brightness stability. It is important to note that the mode of aging (wet or dry aging) has a profound influence on the brightness, whiteness and chromacity values of pulp. The brightness reversion associated with the aging of pulps is summarized in Table 7.

As has been previously discussed, $D_{HT}E(P)DD$ bleaching of pulps provided slightly higher brightness pulps than $D_{HT}E(P)DP$ pulps though the difference is statistically insignificant. Such a conjecture is found true for $D_OE(P)DD$ pulps too.

The measurement of Post-Color (PC) number is a simple way to quantify the brightness retention of pulps after aging (Giertz 1954). Table 8 lists the PC color values for the DD and DP bleached pulps. From Table 8, it seems that DP bleached pulps fared better than DD bleached pulps in terms of retaining their brightness with low brightness reversion as indicated by their PC numbers. However, inferring a conclusion based just on the PC number does not provide a complete picture of the changes happening at the color space. To get the complete picture of the changes happening in the pulp during bleaching as well as after bleaching when the bleached pulp is subjected to thermal and light induced aging conditions, it is important to know the changes in Color Index (CI) of the pulp. Measuring the changes in CI, in addition to tracking the changes in the brightness of pulps, is more useful since CI is a unified measurement and encompasses the changes in whiteness and a* and b* coordinates in the color space. Table 9 summarizes the changes in CI values of the D_o and D_{HT} delignified pulps and bleached by DP and DD processes.

Conventionally delignified (D_o) pulps have shown a higher Color Index (CI) value than the hot chlorine dioxide (D_{HT}) delignified pulps both in DD and DP bleaching. Even within this sub-sect, the DD bleached pulps have a higher CI than the DP bleached pulps but the increase in CI value in DD pulps is due an increase in b* (blue-yellow) values. Therefore, the claim by Lachanel and Chirat (2004 and 2005) that final D-stage has an oxidation effect on the residual lignin generating more quinone structures can be only partially supported because while the CI values are higher for DD pulps over DP pulps, the difference in a* values of before and after aged pulps is infinitesimally small and the difference in b* values is significantly large. Referring to CI equation (1), it should be remembered that that CI is dictated by not only by a* values but also by the b* (blue-yellowish scale) values. The argument that final peroxide treatment could reduce quinone structures to quinhydroxy (colorless) structures thus lowering the chances of reversion of pulps has some validity to it but can be conclusively supported only with additional information and data.

The changes in a* and b* values (Table 9) of the DD and DP bleached pulps before and after aging rather indicates that there are

no simple explanations to the brightness reversion of pulps and the assertion by Lachanel and Chirat (2004 and 2005) can be defended only partially. From Table 9, it is clear that there is very little change in a* (red-green) values of DD and DP pulps whereas the changes in b* (blue-yellow) values are significant, indicating that the DD pulps have a "gray" hue than "red" hue; there are structures other than quinones which may be attributing to the changes in CI for the DD bleached pulps. This is true for both conventionally delignified and hot chlorine dioxide delignified DD bleached pulps. The changes in b* values of D_{HT} delignified pulps are somewhat lower than that of D_o delignified pulps and that applies to both DD and DP bleached pulps. But again DD bleached pulps had a higher b* value than that of the DP bleached pulps. This means in DD bleached pulps in addition to quinone structures, there may be other structures which may be contributing to the brightness reversion of pulps. Whether these groups are persistent ones or their role in brightness reversion can be mitigated is an interesting proposition to study. This has commercial implications since the mills that are contemplating to convert their final D-stage (D2) to peroxide (P) stage have to be prepared themselves for a drop in the final brightness of pulps (at constant OXE applications) since DD bleached pulps provided at least 0.7 percentage point higher brightness than DP bleached pulps. This increment in brightness may look small, but as explained by Reeves and Dence (1996), it requires almost exponential application of bleaching chemicals to gain each brightness point beyond 90 %ISO. If the target brightness is raised to 92 %ISO, the brightness advantage gained from DD bleaching has strong commercial implications over DP bleaching, provided certain means are devised to address the disadvantages of the DD pulps over DP pulps on PC and CI value. In order to address this, D_{HT} E(P)D_1D_2 are subjected to a peroxide treatment (D_{HT}E(P)D_1D_2P) while keeping the overall applied Oxidation Equivalent (OXE) same as that of D_{HT}E(P)D_1P process. This means that the peroxide bleaching in D_{HT}E(P)D_1D_2P is a mere polishing step and not a full blown bleaching step as is the case in E(P)D_1P bleaching. The bleaching results are summarized in Table 10.

The hydrogen peroxide polishing of D_{HT}E(P)D_1D_2 pulps (D_{HT}E(P)D_1D_2P) increased the pulp brightness by as much as 0.8 percentage points over D_{HT}E(P)D_1D_2 pulps and almost 1.0 percentage points over D_{HT}E(P)D_1P pulps. This brightness advantage is maintained irrespective of the aging techniques applied on the pulp. More importantly, the CI values of D_{HT}E(P)D_1D_2P and D_{HT}E(P)D_1P pulps are the same. Another interesting observation is that the addition of a polishing step to a DD bleaching sequence resulted in lower b* value than the peroxide bleaching. Since the applied OXE equivalents for both sequences are the same, the additional gain in brightness by the hydrogen peroxide polishing step may even lead to lowering the chlorine dioxide application in the final D-stages thus allowing mills to gain savings in chlorine dioxide use. Also, mills may not incur any additional capital expenses for this modification since the peroxide polishing step can be carried out in the high density tower.

The lowering of b* values of the pulps when a peroxide polishing is included as a part of the final DD stage bleaching, led us to infer that some of the chromophores generated at the end of final D-stage may not be quinone types but of groups that are easily bleachable by peroxide.

As per Liitia et al (2005), ECF bleaching of hardwood Kraft pulps resulted in non-detectable amount of HexAs in pulp whereas the HexAs in the TCF bleached pulps were rather high. On the other hand, the concentration of carbonyl groups for DD bleaching was higher than that of DP bleaching. Adding a peroxide step after a DD stage did result in decreasing the carbonyl groups significantly. Since carbonyl groups do attribute to brightness reversion of pulps, we do propose a conjecture that in the final D-stage bleaching, there may be certain reactions of chlorine dioxide with carbohydrates resulting in the oxidation of C2 and C3 positions to result in increased C=O groups and that the peroxide polishing step may be reducing the carbonyl groups thus resulting in higher brightness and brightness stability for DD bleached pulps. Further research is needed to prove this conjecture.

Table 11 is a comparison of $D_oE(P)D_1D_2$, $D_oE(P)D_1D_2$, $D_{HT}E(P)D_1D_2$ and $D_{HT}E(P)D_1$P bleaching under optimum conditions. The objective of such comparison is to determine the best alternative between D_0 and D_{HT} stage in the first stage and between D and P in the final bleaching stage. It is observed that a hot chlorine dioxide stage (D_{HT}) is more efficient than a regular chorine dioxide stage (D_0) as the first stage of bleaching. It results in about US$2.0 savings per bdt of pulp with the advantage of producing pulp of higher brightness stability. Although the hot stage causes some viscosity drop in relation to the regular D_0-stage, the final value obtained is still acceptable.

A final chlorine dioxide stage run at pH 9.0 produces bleaching costs similar to those obtained with final hydrogen peroxide stage run at pH 9. The brightness reversions of the bleached pulps are also similar. The major inconvenient of the final D-stage is the presence of a significant residual of chlorine dioxide at the end of bleaching and the slightly lower final pulp viscosity. The residual ClO_2 must be destroyed at the end of bleaching to avoid corrosion and that will result in increased demand of reducing agent, which was not taken into account in the cost calculations of this study. The lower viscosity is caused by the hypochlorous acid formed when chlorine dioxide is run at the higher pH value.

The sequences starting with the hot chlorine dioxide stage tended to produce pulps with lower b* coordinate before and after dry or wet reversion, a fact that may be explained by the lower content of hexenuronic acids of these pulps at the end of bleaching.

Table 12 lists the refineability (as measured by the Canadian Standard Freeness, (CSF) and Schopper-Riegler (°SR) tests) and properties development of $D_oE(P)D_1D_2$, $D_oE(P)D_1D_2$, $D_{HT}E(P)D_1D_2$ and $D_{HT}E(P)D_1$P pulps. The ease of refining of pulps is pH dependent function and the final bleaching carried out at pH 9.0 has shown better refineability by reaching a CSF value of about 200 at less than 35 watts hour (Wh) whereas pulps bleached at final pH of 4.0, in this case the DD pulps (both Do and D_{HT} delignified) required as much as 50 Wh to reach the same freeness level. Since all the P-bleaching is carried out either pH 9.0 or 11.0, the one way to compare the refineability of DD pulps is to compare the final D-bleaching at high pH. When the final D-bleaching is carried out at pH 9.0, it followed the same trend as P-bleached pulps at pH.9.0 indicating that ease of refining of pulp is a pH dependent function and an increase in pH requiring increase in NaOH charge results in strong fiber swelling which results in low Wh requirement to refine pulps to a given Canadian Standard Freeness as against pulps bleached to end acidic pH levels (pH 4.0). The DD bleached pulps (for both Do and D_{HT} delignification) as against DP bleached pulps when compared at the same final stage pH provided a slightly better Tensile and Burst index (adjusted for CSF of 200 ml) but correspondingly the Tear Index was lower. The DD bleached pulps have a better Tensile Energy Absorption (TEA) than DP bleached pulp at a given CSF. This is true irrespective what the final stage pH was. The DD bleaching provided a denser (lower bulk) pulp than DP bleached pulp when compared at constant CSF though the difference was statistically not significant. The % opacity followed the sheet density correspondingly. The difference in Modulus of Elasticity (MOE) of DD and DP bleached pulps were insignificant.

CONCLUSIONS

Final brightness of hardwood pulps, in particular eucalyptus pulps is dictated by the type of delignification employed prior to bleaching. Hot chlorine dioxide delignification (D_{HT}) resulted in higher brightness pulps over conventionally delignified (D_o) pulps. A final chlorine dioxide bleaching though resulted in higher brightness pulp than that of a peroxide bleached pulp, the pulp did not keep this brightness advantage upon aging. As a matter of fact, for DD bleached pulps, the post-color number and color index (CI) values are higher than that of DP pulps. Incorporating a peroxide polishing step to DD bleaching will provide not only higher brightness pulp than that of DP bleaching, but also will provide stable pulps, low in PC number and CI values. All these properties

can be achieved at lower chemical consumption, an advantage the only DD bleached pulps can provide than that of the DP bleached pulp.

Refining of pulps bleached at high end pH is easier than the ones bleached at low pH. Between DD and DP bleached pulps, the former provided a better Tensile and Tear Index at a given CSF than the latter but the difference is found to be statistically insignificant. However, at a given OXE application DD bleaching provided a higher brightness pulps than DP bleached pulps with statistically insignificant changes in brightness reversion, CI and chromacity values. It is estimated that between DD and DP bleaching, the former can bleach pulps to 92% ISO brightness at almost US$ 2 to 3 per ton less than that of the latter, a significant cost advantage of having a final D-stage. By keeping the OXE constant and adding a peroxide polishing step to the DD bleaching will lead to not only high brightness pulps but a pulp optically balanced in a* and b* values and that the papermakers will require to use less OBA to reach "pure" white paper (= 100% whiteness).

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REFERENCES

1. Andrady, A.L., Research Triangle Institute (RTI), Research Triangle Park, North Carolina – Private Discussion (2006)

2. Andrady, A.L., Parthasarathy, V.R., Song, Y., Fueki, K., and Torikai, A., "Photo Yellowing of Mechanical Pulp. Part I. Examining Wavelength Sensitivity of Light-Induced Yellowing Using Monochromatic Light". **TAPPI J 74**: 162-168 (1991).

3. Coledette, J., Oliveria, R.B., Azevedo, M.A.B., de Paula, O.C., Sabioni, L., and Lopes Motta, C.L., "Final D-Stage Versus Final P-Stage for High Brightness ECF Bleaching of Eucalyptus Kraft Pulps, Which is Best?" **Technical Report 027/2006**. Submitted to Canexus Limited (October 2006).

4. Daniel, A.I.D., Evtuguin, D.V., Silvestre, A.J.D., and Pascola Neto, C., "Chemical Features of Hardwood Unbleached Kraft Pulps and Their ECF Bleachability." **J. Pulp. Paper. Sci., 30** (4): 94-98 (2004).

5. Desprez, F., Devenyns, J., and Troughton, N.A., "TCF Bleaching of Softwood Kraft Pulp: The Optimal Conditions for P* Hydrogen Peroxide Bleaching" in **1994 TAPPI Pulping Conference**, Atlanta, 1994. p. 929.

6. Eiras, K.M., Francis, R.C., Colodette, J.L., and Lassell, S., "The Role of Bound Chlorine in the Brightness Reversion of Bleached Hardwood Kraft Pulp." **2005 International Pulp Bleaching Conference (IPBC),** Stockholm, Sweden, 2005. p47.

7. Finar, I.L., **Organic Chemistry**. Ed. I.L. Finar. English Language Book Society (ELBS), London, UK (1956)

8. Forskahl, I., Popoff, T., and Theander, O., "Reactions of D-Xylose and D-Glucose in Alkaline Aqueous Solutions." **Carbohydrate Res., 48**: 13-21 (1976).

9. Gellerstedt, G., and Wafa Al-Dajani, W., "Bleachability of Alkaline Pulps. Part I. The importance of -Aryl Ether Linkages in Lignin." **Holzforschung 54** (6): 609-617 (2000).

10. George, J., Lachanel, D., and Robert, D., "Application of the Principles of Extended Delignification. Effects on Softwood Kraft Residual Lignin." **J. Pulp. Paper. Sci., 26** (8): 271-274 (2000).

11. Gierer, J., "The Reactions of Lignin during Pulping". **Svensk Papperstidn 73**: 571-597 (1970)

12. Giertz, H.W., "The Post-Color Number". **Svensk. Papperstidn 57**: 89-94 (1954).

13. Judd, G.B., and Wyszeci, G., **Color in Science, Business and Industry**, Wiley Interscience, New York, NY 1975.

14. Kumar, K.R., Jacobs, C., Jameel, H., and Chang, H., "Bleachability Difference between RDH and Kraft O2 Pulps – Role of Phenolic Hydroxyl Groups in Residual Lignin". **1996 International Pulp Bleaching Conference (IPBC)**. TAPPI Press. pp 147-162.

15. Kutney, G.W., and Evans, T.D., "Peroxide Bleaching of Mechanical Pulps; Part 1. Alkali Darkening – The Effect of Caustic Soda". **Sven. Papperstidn. 88**: R78-R82 (1985)

16. Lachenal, D., Chirat, C., Benattar, N., Hamzeh, Y., Marlin, N., Mateo, C., and Brochier, B., "Influence of Pulp Color on Bleachability. Ways to Improve the Bleaching Response of Alkaline Pulps." **2005 International Pulp Bleaching Conference (IPBC)**, Stockholm, Sweden, 2005. p181.

17. Lachenal, D., Fernandes, J.C., and Froment, P., "Behavior of Residual Lignin in Kraft during Bleaching." **1993 International Pulp Bleaching Conference (IPBC)**, Vancouver, BC. 1994. p.41

18. Lachenal, D., Servillano, R.M., George, J., and Chirat, C., "Understanding the Structures of Residual Lignin. A Key to Progress in Pulping and Papermaking", **Proceedings in the International Symposium on Wood and Pulping Chemistry**, Japan TAPPI Press 1999. pp 354-357.

19. Liitia, T., Ranua, M., Ohra-aho, T., Hortling, B., Pekkala, O., and Tamminen, T., "Formation of Chromophores during Alkaline Pulping: Effects on Bleachability and Brightness Stability." **2005 International Pulp Bleaching Conference (IPBC)**, Stockholm, Sweden, 2005. pp 194-199.

20. McDonough, T.J., Krishnagopalan, G.A., Rawat, N., Saucedo, V.M., Ragauskas, A.J., Mealander, M., Zawadzki, M., **Proceedings in the International Symposium on Wood and Pulping Chemistry**, Japan TAPPI Press 1999. pp 296-301.

21. Mellander, P., Dahl, M., and Norden, S., "Hot D-Bleaching of Eucalyptus Pulps – Every Pulp is Unique." **2005 International Pulp Bleaching Conference (IPBC),** Stockholm, Sweden, 2005. p25.

22. Miyazaki, K., Smelstorius, J.A., Hardwood, B.J., Stewart, C.M., "The Formation of Uronic Acid during Holocellulose Preparation." **APPITA 24** (6): 452-454

23. Parthasarathy, V.R., Grygotis, R.C., Wahoske, K.W., and Bryer, D.M., "A Sulfur-Free, Chlorine-Free Alternative to Kraft Pulping." **TAPPI J 79** (6): 189-198 (1996).

24. Parthasarathy, V.R., and Christian, M., **"Aracruz-Nexen Chemicals Technology Exchange and Discussion."** May 10, 2005.

25. Parthasarathy, V.R., and Brooks, G., " Final Chlorine Dioxide Bleaching as an Option for the Production of Very High Brightness and Optically Balanced Pulps – Comparison of DD versus DP Bleaching Sequences in the Bleaching of Kraft Pulps" in the Proceedings of **2006 TAPPI Engineering, Pulping and Environmental Conference**, TAPPI Press, Atlanta (2006).

26. Popson, S. J. and Malthouse, D. D., **Measurement and control of the optical properties of paper**, 4th publication, Technidyne Corp., New Albany, IN, 1990, p.35.

27. Reeves, D., and Dence, C., in **"Pulp Bleaching – Principles and Practice".** TAPPI Press. Atlanta, GA (1996).

28. Stewart, C.M., and Smelstorius, J.A., in **Chem & Ind** 1968. p.618.

29. TAPPI T 524 om-94 "Color of paper and paper board (45°/0° geometry)."

30. Teder, A., and Tormund, D., "Mathematical Model for Chlorine Dioxide Bleaching and Its Applications". **AIChE Symposium Series No 200**, Volume 76, 1980, p.133.

31. Voiron, T., Kuligowski, C., Berthome, G., and Lachenal, D., "Impact of Chromophores in Chemical Pulps on Bleachability." **2005 International Pulp Bleaching Conference (IPBC),** Stockholm, Sweden, 2005. p288.

32. Zeronian, S.H., and Inglesby, M,K., "Bleaching of Cellulose by Hydrogen Peroxide." **Cellulose 2** :265-272 (1995).

TABLE 2: Bleaching of Pulps by D$_o$E(P)DP and D$_o$E(P)DD Processes: L*a*b*, Brightness and Brightness Reversion Values.

Wet Reversion Test: 60ºC, 7days, 90% Relative Humidity
Do(EP)D$_1$P Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90.6	90.4	90.5
Reverted Brightness, % ISO	87.5	87.9	88.3
Reversion, % ISO	**3.1**	**2.5**	**2.2**
L* before reversion	98	97.92	97.89
a* before reversion	-0.13	-0.1	-0.08
b* before reversion	3.07	3.06	3.02
L* after reversion	97.03	97.15	97.22
a* after reversion	0.19	0.19	0.17
b* after reversion	3.67	3.59	3.43

Dry Reversion Test: 105ºC, 4 hours, 0% Relative Humidity
Do(EP)D$_1$P Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90.6	90.4	90.5
Reverted Brightness, % ISO	88.4	88.3	88.5
Reversion, % ISO	**2.2**	**2.1**	**2**
L* before reversion	98	97.92	97.89
a* before reversion	-0.13	-0.1	-0.08
b* before reversion	3.07	3.06	3.02
L* after reversion	97.5	97.44	97.54
a* after reversion	-0.13	-0.09	-0.15
b* after reversion	3.74	3.89	3.94

Do(EP)D$_1$D$_2$ Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.7	90.3
Reverted Brightness, % ISO	85.5	86.6	87.2
Reversion, % ISO	**5.1**	**4.1**	**3.1**
L* before reversion	97.93	98.08	97.85
a* before reversion	-0.09	-0.18	-0.09
b* before reversion	3.1	3.24	3.09
L* after reversion	96.4	96.75	96.87
a* after reversion	0.59	0.29	0.23
b* after reversion	4.03	3.89	3.68

Do(EP)D$_1$D$_2$ Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.7	90.3
Reverted Brightness, % ISO	87.8	87.9	88
Reversion, % ISO	**2.8**	**2.8**	**2.3**
L* before reversion	97.93	98.08	97.85
a* before reversion	-0.09	-0.18	-0.09
b* before reversion	3.1	3.24	3.09
L* after reversion	97.33	97.4	97.4
a* after reversion	0.05	-0.06	-0.06
b* after reversion	4.09	4.15	4.06

Wet Reversion Test: 60ºC, 7days, 90% Relative Humidity
Do(EP)D$_1$P Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90	90.6	90.5
Reverred Brightness, % ISO	86.8	88.3	88.5
Reversion, % ISO	**3.2**	**2.3**	**2**
L* before reversion	97.8	97.93	97.91
a* before reversion	-0.07	-0.08	-0.1
b* before reversion	3.29	2.99	2.98
L* after reversion	96.83	97.23	97.3
a* after reversion	0.33	0.19	0.16
b* after reversion	3.99	3.48	3.46

Dry Reversion Test: 105ºC, 4 hours, 0% Relative Humidity
Do(EP)D$_1$P Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90	90.6	90.5
Reverred Brightness, % ISO	87.2	88.6	88.5
Reversion, % ISO	**2.8**	**2**	**2**
L* before reversion	97.8	97.93	97.91
a* before reversion	-0.07	-0.08	-0.1
b* before reversion	3.29	2.99	2.98
L* after reversion	97.22	97.56	97.54
a* after reversion	-0.08	-0.17	-0.17
b* after reversion	4.33	3.89	3.9

Do(EP)D$_1$D$_2$ Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.8	90.3
Reverred Brightness, % ISO	85.7	87	87.4
Reversion, % ISO	**4.9**	**3.8**	**2.9**
L* before reversion	98.04	98.06	97.95
a* before reversion	-0.11	-0.14	-0.07
b* before reversion	3.15	3.09	3.27
L* after reversion	96.42	96.85	97.02
a* after reversion	0.63	0.35	0.24
b* after reversion	3.94	3.77	3.71

Do(EP)D$_1$D$_2$ Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.8	90.3
Reverred Brightness, % ISO	87.5	87.7	87.5
Reversion, % ISO	**3.1**	**3.1**	**2.8**
L* before reversion	98.04	98.06	97.95
a* before reversion	-0.11	-0.14	-0.07
b* before reversion	3.15	3.09	3.27
L* after reversion	97.25	97.25	97.21
a* after reversion	0.02	-0.01	-0.06
b* after reversion	4.15	4.09	4.06

TABLE 3: Bleaching of Pulps by $D_{HT}E(P)DP$ and $D_{HT}E(P)DD$ Processes – L*a*b*, Brightness and Brightness Reversion Values

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	91	90.9	90.9
Reverted Brightness, % ISO	88.6	89	89
Reversion, % ISO	**2.4**	**1.9**	**1.9**
L* before reversion	97.97	97.95	97.95
a* before reversion	-0.12	-0.09	-0.06
b* before reversion	2.77	2.78	2.77
L* after reversion	97.25	97.41	97.39
a* after reversion	0.08	0.12	0.1
b* after reversion	3.05	3.22	3.19

$D_{HT}(EP)D_1D_2$ Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.2	90.7
Reverred Brightness, % ISO	87.6	88.4	88.7
Reversion, % ISO	**3.9**	**2.8**	**2**
L* before reversion	98.13	98.14	97.95
a* before reversion	-0.09	-0.13	-0.03
b* before reversion	2.66	2.95	2.95
L* after reversion	96.94	97.29	97.32
a* after reversion	0.45	0.21	0.16
b* after reversion	3.46	3.5	3.3

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	91	90.9	90.9
Reverted Brightness, % ISO	89.1	89	89.4
Reversion, % ISO	**1.9**	**1.9**	**1.5**
L* before reversion	97.97	97.95	97.95
a* before reversion	-0.12	-0.09	-0.06
b* before reversion	2.77	2.78	2.77
L* after reversion	97.64	97.56	97.69
a* after reversion	-0.1	-0.09	-0.08
b* after reversion	3.5	3.52	3.49

$D_{HT}(EP)D_1D_2$ Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.2	90.7
Reverred Brightness, % ISO	88	87.9	88.4
Reversion, % ISO	**3.5**	**3.3**	**2.3**
L* before reversion	98.13	98.14	97.95
a* before reversion	-0.09	-0.13	-0.03
b* before reversion	2.66	2.95	2.95
L* after reversion	97.26	97.26	97.36
a* after reversion	0.08	-0.05	-0.02
b* after reversion	3.74	3.83	3.68

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	91	91.1	91.3
Reverted Brightness, % ISO	88.7	89.2	89.5
Reversion, % ISO	**2.3**	**1.9**	**1.8**
L* before reversion	98.06	98.03	98.08
a* before reversion	-0.11	-0.12	-0.1
b* before reversion	2.84	2.79	2.73
L* after reversion	97.33	97.43	97.56
a* after reversion	0.11	0.08	0.08
b* after reversion	3.32	3.16	3.05

$D_{HT}(EP)D_1D_2$ Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	87.7	88.2	88.8
Reversion, % ISO	**3.8**	**2.9**	**2**
L* before reversion	98.13	98.11	98.01
a* before reversion	-0.1	-0.11	-0.05
b* before reversion	2.67	2.92	2.98
L* after reversion	97.01	97.21	97.38
a* after reversion	0.47	0.23	0.17
b* after reversion	3.45	3.5	3.35

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	91	91.1	91.3
Reverted Brightness, % ISO	89.3	89.7	89.9
Reversion, % ISO	**1.7**	**1.4**	**1.4**
L* before reversion	98.06	98.03	98.08
a* before reversion	-0.11	-0.12	-0.1
b* before reversion	2.84	2.79	2.73
L* after reversion	97.74	97.82	97.82
a* after reversion	-0.1	-0.12	-0.11
b* after reversion	3.59	3.5	3.41

$D_{HT}(EP)D_1D_2$ Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	88.1	88	87.8
Reversion, % ISO	**3.4**	**3.1**	**3**
L* before reversion	98.13	98.11	98.01
a* before reversion	-0.1	-0.11	-0.05
b* before reversion	2.67	2.92	2.98
L* after reversion	97.33	97.35	97.19
a* after reversion	-0.02	-0.04	-0.05
b* after reversion	3.81	3.93	3.78

TABLE 4: Chromacity Values for Do Delignified and DP and DD Bleached Pulps

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
Do(EP)D₁P. Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90.6	90.4	90.5
Reverted Brightness, % ISO	87.5	87.9	88.3
Reversion, % ISO	**3.1**	**2.5**	**2.2**
Chromacity Value			
Before Reversion	**3.1**	**3.1**	**3.0**
After Reversion	**3.7**	**3.6**	**3.4**

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
Do(EP)D₁P. Final Stage Temperature 70ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90.6	90.4	90.5
Reverted Brightness, % ISO	88.4	88.3	88.5
Reversion, % ISO	**2.2**	**2.1**	**2.0**
Chromacity Value			
Before Reversion	**3.1**	**3.1**	**3.0**
After Reversion	**3.7**	**3.9**	**3.9**

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
Do(EP)D₁D₂. Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.7	90.3
Reverred Brightness, % ISO	85.5	86.6	87.2
Reversion, % ISO	**5.1**	**4.1**	**3.1**
Chromacity Value			
Before Reversion	**3.1**	**3.2**	**3.1**
After Reversion	**4.1**	**3.9**	**3.6**

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
Do(EP)D₁D₂. Final Stage Temperature 70ºC

pH	4.0	6.5	9.0
Brightness, % ISO	90.6	90.7	90.3
Reverred Brightness, % ISO	87.8	87.9	88
Reversion, % ISO	**2.8**	**2.8**	**2.3**
Chromacity Value			
Before Reversion	**3.1**	**3.2**	**3.1**
After Reversion	**4.1**	**4.2**	**4.1**

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
Do(EP)D₁P. Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90	90.6	90.5
Reverred Brightness, % ISO	86.8	88.3	88.5
Reversion, % ISO	**3.2**	**2.3**	**2.0**
Chromacity Value			
Before Reversion	**3.2**	**3.0**	**3.0**
After Reversion	**4.0**	**3.5**	**3.5**

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
Do(EP)D₁P. Final Stage Temperature 90ºC

pH	9.0	10.0	11.0
Brightness, % ISO	90	90.6	90.5
Reverred Brightness, % ISO	87.2	88.6	88.5
Reversion, % ISO	**2.8**	**2.0**	**2.0**
Chromacity Value			
Before Reversion	**3.2**	**3.0**	**3.0**
After Reversion	**4.3**	**3.9**	**3.9**

Wet Reversion Test:
60ºC, 7days, 90% Relative Humidity
Do(EP)D₁D₂. Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	87.7	88.2	88.8
Reversion, % ISO	**3.8**	**2.9**	**2.0**
Chromacity Value			
Before Reversion	**2.7**	**2.9**	**3.0**
After Reversion	**3.5**	**3.5**	**3.4**

Dry Reversion Test:
105ºC, 4 hours, 0% Relative Humidity
Do(EP)D₁D₂. Final Stage Temperature 90ºC

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	88.1	88	87.8
Reversion, % ISO	**3.4**	**3.1**	**3.0**
Chromacity Value			
Before Reversion	**2.7**	**2.9**	**3.0**
After Reversion	**3.8**	**3.9**	**3.8**

TABLE 5: Chromacity Values for D_{HT} Delignified and DP and DD Bleached Pulps.

Wet Reversion Test:
60°C, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 70°C

pH	9.0	10.0	11.0
Brightness, % ISO	91	90.9	90.9
Reverred Brightness, % ISO	88.6	89	89
Reversion, % ISO	**2.4**	**1.9**	**1.9**
Chromacity Value			
Before Reversion	**2.8**	**2.8**	**2.8**
After Reversion	**3.0**	**3.2**	**3.2**

Dry Reversion Test:
105°C, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 70°C

pH	9.0	10.0	11.0
Brightness, % ISO	91	90.9	90.9
Reverred Brightness, % ISO	89.1	89	89.4
Reversion, % ISO	**1.9**	**1.9**	**1.5**
Chromacity Value			
Before Reversion	**2.8**	**2.8**	**2.8**
After Reversion	**3.5**	**3.5**	**3.5**

Wet Reversion Test:
60°C, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1D_2$. Final Stage Temperature 70°C

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.2	90.7
Reverred Brightness, % ISO	87.6	88.4	88.7
Reversion, % ISO	**3.9**	**2.8**	**2**
Chromacity Value			
Before Reversion	**2.7**	**3.0**	**3.0**
After Reversion	**3.5**	**3.5**	**3.3**

Dry Reversion Test:
105°C, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1D_2$. Final Stage Temperature 70°C

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.2	90.7
Reverred Brightness, % ISO	88	87.9	88.4
Reversion, % ISO	**3.5**	**3.3**	**2.3**
Chromacity Value			
Before Reversion	**2.7**	**3.0**	**3.0**
After Reversion	**3.7**	**3.8**	**3.7**

Wet Reversion Test:
60°C, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 90°C

pH	9.0	10.0	11.0
Brightness, % ISO	91	91.1	91.3
Reverred Brightness, % ISO	88.7	89.2	89.5
Reversion, % ISO	**2.3**	**1.9**	**1.8**
Chromacity Value			
Before Reversion	**2.8**	**2.8**	**2.7**
After Reversion	**3.3**	**3.2**	**3.1**

Dry Reversion Test:
105°C, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1P$. Final Stage Temperature 90°C

pH	9.0	10.0	11.0
Brightness, % ISO	91	91.1	91.3
Reverred Brightness, % ISO	89.3	89.7	89.9
Reversion, % ISO	**1.7**	**1.4**	**1.4**
Chromacity Value			
Before Reversion	**2.8**	**2.8**	**2.7**
After Reversion	**3.6**	**3.5**	**3.4**

Wet Reversion Test:
60°C, 7days, 90% Relative Humidity
$D_{HT}(EP)D_1D_2$. Final Stage Temperature 90°C

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	87.7	88.2	88.8
Reversion, % ISO	**3.8**	**2.9**	**2.0**
Chromacity Value			
Before Reversion	**2.7**	**2.9**	**3.0**
After Reversion	**3.5**	**3.5**	**3.4**

Dry Reversion Test:
105°C, 4 hours, 0% Relative Humidity
$D_{HT}(EP)D_1D_2$. Final Stage Temperature 90°C

pH	4.0	6.5	9.0
Brightness, % ISO	91.5	91.1	90.8
Reverred Brightness, % ISO	88.1	88	87.8
Reversion, % ISO	**3.4**	**3.1**	**3.0**
Chromacity Value			
Before Reversion	**2.7**	**2.9**	**3.0**
After Reversion	**3.8**	**3.9**	**3.8**

TABLE 6: Brightness and Whiteness of D_o and D_{HT} Delignified Pulps Subjected to DD or DP Bleaching

Hot Chlorine Dioxide Delignification (D_{HT}) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	End pH	Brightness % ISO	Lightness or Whiteness (L*)	
$D_{HT}E(P)D_1P$	70.0	9.0	91.00	97.97	
		10.0	90.90	97.95	
		11.0	90.90	97.95	
			90.93	**97.96**	Average
	90.0	9.0	91.00	98.06	
		10.0	91.10	98.03	
		11.0	91.30	98.08	
			91.13	**98.06**	Average
$D_{HT}E(P)D_1D_2$	70.0	4.5	91.50	98.13	
		6.0	91.20	98.14	
		9.0	90.70	97.95	
			91.13	**98.07**	Average
	90.0	4.5	91.50	98.13	
		6.0	91.10	98.11	
		9.0	90.80	98.01	
			91.13	**98.08**	Average

Conventional Chlorine Dioxide Delignification (D_O) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	End pH	Brightness % ISO	Lightness or Whiteness (L*)	
$D_OE(P)D_1P$	70.0	9.0	90.60	98.00	
		10.0	90.40	97.92	
		11.0	90.50	97.89	
			90.50	**97.94**	Average
	90.0	9.0	90.00	97.80	
		10.0	90.60	97.93	
		11.0	90.50	97.91	
			90.37	**97.88**	Average
$D_OE(P)D_1D_2$	70.0	4.5	90.60	97.93	
		6.0	90.70	98.08	
		9.0	90.30	97.85	
			90.53	**97.95**	Average
	90.0	4.5	91.50	98.13	
		6.0	91.10	98.11	
		9.0	90.80	98.01	
			91.13	**98.08**	Average

TABLE 7: Summary of Brightness Reversion of D_o- and D_{HT}-Delignified and DD and DP Bleached Pulps.

Hot Chlorine Dioxide Delignification (D_{HT}) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	End pH	Brightness % ISO	Brightness Reversion	
				Wet Method*	Dry Method**
$D_{HT}E(P)D_1P$	70.0	9.0	91.00	88.60	89.10
		10.0	90.90	89.00	89.00
		11.0	90.90	89.00	89.40
			90.93	**88.87**	**89.17**
	90.0	9.0	91.00	88.70	89.30
		10.0	91.10	89.20	89.70
		11.0	91.30	89.50	89.90
			91.13	**89.13**	**89.63**
$D_{HT}E(P)D_1D_2$	70.0	4.5	91.50	87.60	88.00
		6.0	91.20	88.40	87.90
		9.0	90.70	88.70	88.40
			91.13	**88.23**	**88.10**
	90.0	4.5	91.50	87.70	88.10
		6.0	91.10	88.20	88.00
		9.0	90.80	88.80	87.80
			91.13	**88.23**	**87.97**

Conventional Chlorine Dioxide Delignification (D_O) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	End pH	Brightness % ISO	Brightness Reversion	
				Wet Method*	Dry Method**
$D_OE(P)D_1P$	70.0	9.0	90.60	87.50	88.40
		10.0	90.40	87.90	88.30
		11.0	90.50	88.30	88.50
			90.50	**87.90**	**88.40**
	90.0	9.0	90.00	86.80	87.20
		10.0	90.60	88.30	88.60
		11.0	90.50	88.50	88.50
			90.37	**87.87**	**88.10**
$D_OE(P)D_1D_2$	70.0	4.5	90.60	85.50	87.80
		6.0	90.70	86.60	87.90
		9.0	90.30	87.20	88.00
			90.53	**86.43**	**87.90**
	90.0	4.5	91.50	87.70	88.10
		6.0	91.10	88.20	88.00
		9.0	90.80	88.80	87.80
			91.13	**88.23**	**87.97**

*Wet Reversion Test: 60°C, 7 Days, 90% Relative Humidity
**Dry Reversion Test: 105°C, 4 Hours, 0% Relative Humidity

TABLE 8: Post-Color Numbers of DP and DD Bleached Pulps.

Hot Chlorine Dioxide Delignification (D_{HT}) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	Brightness % ISO	Brightness Reversion		Post-Color Number	
			Wet Method*	Dry Method**	Wet Method*	Dry Method**
$D_{HT}E(P)D_1P$	70.0	90.93	88.87	89.17	0.212	0.196
	90.0	91.13	89.13	89.63	0.208	0.181
Average		91.03	89.00	89.40	0.210	0.188
$D_{HT}E(P)D_1D_2$	70.0	91.13	88.23	88.10	0.250	0.256
	90.0	91.13	88.23	87.97	0.250	0.261
Average		91.13	88.23	88.03	0.250	0.259

Conventional Chlorine Dioxide Delignification (D_O) and Multi-stage Bleaching

Bleaching Sequence	Final Stage Temperature °C	Brightness % ISO	Brightness Reversion		Brightness Reversion	
			Wet Method*	Dry Method**	Wet Method*	Dry Method**
$D_oE(P)D_1P$	70.0	90.50	87.90	88.40	0.238	0.214
	90.0	90.37	87.87	88.10	0.234	0.223
Average		90.43	87.88	88.25	0.236	0.218
$D_oE(P)D_1D_2$	70.0	90.53	86.43	87.90	0.298	0.239
	90.0	91.13	88.23	87.97	0.250	0.261
Average		90.83	87.33	87.93	0.274	0.250

TABLE 9: Summary of Color Index Values of DP and DD Bleached Pulps.

Hot Chlorine Dioxide Delignification (D_{HT}) and Multi-stage Bleaching

Bleaching Sequence		Whiteness, % (L*)		Chroma Values a*		b*		Color-Index		Average	Delta[1] (between DP and DD bleaching)
		Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**		
$D_{HT}E(P)D_1P$	Before Aging	98.01	98.01	-0.10	-0.10	2.78	2.78				
	After Aging	97.40	97.71	-0.10	-0.10	3.17	3.50	0.72	0.78	0.75	
$D_{HT}E(P)D_1D_2$	Before Aging	98.08	98.08	-0.08	-0.08	2.86	2.86				
	After Aging	97.19	97.29	0.28	-0.02	3.43	3.80	1.12	1.23	1.17	-0.42

Conventional Chlorine Dioxide Delignification (D_O) and Multi-stage Bleaching

Bleaching Sequence		Whiteness, % (L*)		Chroma Values a*		b*		Color-Index		Average	Delta[1] (between DP and DD bleaching)
		Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**		
$D_oE(P)D_1P$	Before Aging	97.9	97.91	-0.09	-0.09	3.07	3.07				
	After Aging	97.1	97.35	0.21	-0.02	3.60	3.83	0.99	0.95	0.97	
$D_oE(P)D_1D_2$	Before Aging	98.0	98.02	-0.10	-0.10	3.00	3.00				
	After Aging	96.9	97.20	0.33	0.09	3.65	3.86	1.33	1.20	1.27	-0.30

1. Delta is calculated between DP and DD bleaching between likely testing events (before aging and after aging events)

TABLE 10: Properties of Bleached Pulps from $D_{HT}E(P)D_1D_2P$ and $D_{HT}E(P)D_1P$ Processes.

Bleaching Sequence		Brightness, %ISO	Whiteness, % (L*)		Chroma Values a*		b*		Color-Index		Average
			Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**	Wet Method*	Dry Method**	
$D_{HT}E(P)D_1D_2P$	Before Aging	92.0	98.31	98.41	-0.11	-0.09	2.74	2.54			
	After Aging	89.7	97.59	98.01	-0.09	-0.10	2.93	3.20	0.74	0.77	0.76
$D_{HT}E(P)D_1P$	Before Aging	91.0	98.01	98.01	-0.10	-0.10	2.78	2.78			
	After Aging	89.2	97.40	97.71	-0.10	-0.10	3.18	3.50	0.73	0.78	0.75

TABLE 11: Comparison between the sequences D(EP)DD, D_{HT}(EP)DD, D(EP)DP and D_{HT}(EP)DP under optimum conditions

Conditions and Results	D(EP)DD	D_{HT}(EP)DD	D(EP)DP	D_{HT}(EP)DP
[1]Total Active Chlorine, kg/bdt	5.23	4.73	5.25	4.75
[2]Bleachability, K #/% act Cl	2.39	2.64	2.38	2.63
[3]Chemical Cost, US$/bdt	28.3	26.0	28.5	26.2
Final pH Last Stage	**9.0**	**9.0**	**9.3**	**9.3**
Oxidant Cosumed at Last Stage , %	**81**	**87**	**100**	**100**
Kappa No.	0.5	0.2	0.8	0.4
Viscosity, cP	15.5	12.0	17.8	15.2
Final Brightness, % ISO	90.3	90.7	90.6	91.0
Dry Reverted Brightness, % ISO	88.0	88.4	88.4	89.1
Wet Reverted Brightness, % ISO	87.2	88.7	87.5	88.6
[4]Dry Reversion, % ISO	2.3	2.3	2.2	1.9
[5]Wet Reversion, % ISO	3.1	2.0	3.1	2.4
HexA´s, mmol/kg	5.1	1.9	5.7	2.2
Cumulative TOC, kg C/bdt	11.2	11.0	11.4	11.1
[6]Cumulative Bleaching Yield, %	97.2	97.2	97.2	97.2
OX, kg Cl⁻/bdt	0.12	0.12	0.13	0.11
L* before reversion	97.9	98.0	98.0	98.0
a* before reversion	-0.09	-0.03	-0.13	-0.12
b* before reversion	3.1	3.0	3.1	2.8
L* after **Dry** reversion	97.4	97.4	97.5	97.6
a* after **Dry** reversion	-0.06	-0.02	-0.13	-0.10
b* after **Dry** reversion	4.1	3.7	3.7	3.5
L* after **Wet** reversion	96.9	97.3	97.0	97.3
a* after **Wet** reversion	0.23	0.16	0.19	0.08
b* after **Wet** reversion	3.7	3.3	3.7	3.1

[1] Total Active Chlorine = (ClO2*2.63 + H_2O_2*2.09);
[2] Original pulp kappa No./ total active chlorine;
[3] Based on prices listed in Item 3.2.;
[4] Reversion Test: 60ºC, 7days, 90% Relative Humidity
[5] Dry Reversion Test: 105ºC, 4 hours, 0% Relative Humidity
[6] Calculated from TOC values through the following equation: Yield loss (%) = 0.0812*TOC (kg C/bdt) + 1.913.

TABLE 12: Properties of Bleached Pulps from $D_{HT}E(P)D_1D_2P$ and $D_{HT}E(P)D_1P$ Processes.

Samples	Mill Revo-lutions	Energy Consumption Wh	Freeness ml	°SR	Tensile Index N.m/g	Burst Index kPa.m²/g	Tear Index mN.m²/g	Stretch %	Air Resistance s/100cm³	Thickness sµm	Density kg/m³	Bulk cm³/g	T.E.A. J/m²	M.O.E. MNm/kg	Opacity %
D(EP)DD Ph = 4	0	0	550	15.0	17.15	0.72	3.57	1.16	0.52	150	410.67	2.44	9.10	3.31	81.05
	1500	18	400	24.0	51.18	3.14	10.72	2.53	3.54	105	605.26	1.65	57.16	5.95	77.70
	3000	38	270	36.0	69.31	5.47	11.30	3.20	18.86	90	694.20	1.44	96.36	6.42	73.52
	4500	57	190	48.0	76.81	6.10	10.89	3.31	66.73	85	737.49	1.36	109.67	6.75	69.94
D(EP)DD Ph = 9	0	0	500	18.0	21.76	1.01	4.82	1.25	0.75	143	447.76	2.23	12.29	3.87	81.20
	1000	12	370	26.0	49.30	3.31	11.41	2.55	4.09	107	582.88	1.72	56.76	5.67	75.46
	2000	24	250	38.0	67.66	4.87	11.54	3.10	27.39	95	669.81	1.49	93.08	6.41	72.88
	3000	36	160	52.0	70.43	5.76	10.61	3.12	116.49	86	743.72	1.34	97.18	6.44	69.44
D*(EP)DD Ph = 4	0	0	610	13.0	16.27	0.79	4.00	1.03	0.55	150	410.68	2.43	7.47	3.26	80.59
	1500	19	420	23.0	50.37	3.36	9.54	2.46	4.85	100	635.80	1.57	56.64	5.98	77.24
	3000	36	320	31.0	62.11	4.47	9.78	3.10	17.67	90	700.00	1.42	90.10	6.31	71.64
	4500	55	180	48.0	72.50	5.41	8.67	3.65	76.94	83	754.18	1.32	118.50	6.48	69.00
D*(EP)DD Ph = 9	0	0	510	18.0	17.11	0.80	3.97	0.96	0.48	150	421.40	2.38	7.24	3.40	81.11
	1000	12	370	25.0	44.45	3.19	8.96	2.25	3.92	105	597.56	1.67	44.94	5.46	78.04
	2000	24	270	35.0	60.33	4.00	9.31	2.43	13.71	95	664.36	1.51	79.13	6.41	73.58
	3000	37	180	50.0	65.56	4.31	9.10	3.08	69.54	84	733.83	1.36	92.35	6.57	70.93
D(EP)DP Ph = 9	0	0	510	17.0	16.67	0.76	3.75	0.89	0.49	155	414.45	2.41	6.34	3.42	81.39
	1000	12	400	24.0	46.34	3.01	10.34	2.16	2.72	107	584.46	1.71	44.84	5.69	77.16
	2000	24	280	33.0	66.89	4.71	10.95	3.11	12.86	95	652.53	1.53	91.31	6.38	73.80
	3000	36	190	46.0	78.24	5.81	10.65	3.73	39.96	87	713.33	1.40	106.72	6.44	71.09
D(EP)DP Ph = 11	0	0	530	15.0	17.40	0.71	4.71	1.05	0.53	155	407.38	2.45	7.94	3.39	81.19
	1000	12	350	26.0	50.10	3.18	10.58	2.49	3.96	110	578.38	1.72	55.49	5.69	77.06
	2000	24	270	35.0	67.63	4.60	11.54	3.33	14.76	93	675.44	1.48	98.83	6.03	74.10
	3000	36	180	48.0	71.57	5.25	11.55	3.41	45.71	87	720.40	1.39	107.27	6.27	71.17
D*(EP)DP Ph = 9	0	0	510	18.0	17.99	0.83	4.44	1.28	0.61	150	422.16	2.37	10.76	3.39	80.75
	1000	13	400	24.0	42.37	2.40	10.46	2.44	2.55	110	582.63	1.72	47.80	5.25	77.33
	2000	25	290	32.0	54.11	3.38	10.66	2.56	10.92	100	640.60	1.56	63.97	6.33	74.13
	3000	37	200	46.0	64.45	4.83	9.53	3.03	54.57	89	713.73	1.40	87.61	6.36	73.09
D*(EP)DP Ph = 11	0	0	540	17.0	18.81	0.93	4.25	1.01	0.70	150	433.83	2.31	8.20	3.60	81.93
	1000	12	400	24.0	41.20	2.61	9.57	2.19	2.42	110	569.88	1.75	41.12	5.33	77.69
	2000	24	290	32.0	56.98	3.74	9.75	2.76	13.58	95	652.53	1.53	72.32	6.26	74.89
	3000	36	190	45.0	66.16	5.03	9.60	2.94	57.54	87	721.79	1.38	87.87	6.51	69.60

NOTE: SR⁰= Schopper Riegler. T.E.A.= Tensile Energy Absorption. M.O.E. = Modulus of Elasticity.