

CHALLENGES AND OPPORTUNITIES IN MEASURING AND MAINTAINING BRIGHTNESS OF BLEACHED EUCALYPT KRAFT PULP

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SUMMARY

One of the most important tasks of present wood chemical and pulping process research is to better understand the mechanisms behind the yellowing of chemical pulp and to find ways to counteract it. Market pulp producers in tropical areas far from the paper mill customers are evidently those most concerned with the problem of yellowing. The causes behind yellowing can be divided into two categories, one relating to the chemical composition of the pulp and the other to the physical conditions to which the pulp bale is exposed on its way from the pulp dryer to the re-pulper. In the present paper these two categories are further discussed and practical advice based on a literature review given. Significant attention is also given to the confused area of standard methods for measuring yellowing of chemical pulp and for reporting the results of such studies. It is proposed that a standard method is developed and that a normalised ISO unit at 90 % brightness is introduced as the unit in which yellowing of a fully bleached chemical pulp is to be reported.

BACKGROUND

Pulp is traded based on brightness, where a brighter pulp can be sold at a higher price. The papermaker uses the pulp to make paper of a certain whiteness, where the brightness of the pulp and the addition of optical whiteners gives the whiteness. The brighter the pulp, the lower is the requirement for whiteners and accordingly the lower the cost for the papermaker. These facts together call for the importance of A.) Correct measurement of the brightness B.) lowest possible brightness reversion. Whereas there is an easy fix to the former problem, the latter is a notoriously difficult thing. It is well-known that yellowing is strongly affected by heat, moist and storage time.

In the present paper the methods of studying yellowing in the laboratory are at first discussed followed by a critical way of reporting yellowing results. Following this a review of a number of recent papers devoted to the chemical origin.

METHODS TO STUDY YELLOWING

An industrially relevant study on yellowing of chemical pulp should use the actually yellowed pulp as raw material. Although yellowed pulp from certain shipments may be a suitable source, the problem is that the precise conditions that have caused this particular yellowing are often not known in detail. This leads to difficulties in the interpretation of the results. Instead laboratory-yellowed pulp is often used.

Such pulp is said to have been subjected to an *accelerated yellowing procedure*.

Although there has long been a quest for a standard method for accelerated yellowing of *pulp*, no method has yet been standardised, in spite of the fact that organisations like Tappi and SCAN-test have made serious attempts to develop such. The only method describing a procedure for measuring yellowing of pulp issued by a standardisation organisation is the Tappi um 200 entitled “Test for reversion of bleached pulp”. In this method, without any explanation or reference to the literature, it is simply claimed that yellowing is measured by keeping a brightness sheet in an oven with circulating air at 105 °C for 4 h. The loss of brightness is then a measure of the yellowing. The humidity level in the oven is not considered as a variable in the test, neither is the sheet formation or the handling procedure for the sheet described. In order to reduce the time required, treatment for 3 h instead of 4 h under these conditions is also widely practised. All this opens up for big differences in results from different laboratories, although within one laboratory results show a good reproducibility.

If the scope is slightly widened also to include standard methods for measurement of yellowing of *paper and paper products* another three standard methods are found, all of which are issued by ISO, being 5630-1:1991, 5630-3:1996 and 5630-4:1986. The latter is aimed for electro-technical paper grades using very high temperatures and here not further discussed. ISO 5630-1 is a dry treatment at 105 °C, whereas ISO 5630-3 is a moist treatment at 80 °C and 65 % relative humidity. The difference might seem semantic, but it is a problem that these ISO methods do not specify that yellowing, or more precisely ageing, of *pulp* also could be measured in addition to that of paper and board. Unlike the Tappi um 200, the ISO 5630-1 specifies how the sample should be put in the oven and how the circulation of air inside the oven should take place. The preferred yellowing time according to the standard is 72 h, but also 24 h, 48 h and 144 h are accepted. This standard also specifies the way the conditioning of the sample should be made after taking it out from the oven. The moist method, ISO 5630-3 specifies a humidity of 65 % during the yellowing procedure and the same time four treatment times as in ISO 5630-1.

In the introduction of ISO 5630-1 it is anticipated that this dry method does not rank papers as accurately as the moist method in relation to their actual yellowing. It is near-at-hand to believe that the accuracy will be better if pulps bleached in one bleaching sequence are compared, than if pulps bleached in different sequences are compared. Yet, a

good correlation between a dry and a moist yellowing procedure (though not carried out according to the above mentioned ISO standards), has been shown in the literature (1) in a comparative study of 13 different ECF and TCF bleaching sequences applied to the same oxygen delignified Eucalypt kraft pulp (Figure 1). With one exception, the sequence (DQ)(PO), a good correlation between the yellowing obtained with the dry and moist methods was shown.

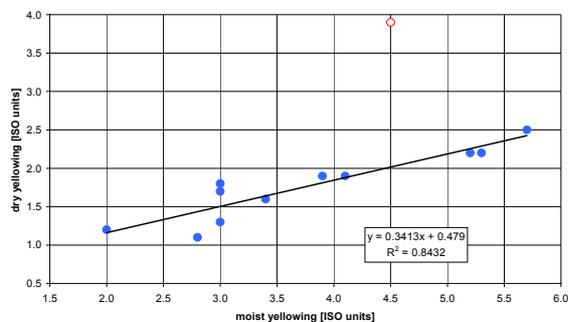


Figure 1. A good correlation between the dry yellowing and the moist yellowing was found in the study comparing different bleaching sequences applied to one and the same oxygen delignified Eucalypt kraft pulp.

The advantages of a dry method in general are identified in ISO 5630-1 as “simple” and “sufficiently adequate for many purposes”. From a practical fiberline trimming perspective the stipulated long yellowing times of ISO 5630-1 compared to those of Tappi um 200 presents a problem, as also noted in the literature (2). It is proposed that the ISO 5630-1 is modified whereby the scope is extended also to apply to pulp whereby a short yellowing time of 4 h is added to the list of allowed yellowing times. In this extended method special attention also needs to be paid to the surface weight of the pulp sheet. This is important since moist increases the yellowing and the higher the surface weight of the pulp sample, the longer time the treatment in the oven will involve more or less moist conditions.

When testing a paper or a board the surface weight of the test sample is obviously the same as that of the product, but for pulp the case is different. Often the yellowing is studied after the last bleaching stage where no surface weight is defined by the process, but even if the pulp is sampled after the drying machine it is problematic since in addition to sheet drying also flash dryers prevail.

A standard method for yellowing of *pulp* thus must specify a certain surface weight of the lab sheet prepared from the studied pulp sample. To merely refer to the ISO standard describing how to prepare a paper sheet for ISO brightness measurement is not sufficient, since ISO 3688:1999 in addition to a hand sheet also allows a sheet of not so well defined surface weight prepared on a Buchner funnel to be used.

PROPERTIES AND UNITS

Yellowing is often reported as PC number (post colour number) (3). It is important to note that the PC number

is a unit, not a property, a fact that is not rarely missed. Without a clear description of which method that has been used the PC number in itself thus does not tell anything.

Basically there are two different ways how yellowing is reported, either as loss of (ISO) brightness units or after a recalculation as PC number. In addition Tran (4) has proposed that yellowing should be expressed in terms of Δb^* instead of ΔR_{∞} , i.e. ISO units. It is argued that this way of measuring would be more indicative for the paper application. Returning to the two common ways, the loss of ISO units way has two clear advantages. One is that it is simple, the other that it is easy to understand the magnitude. However, this approach is only meaningful as long as pulps having the same (ISO) brightness are to be compared. This is true since the chromophore concentration is not linearly related to the (ISO) brightness, but is linked to it via the Kubelka–Munk equation (5).

$$\frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$

(k is the absorption coefficient, s the scattering coefficient and R_{∞} is the ISO brightness). Calculating the yellowing factor according to

$$y_{\text{factor}} = \frac{R_{\infty} - R_y}{R_{\infty}}$$

as proposed by some authors (6, 7), suffers from the same problem (R_y is the brightness after yellowing). In order to enable a comparison of the magnitude of yellowing of pulps with different (ISO) brightness a recalculation is therefore necessary. The PC number here shows the way

$$PC \text{ number} = 100 \left[\left(\frac{k}{s} \right)_{\text{after yellowing}} - \left(\frac{k}{s} \right)_{\text{before yellowing}} \right]$$

where the scattering coefficient, s , obviously is unaffected by the yellowing. One clear drawback of the PC number also appears, being the difficulty of understanding what a certain PC number value actually means. The sense for the importance of a change in PC number from 0.15 to 0.17 is hard to gain. It is therefore now time to propose a way forward from the present confused situation combining the accuracy of the PC number approach with the ease of interpretation of the ISO brightness units loss approach.

The vast majority of all bleached chemical pulp in the world today is bleached to a final ISO brightness of 90 %, the variation being 88–92 %. Although small, this variation still is too big to allow the first approach directly, as will be shown. Instead it is proposed that the PC number is first calculated for a pulp to be compared, where after the PC number achieved is used to calculate which ISO brightness unit loss this would mean if the final ISO brightness had been 90.0 %. A reference final brightness level of 90 % ISO is thus established and the yellowing of all pulps normalised to reflect the yellowing at this particular final ISO brightness. Figure 2 shows the relation between the

yellowing at 90 % ISO brightness expressed in ISO units and the PC number.

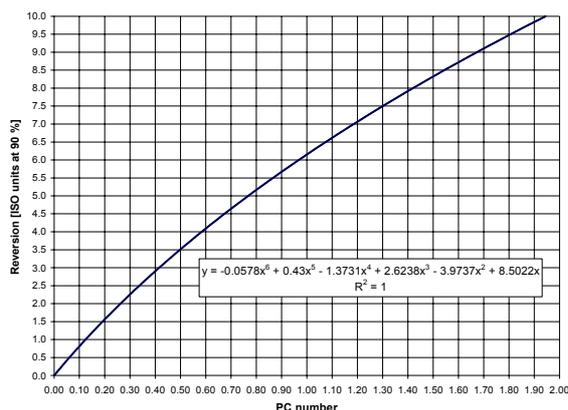


Figure 2. The normalised reversion at an ISO brightness of 90 % as a function of the PC number.

The relation could also be expressed mathematically such that

$$y_{90} = 8.5022 p - 3.9737 p^2 + 2.6238 p^3 - 1.3731 p^4 + 0.43 p^5 - 0.0578 p^6$$

where y_{90} is the yellowing at 90 % ISO brightness and p is the calculated PC number. An example aimed at illustrating the importance of the recalculation and the strength of the proposed approach is shown in Table 1.

Table 1. At a measured yellowing of 2.0 ISO units, the pulp with the highest brightness has yellowed the least and vice versa. It is important to understand that the chromophore concentration is not linearly related to the ISO brightness. Recalculating the yellowing to PC number gives a fair measure, but a measure hard to understand. It is here instead proposed that the PC number is used to calculate the yellowing expressed in ISO units at an ISO brightness of 90.0 %.

ISO brightness [%]	Reversion [ISO units]	PC number	Normalised ISO units at 90 %
90.5	2.0	0.25	1.9
88.6	2.0	0.30	2.3
92.3	2.0	0.20	1.6
80.4	2.0	0.59	4.0

In a recent article (8) it is proposed that the causes of yellowing of a fully bleached pulp could be more easily discovered if the yellowing characteristics not only of the fully bleached pulp, but also of semi-bleached samples are studied. To do so, a normalised reporting of the yellowing is required, and the PC number has so far been used.

EXPERIMENTAL

A lab cooked Chinese Eucalypt kraft pulp was oxygen delignified and bleached in the sequence DED in the laboratory. The bleached pulp had a kappa number of 1.8 and an ISO brightness of 89.4 %. A large number of sheets were made of the bleached pulp and these were treated in different ways in order to measure the effect on the yellowing. One series was made in an oven at 105 °C for 30 min, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h, 26 h and 53 h. A second series was made for 4 h in an

oven at 75 °C, 85 °C, 95 °C, 105 °C, 115 °C, 125 °C and 135 °C.

In a second set of trials the effect on the yellowing of a treatment of oxygen and alkali taken together or alone was investigated for the same pulp. Alkaline oxygen bleaching was carried out for 60 min at 105 °C, at 90 °C for 20 min and (OP)-stages for 60 min at 105 °C with a hydrogen peroxide charge of up to 3 kg/ADt.

ISO brightness (2470:1999) was determined according to the ISO standard method

CAUSES OF YELLOWING

Chemical factors

Historically, yellowing has been ascribed to nearly every constituent of pulp and paper including cellulose itself (9). Towards such a background it is near-at-hand to question the meaningfulness of all research on the yellowing phenomenon following this first statement. However, the discussion has developed significantly in the past 15 years. With a focus on Brazilian Eucalypt kraft pulp it is e.g. interesting to have a closer look at a study by Redko et al. (10). In 1992 they reported the main cause of yellowing of the studied Eucalypt kraft pulp to be related to the fraction of chlorine gas used in the (D/C)-stage. Their recommendation in order to minimise yellowing was to keep the charge of chlorine gas low.

In the present study it has been considered appropriate to review only works on yellowing published in the past decade to ensure that the bleaching sequences investigated are of ECF or TCF type. It should, however, be kept in mind that since the yellowing area suffers from lack of general and universally applied methods for measuring and for reporting, results which at a first glance seem contradictory might in the end well not be so. Reading the mere conclusions of an article therefore also risks leading the reader in the wrong direction.

Chirat and de la Chapelle (6) join this author in a call for a universally applied standard method for yellowing studies, stating that as a result "it is almost impossible to link the conclusions to each other and no general mechanism has been proposed so far". The authors conclude that TCF bleached pulp usually has a higher residual kappa number and usually has a higher yellowing (dry method). However, a TCF bleached pulp from one mill might well have a lower yellowing than an ECF bleached pulp from another mill. Ketones present in the bleached pulp are identified as detrimental for the brightness stability and the simultaneous presence of ketone and aldehyde groups at C_1 or C_6 as potentially even more detrimental. However, it should also be said that a part of these conclusions are drawn based on a comparison of the yellowing fraction starting from such different final brightness levels as 91.3 % and 86.4 %. Against this background it is difficult to tell the validity of these conclusions. It should also be pointed out that the TCF

sequence studied in the paper involved ozone, an important information in the light of the effect of keto-groups on the yellowing. It is *e.g.* very likely that the results could have been different if a TCF sequence not involving the use of ozone instead had been investigated. This fact should call for a more appropriate use of bleaching sequence nomenclature in the study of yellowing, giving the sequence and using general terms like ECF and TCF sparsely.

The importance of hexenuronic acid (HexA) for the yellowing of kraft pulp has been shown and also thoroughly discussed (11-13).

Tran (4) notes an increased yellowing (dry method) when the bleaching sequence is changed from C(EO)HD to D(EO)HD. In the study the author use Δb^* to report the results of a dry yellowing. The presence of chloride ions are singled out not to affect the yellowing, whereas the importance of studying the effect also of very low concentrations of transition metal ions for the yellowing is emphasized. Increasing the charge factor of chlorine dioxide to the D₀ stage resulted in a yellowing even lower than that of the reference C(EO)HD sequence. However, it remains unclear which parameter was instead reduced since the pulps were compared at the same brightness level. A pre-treatment of the pulp under hot acidic conditions or with xylanase reduced the yellowing and a fairly good correlation between the yellowing expressed in Δb^* and the residual kappa number could be established. Perhaps it could be added that this correlation between yellowing and residual kappa number probably prevails when different chemical charges within one sequence are studied, whereas the study of different sequences usually give a more scattered correlation. Merely lowering the kappa number of the pulp into the bleaching did not prove efficient for reducing the yellowing. A fair correlation between the copper number, aimed at measuring the total amount of reducing groups in the pulp, and the yellowing expressed as Δb^* is also reported. The author seem to conclude that remaining lignin is the main cause of yellowing, but calls for more detailed studies on the effect of reducing groups in the lignin and carboxylic groups in the pulp as a whole in addition to the effect of even of very low concentrations of transition metal ions.

Tessier and Savoie (14) showed that when the chlorine dioxide has been consumed in a D₀ stage the brightness starts to decrease. This is a well-known phenomenon of great importance in the practical operation of a D₁ or a D₂ stage, but hardly of a D₀-stage. The authors also themselves note that the brightness has recovered after the subsequent extraction stage. The conclusion of that study is therefore rather that brightness is an inappropriate control parameter early in the sequence, where priority should be given to the kappa number.

Colodette *et al.* (2) investigated the importance of wood supply and alkali consumption in the kraft cook of different Eucalypt raw material for the yellowing. The type of Eucalypt was not found to be an important factor. Instead a good correlation was found between the dry yellowing and the concentration of carbonyl

and carboxyl groups in addition to the permanganate number, *i.e.* reasonably also with the kappa number. The authors also noted that strategies aiming at kappa number 0 risk leading to a higher carboxyl concentration, whereas strategies aiming at minimising the carboxyl concentration could lead to increased carbonyl concentrations.

Kawamura and Uchida (15) studied moist yellowing of an oxygen delignified DEPD bleached hardwood kraft pulp. The yellowing was reported as Δb^* . Two phases of the yellowing were identified, where the initial was found to be depending on heat, whereas the second phase was depending more on moist. A clear correlation between HexA remaining in the pulp and the yellowing as Δb^* was also reported (Figure 3).

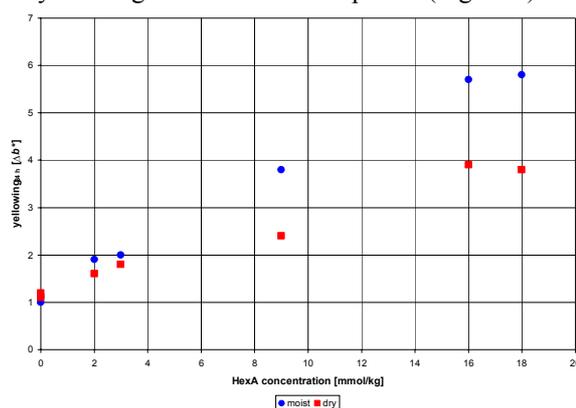


Figure 3. A good correlation between the yellowing and the HexA remaining in the pulp was shown by Kawamura and Uchida (15).

It was proposed that the initial phase of yellowing relates to the cleavage of the HexA from the xylan backbone, whereas the second phase relates to the reactions of the smaller degradation product, 5-formyl-2-furoic acid, with the residual lignin.

Beyer *et al.* (7) seem to agree on these results, concluding that the yellowing proceeds in two steps. The initial step then means a decay of an unstable carbohydrate structure followed by condensation reactions to form coloured substances. Glucuronic acid was identified as one particularly problematic structure, from which reductive acid could be formed (16) and dark colour quickly appear. According to one hypothesis (17), HexA is converted into reductive acid and similar components by metal-ion-catalysed reactions during yellowing, and eventually to low molecular weight carboxylic acids, which can form strongly coloured complexes with transition metal ions.

Dyer and Ragauskas (18) studied the origins of colour of a kraft pulp after cooking and found that almost half of it could be removed by a cold acid treatment, indicating the importance of transition metal ions for this kind of colour.

Ragnar *et al.* (19) used a novel method (8) to investigate the origin of yellowing by measuring the yellowing after each stage of a bleaching sequence and plotting the yellowing against the ISO brightness. Comparing different sequences with initial ozone, standard chlorine dioxide, hot chlorine dioxide and hot

acid treatment stages it could be concluded that the yellowing tendency increased dramatically after an initial treatment with an oxidising bleaching chemical. As the reaction proceeded, the yellowing tendency started to decrease, particularly with a hot chlorine dioxide stage. A treatment under acidic conditions in the absence of oxidising bleaching chemicals was not found to lead to any increased yellowing. Prior to treatment in an acidic and oxidising bleaching stage, the correlation between the yellowing and the HexA content was very weak. In contrast a strong correlation after e.g. a chlorine dioxide or an ozone stage was reported, Figure 4.

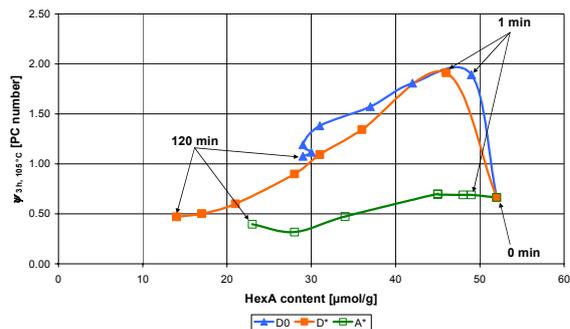


Figure 4. Yellowing tendency plotted against the HexA content for an oxygen delignified Eucalypt kraft pulp treated in an initial stage with D_0 , D^* and A^* (19).

To summarise the recent conclusions on chemical origins of yellowing of bleached hardwood kraft pulp is a difficult task since many different methods and ways to report the results have been used. In addition some of those ways may even be misleading and a different way of evaluation could have given a different conclusion. Still, it is fair to assume that carbonyls and carboxyls in the bleached pulp are important for the yellowing. These structures could prevail in the lignin as well as in the carbohydrates. Lignin remaining in the bleached pulp contributes to the yellowing just as does HexA. The copper number might be an interesting complimentary measure to estimate the yellowing apart from the kappa number. Two different reports on the correlation between the yellowing of a kraft pulp and the remaining kappa number are shown in Figures 5 and 6.

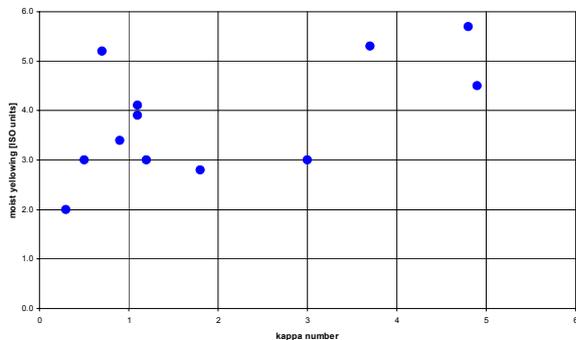


Figure 5. The moist yellowing plotted against the kappa number for a Eucalypt kraft pulp bleached in 13 different bleaching sequences (1).

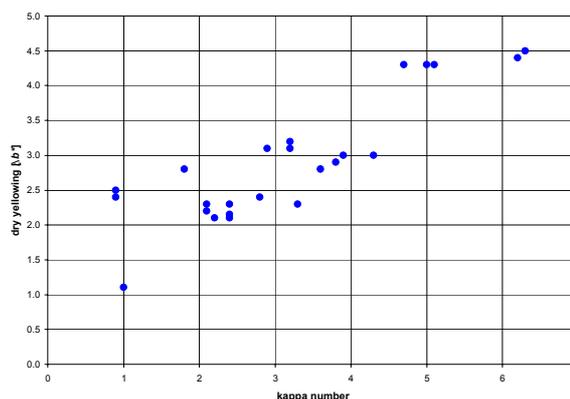


Figure 6. The dry yellowing expressed in Δb^* plotted against the kappa number, data adopted from Tran (4).

HexA plays an important role, but more exactly which remains uncertain. It also remains uncertain whether HexA is particularly detrimental or just as detrimental as any other glucuronic acid structure in the pulp. Transition metal ions seem to be involved in somehow, maybe as catalytic species in the degradation of organic structures, maybe to combine with small organic fragments forming strongly coloured compounds.

Physical factors

Physical factors well-known to affect yellowing of chemical pulp include humidity, temperature and time. In order to illustrate the effect of the former two a laboratory study was performed. In Figure 7 the effect of the retention time at 105 °C on the yellowing is shown.

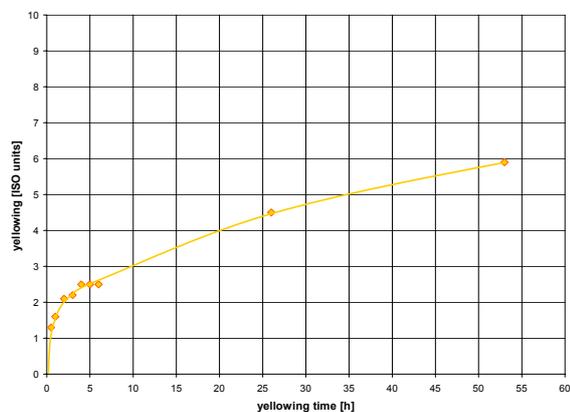


Figure 7. The yellowing (dry method) of a bleached hardwood kraft pulp plotted against the yellowing time in an oven at 105 °C.

The figure shows that the yellowing continues to increase as the retention time increases. Initially the yellowing is very rapid and then enters a second and slower phase, but it shows no sign to level off even after more than 2 days.

Figure 8 instead shows the yellowing plotted against the temperature.

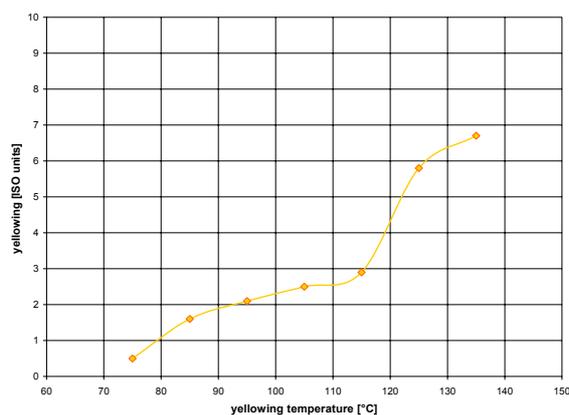


Figure 8. The yellowing (dry method) of a bleached hardwood kraft pulp plotted against the yellowing temperature when treated in an oven for 4 h.

The figure has a somewhat peculiar shape indicating a fairly stable relation between the yellowing and the temperature in the range 100–110 °C. From 115 °C the importance of the temperature increases drastically. This could be a possible explanation in a case where high yellowing is recorded on a drying machine, which well could operate in this field.

When it comes to the importance of humidity has been illustrated in a very clear way in the literature (20), Figure 9.

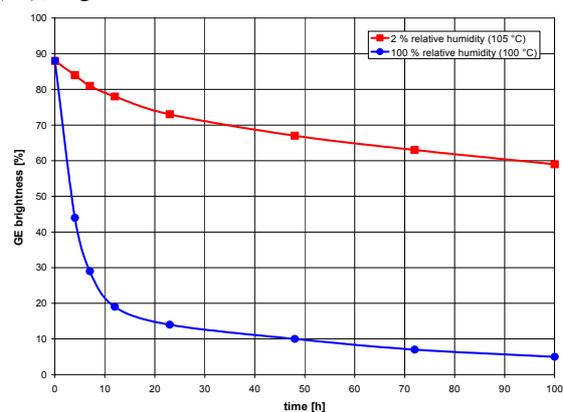


Figure 9. The GE brightness plotted against the yellowing time at two different humidity levels.

Colodette *et al.* (2) has also reported that the dry yellowing expressed in loss of ISO units was decreased from 1.70 to 0.98 when the dryness of the lab sheet was increased from 88.5 % to 91.0 %. This finding emphasizes the great importance of moist in the pulp for the yellowing to take place.

WAYS TO AFFECT

Chemical factors

Choice of sequence

Based on the previous section it could be advised that, in order to reach a low yellowing, bleaching should be made in a way aiming at a low final kappa number, a low HexA content and a low carbonyl and carboxyl content. In practice this implies that hardwood kraft

pulp should benefit from either a hot acid treatment, a hot chlorine dioxide bleaching or an ozone bleaching as the initial stage and that the bleaching should aim at a low final kappa number, though not zero. Although ozone is efficient in degrading HexA a final ozone stage should be avoided, since ozone also efficiently introduces carbonyl functions to the carbohydrates. Similarly there is a risk for “over bleaching” meaning oxidation of the carbohydrates if the bleaching is extended too close to kappa number 0. A final hydrogen peroxide stage should on the other hand be particularly interesting from the point of view that peroxide effectively degrades carbonyl functions including quinones in the pulp, as pointed out *e.g.* by Suess *et al.* (21).

An alternative to hydrogen peroxide as the final stage might also be alkaline oxygen bleaching as recently proposed (22). In this study the effect of alkaline oxygen bleaching on the yellowing of a bleached Eucalypt kraft pulp was investigated. As is shown in Figure 10, the effect on the yellowing was dramatic already at short treatment times and 90 °C, whereas tougher conditions also significantly increased the ISO brightness.

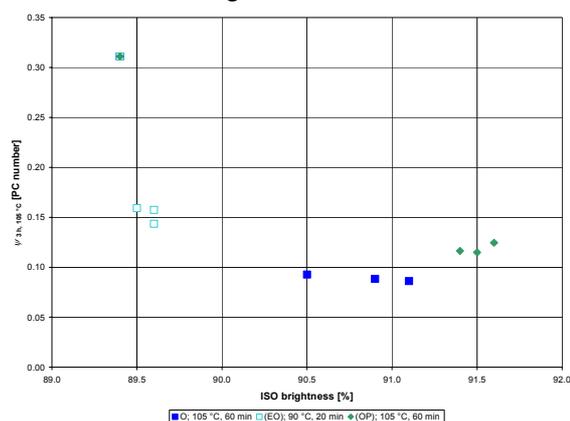


Figure 10. The yellowing (dry method) plotted against the ISO brightness for a 4th stage treatment of a DED bleached Eucalypt kraft pulp.

Post treatments

If the yellowing is not handled within the bleaching sequence as such a post treatment is also possible. For such a treatment some important requirements could be put up. Apart from the obvious requirement, that the treatment really affects the yellowing, the post-treatment should not reduce the brightness of the treated pulp. Even better is if it could increase the brightness. And if it should be defined as a post-treatment no additional washing should be required after the treatment, which preferably should take place in an existing storage tower. This is true since *if* washing is required after the treatment stage the treatment in effect means an extension of the bleaching sequence and the cost-effectiveness of the treatment then must be compared to that of an additional bleaching stage using *e.g.* hydrogen peroxide. In practice it is hard to foresee many true post-treatments not requiring a subsequent washing. The use of enzymes could perhaps fulfil the demands.

Physical factors

It seems unproblematic to state that from a yellowing perspective the drying should be made at a low temperature, where low is defined as <115 °C. Moreover, the pulp should be stored as short time as possible and preferably away from sunlight. Provided that the drying temperature is not changed it seems attractive to dry the pulp to a high dry content in order to obtain a low yellowing. Doing so, however, also affects the steam requirement significantly meaning that there are more factors than the yellowing to consider here.

CONCLUSIONS

The causes behind yellowing can be divided into two categories, one relating to the chemical composition of the pulp and the other to the physical conditions to which the pulp bale is exposed on its way from the pulp dryer to the re-pulper. The pulp manufacturer is usually able to influence the latter category. This study indicates that it might be particularly important to limit the temperature in the dryer to below 115 °C.

The chemical causes behind yellowing are difficult to conclude clear upon. Carbonyl and carboxyl functions in both remaining lignin and carbohydrates are important. The kappa number as well as the copper number might provide rough indications of the yellowing ability of a pulp, but better methods are required.

A final hydrogen peroxide stage seems to be the best proposal so far as to how to practically affect the chemical reasons to yellowing, due to its ability to reduce the carbonyl structures in the pulp.

The whole area of yellowing research suffers hard from a lack of a universally accepted standard method. The situation is further complicated by the many different ways of reporting the result of a yellowing test prevailing in the literature. Some of these merely mislead the reader and should be avoided. It is proposed that yellowing of a fully bleached chemical pulp should be reported in normalised ISO units at 90 % according to a formula given in this paper.

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