Cellulose (2019) 26:429–444
https://doi.org/10.1007/s10570-018-2200-x

ORIGINAL PAPER

Yellowing and brightness reversion of celluloses: CO or COOH, who is the culprit?

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Received: 26 October 2018 / Accepted: 14 December 2018 / Published online: 10 January 2019

Abstract Literature is strongly contradictory about the molecular reasons for yellowing and brightness reversion of pure (lignin- and hemicellulose-free) celluloses, such as in highly bleached pulps, bacterial cellulose, or cotton linters. While oxidized groups—carbonyls (CO) and carboxyls (COOH)—have been recognized as the initiators of yellowing, they are generally always found together; thus, their effects are permanently superimposed in real-world cellulose. For this reason, their individual contributions could not be reliably determined. To tackle this conundrum, we have used a two-stage study: the employment of glucopyranose-derived model compounds and the use of special cellulosic pulps. Both substrates had either only carbonyl functions, only carboxyl functions, or defined ratios of both functionalities present at the same time. The model compounds alone already provided strong indications of the CO-related and COOH-related effects, and further confirmation was obtained by the pulp study. Here, in regard to the polymer case, the carbonyl groups are the minimum functional unit in cellulose responsible for chromophore generation (termed as the "CO effect"). The carbonyl groups are the precursors for the chromophores that are formed later upon yellowing/aging. Chromophore formation increases strictly linearly with the carbonyl content at a constant given carboxyl content. Carboxyl groups alone (i.e., in the absence of carbonyl groups) are fully innocent regarding the color generation. However, they have a

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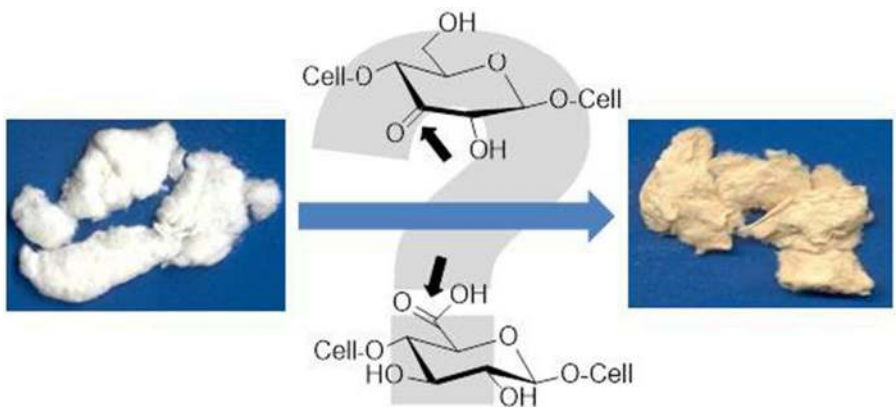
strong promotive action when carbonyl groups are present (termed as the "COOH effect"), which includes acidic catalysis and an additional activation by electronic effects. The general roles of CO and COOH are the same for all aging types (e.g., thermal, acidic, or alkaline), while the respective rates of chromophore generation evidently depend on various parameters such as the temperature, medium, and pH value.

Graphical abstract



Keywords Aging · Brightness · Brightness reversion · Carbonyl groups · Carboxyl groups · Cellulose · Chromophores · Yellowing

Introduction

Yellowing and brightness reversion of celluloses, two easily recognizable aspects of the more general term "cellulose aging," have always been linked to oxidation phenomena. In the case of real-world pulps, the underlying chemistry is, in principle, rather simple. There are only two relevant reactions in cellulose which—in a most simplifying way—can be conceived as a polyol with multiple primary and secondary hydroxyl groups: the oxidation of secondary alcohols (at C2 and C3) to keto groups and the oxidation of primary alcohols (C6) to aldehyde functions and further to carboxylic acids. The oxidation of the only reducing chain end of cellulose (a hemiacetal) to the carboxylic acid is of little importance but might become more significant upon cellulose hydrolysis, which generates the new reducing ends of the shortened cellulose chains. The factors that cause the yellowing and aging of pulp and pure cellulose have been well-studied. These include (naturally) oxidative conditions, such as contact with gases (e.g., O_2, O_3, and halogens), aggressive chemicals from the surroundings, light and irradiation, or increased temperatures. Commonly, the yellowing of celluloses is thought to be caused by three stress factors: chemical (oxidative and/or hydrolytic) stress, photostress (light and irradiation), and thermal stress (high temperatures). These factors cause the yellowing individually or in combination. As a consequence of these physical and chemical influences, molecular changes arise in the cellulose material, which are reflected by losses in molecular weight (and often crystallinity) (Wilson and Parks 1979; Ahn et al. 2013; Area and Cheradame 2011; Lewin 1965) and by a more or less pronounced discoloration, that is, the yellowing of the material, originating from the formation of chromophores (Rosenau et al. 2011). Considering the role of the pulp and paper industries as a mainstay in many economies worldwide, the importance of bleaching processes in the pulp and paper industries, and the customer's notion that bright white materials are of high quality and purity, it is evident that yellowing and brightness reversion of celluloses have been a topic of great interest (Suess 2010).

It should be noted that the following discussion only refers to pure celluloses. Evidently, other contributors, such as residues from bleaching

chemicals (Eiras et al. 2009), hexeneuronic acid (HexA) and similar compounds (Sevastyanova et al. 2006; Vuorinen et al. 1999), lignin residues (Jääskeläinen et al. 2009), or the hemicellulose content can be important factors causing significant color generation in pulp used for real-world applications. Hemicellulose, for instance, has been linked to discoloration in the work of Zhou et al. (2011), where they showed a linear correlation between its content and increasing color after processing. Certainly, the formation of HexA and other organic acids (5-formyl-2-furancarboxylic acid) (Sevastyanova et al. 2006; Vuorinen et al. 1999) or aromatic residuals from lignin still present in the cellulose (Jääskeläinen et al. 2009) can also not be neglected when addressing chromophore formation in cellulose. In fact, these external factors may in many cases be more significant than the internal triggers of yellowing that originate in cellulose itself. However, as relevant as the external triggers might be from a product perspective, they are not pertinent from a mechanistic perspective when addressing the polymer cellulose as such. Hemicelluloses, HexA or lignin represent common "impurities" in real-world pulps—they are absent in pure cellulose.

Although it is known that oxidations cause the yellowing effects in celluloses, the nature of the initial precursors for chromophore formation is still an aspect of the ongoing debate in the cellulose research community, where it comes down to the question of which functional group is the actual trigger of the yellowing. In general, the opinions on which moieties introduced by aging processes cause cellulose discoloration can be parted in three groups: (1) researchers who designate the largest influence to the carbonyl (keto and aldehyde) functions (Zhou et al. 2011; Smith 2012; Mosca Conte et al. 2012a, b, Pouyet et al. 2014), (2) researcher who believe it is the formation of carboxylic groups (Virkola et al. 1958; Chirat et al. 2000; Beyer et al. 2006; Arney and Chapdelaine 1981), and (3) researchers who do not have a definite conclusion (Barbosa et al. 2013; Lewin 1965, 1997; Achwal and Murali 1986; Suess and Filho 2003). In addition, the bleaching method and the bleaching pH also have an important influence on the oxidized moieties present in cellulose (Lewin 1965). Reportedly, hypochlorite and ozone oxidation introduce all three moieties (carboxyl, aldehyde, and ketone groups), their relative content depending on the reaction conditions, while hydrogen peroxide oxidation resulted mostly in ketone functions being introduced (Lewin and Epstein 1962).

Mosca Conte et al. (2012a) investigated the aging processes in paper by linking computational chemistry with UV/Vis spectroscopy. This allowed the determination of carbonyl groups in the form of aldehyde moieties and conjugated diketones, which are closely related to structures identified in previous studies as key chromophores derived from polysaccharides and as the cause of lowered optical quality in pulps and paper (Rosenau et al. 2004). Further results by Mosca Conte et al. (2012b) did not indicate any contribution to yellowing from COOH groups. In contrast, the acidity of paper has been proposed as the main reason for its yellowing by Arney and Chapdelaine (1981). In this work, thanks to manifold kinetic analyses, it was possible to propose an empirical rate law that expresses the total rate of degradation as the sum of two oxidation processes: one atmospheric process and one oxygen-independent process. These oxidation processes were found to increase linearly with the decreasing pH of paper, and therefore, depend on the carboxylic acid content in paper. A connection between the yellowing of paper and both oxidized moieties (COOH and CO)—the latter even in the form of lactones (Lewin 1997)—has been suspected by several groups and also connected to a loss in molecular weight of the cellulose (Barbosa et al. 2013; Eiras et al. 2009). Earlier mechanistic studies of cellulose discoloration and chromophore formation (Krainz et al. 2010a), by means of model compounds, pointed at different but still undefined roles of carbonyls and carboxyls in those processes.

There are two possible explanations for the apparently controversial views in the above-mentioned literature. The first involves the fact that real-world celluloses always contain both carbonyl and carboxyl groups, making it arduous to separate their individual effects and contributions reliably. The second explanation involves the generally low concentration of carbonyls and carboxyl groups—in most cases below 50 µmol/g—which requires very accurate and reliable analytical methodology that would by far exceed the performances of usual titration approaches (for COOH) or sum parameter methods (e.g., "copper number" for carbonyls).

In this study, the two difficulties mentioned in the two above-mentioned explanations have been resolved. As our experimental data shows, the research

assigning different action modes to CO and COOH was indeed pointing to the right direction. With the presented work, we are able to offer a final conclusion to this decade-old discussion: Which of the two oxidized functions in celluloses - carbonyls or carboxyls - is the culprit responsible for yellowing and brightness reversion of celluloses?

Results and discussion

Analytical methodology

Studying oxidized groups in pulps requires an accurate and reliable method to quantify the content of CO and COOH. With the advent of the "CCOA method" for carbonyls (Röhrling et al. 2002a, b, Potthast et al. 2003) and the "FDAM method" for carboxyls (Bohrn et al. 2006), the methodology to accurately quantify oxidized groups relative to the molecular weight distribution has been realized, that is, they provide molecular weight related profiles of the oxidized groups (Potthast et al. 2006). Other alternative quantification methods only obtain sum parameters (i.e., the overall content), and therefore, miss the important information of how the oxidized groups are distributed over the different molecular weight regions (Potthast et al. 2007). This information is conveniently displayed as degree of substitution (DS) plots, which perceive the oxidized groups as "substituents" along the cellulose chain and can make therefore use of the usual DS concept. DS-difference (ΔDS) plots show the difference in carbonyl/carboxyl profiles between two pulps, which is especially useful to monitor the effect of various cellulose treatments (e.g., in bleaching). For example, a process that decreases the carbonyl content in the low-molecular-weight region while simultaneously increasing the content by the same amount in the high-molecular-weight region can be imagined. The CCOA method reliably reports such an alteration, best visualized by means of the ΔDS_{CO} plots, whereas these dynamic changes would remain unnoticed when using conventional quantification methods that only report sum parameters and would only see the two cellulose samples as equal. Besides the functional group profiles, both methods also provide the overall content of oxidized groups. This amount of these oxidized groups usually ranges between 5 and 40 µmol/g for most real-world celluloses, whereas their content in deliberately oxidized celluloses (including extensively bleached ones) can well exceed 100 µmol/g.

Both CCOA and FDAM methods are based on group-selective fluorescence labeling of the cellulosic substrate followed by dissolution and gel permeation chromatography (GPC) in the standard solvent *N*,*N*-dimethylacetamide (DMAc)/LiCl (Potthast et al. 2015). The methods can therefore only be applied to pulps that are soluble in this solvent system, excluding for example pulps with high lignin contents (kappa numbers). However, this dissolution methodology has been extensively optimized (Henniges et al. 2011, 2014), so that previously "difficult" substrates such as certain hardwood pulps or spun cellulosic fibers (viscose fibers/rayon, Lyocell fibers) (Siller et al. 2014) are now also dissolvable. Overall, the CCOA and FDAM methods to analyze carbonyl and carboxyl group profiles in celluloses can be very powerful tools to investigate the effect of these functionalities on cellulose yellowing and aging.

Pulp studies

Model pulps used

In our pulp studies, different sets of pulps were used. Two sets contained either of the two functionalities (carbonyl or carboxyl) exclusively: all specimen in the first set had no carboxyl groups, but an increasing content of carbonyl groups, while the second group of pulps was "opposite", i.e., free of carbonyl groups at an increasing carboxyl content. A third set contained varying amounts of carbonyl groups at constant carboxyl contents (Fig. 1). It should be noted that "no carbonyl groups" and "no carboxyl groups" refer to the detection limits of the CCOA and FDAM methods, respectively. Evidently, the functional group content was not absolutely zero, but at or below the detection limit of the respective oxidized functionalities.

For the introduction of oxidized groups into the pulps, four oxidation methods were used: periodate oxidation, Swern oxidation, hypochlorite oxidation, and 2,2′,6,6′-tetramethylpiperidine-1-oxyl (TEMPO) oxidation. The introduced carbonyl functions can readily be re-reduced to hydroxyl groups, while carboxyl groups, once generated, are rather hard to reconvert to the alcohol stage in a simple way that

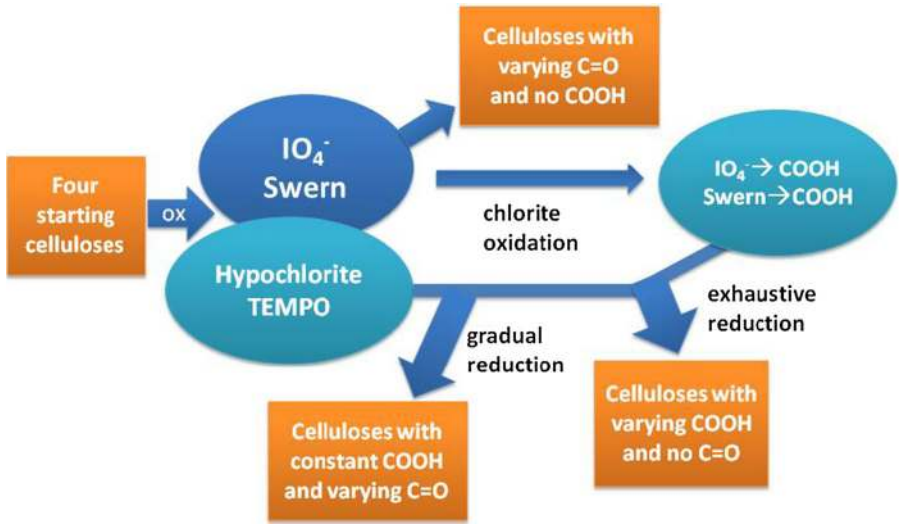


Fig. 1 Schematic representation of the redox processes used to prepare the test pulps with different contents of oxidized functionalities (carbonyl and/or carboxyl groups)

would leave the cellulose backbone unaffected. This subsequent reduction step offers a way to adjust the carbonyl content at a given carboxyl content that is not affected by the reduction. In this study, two different reduction methods were employed: treatment with sodium borohydride or with *tert*-butylamine-borane complex. While the former is generally more effective and offers faster reactions, it only functions in alkaline media. This causes (often severe) cellulose degradation by beta-alkoxy elimination, starting from carbonyl groups along the cellulose chain. Additionally, this cellulose degradation process might already commence at a pH as low as 8 and becomes quite severe at higher alkalinities. In this regard, the *tert*-butylamine-borane complex method offers the advantage of working in a neutral aqueous medium, avoiding cellulose degradation, but at the expense of lower reaction rates.

The introduction of carbonyl groups into the pulps without causing simultaneous generation of COOH was accomplished by periodate oxidation and Swern oxidation (Fig. 1). In this regard, periodate oxidation causes cleavage of the C2–C3 bond in the anhydroglucose units (AGUs) of cellulose. Both C2 and C3 are converted concomitantly into formal aldehyde functions, which are present as masked aldehydes in the form of hydrates, hemiacetals, and hemialdals. However, periodate oxidation does not affect the C6-hydroxymethyl group. In contrast, Swern oxidation converts C6 into an aldehyde and C2/C3 into carbonyl groups. All of these functions are mainly present in their masked forms (i.e., hydrates, hemiacetals or hemiketals). The respective carbonyl carbons do not exhibit a C=O double bond, but four single bonds instead—they are sp^3-hybrids rather than sp^2-hybrids. Nevertheless, the masked carbonyls exhibit the same reactivity as the parent aldehydes/ketones and show their typical reactions, which has been addressed by Rosenau et al. (2005) previously. Important to note is that neither periodate nor Swern procedures introduce carboxyl groups into cellulose.

Pulp specimens containing carboxyl groups without carbonyl groups were obtained by exhaustive reduction of previously oxidized pulps (Fig. 1). Hypochlorite oxidation and TEMPO oxidation generate both carbonyl and carboxyl groups. Hypochlorite oxidation is the least selective of the oxidation methods used. It introduces keto (at C2 and C3) as well as aldehyde and carboxyl groups (at C6). TEMPO oxidation is reasonably selective for C6 (primary alcohols) and generates carboxyl groups in this position. However, about 5% of keto groups (relative to the introduced carboxyls) are also introduced. The amount of carbonyls relative to the introduced carboxyls is thus much lower with the TEMPO method than with the hypochlorite one. Both hypochlorite-oxidized and TEMPO-oxidized pulps (one-step oxidation) contain carbonyls and carboxyls and can be directly reduced, leaving only carboxyls behind. Periodate-oxidized or Swern-oxidized cellulose do not contain carboxyls from the beginning and require a pre-oxidation by chlorite for their generation. Chlorite converts the (masked)

aldehydes to the corresponding carboxylic acids, while having the present keto functions unaffected. After the preceding one-step (hypochlorite or TEMPO) or two-step oxidation (periodate/chlorite or Swern/chlorite), the exhaustive reduction removes carbonyls so that only carboxyls remain.

Pulps containing different amounts of carbonyl groups at pre-set carboxyl contents were prepared by gradually lowering the concentration of the carbonyl groups by a step-by-step reductive treatment with either sodium borohydride or the *tert*-butylamino-borane complex (Fig. 1). Importantly, residual carbonyls will remain when this reduction is not executed in an exhaustive manner (see above). The reduction converts keto and aldehyde groups into the corresponding (secondary and primary) alcohols while leaving carboxyl groups unchanged throughout. This gradual reduction produced pulps with a constant carboxyl content but with a varying carbonyl content. The same starting pulps as for the carboxyl-only pulps via a comprehensive reduction (see above) were used. All types of pulps were briefly washed with diluted HCl (1 mM, pH = 3) to assure that the contained carboxyl groups were present in their protonated form and then washed neutral with distilled water, followed by air-drying and placing them at −20 °C in the dark for storage. The oxidation/reduction approaches to produce the different pulp specimens are schematically summarized in Fig. 1.

The effect of carbonyl groups

Four series of cellulosic pulps were obtained, for which all pulps within a series had the same carboxyl content. However, the carboxyl content between the four series varied: 0, 7, 16, and 45 µmol/g. Within each of the series, there were seven to nine individual pulps with increasing (keto) carbonyl contents ranging between 0 and 96 µmol/g (Fig. 2). All of the pulps, in the form of standard handsheets, were subjected to accelerated aging according to standardized conditions (see the "Materials and methods" section). The chromophore formation, better known as "brightness reversion," was quantified by UV measurement at 457 nm according to the ISO brightness standard method (2009). The gain in UV absorption, or in other words the loss of UV remission, increased linearly over time within the first 3–4 h. The slope of this linear increase was taken as the yellowing rate (i.e., the chromophore formation rate) for the respective pulp, see the data points in Figs. 2 and 3.

Figure 2 shows the chromophore formation rate for all four series of pulps. The pulps with zero carboxyl content (series A) showed a linear carbonyl content

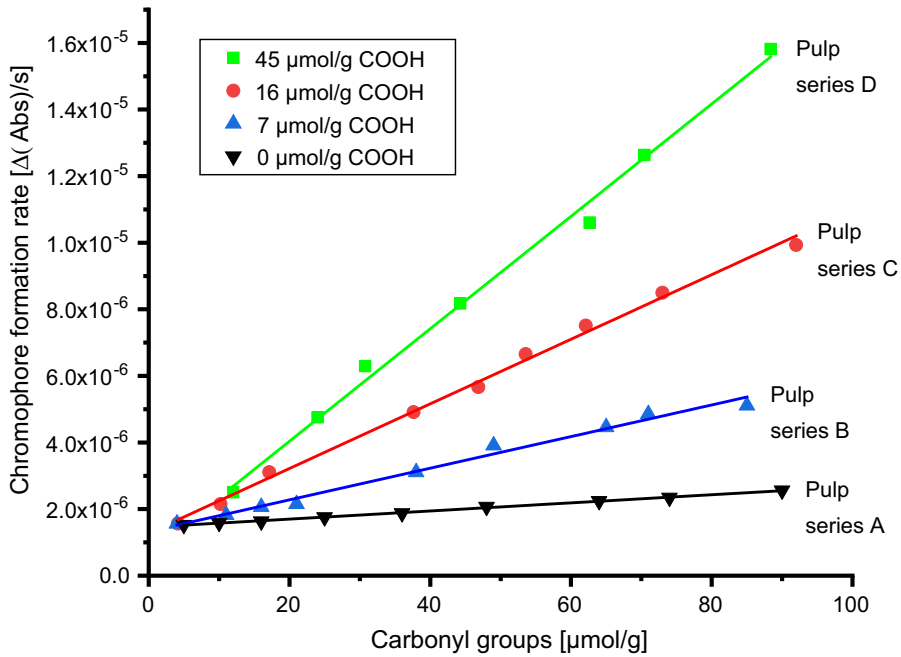


Fig. 2 Chromophore formation from four pulp series A–D with constant carboxyl contents of 0, 7, 16, and 45 µmol/g, respectively. Pulps specimen within each series have increasing amounts of carbonyl groups

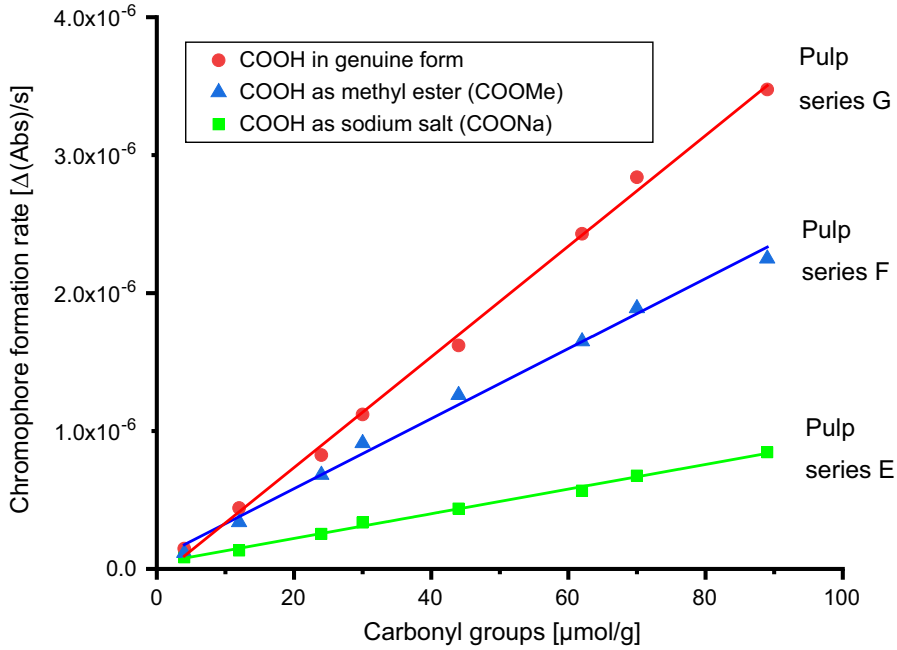


Fig. 3 Influence of the nature of the COOH groups (protonated form COOH vs. salt form COONa vs. methyl ester COOMe) on their catalytic effect of chromophore formation from carbonyl groups. Chromophore formation from three pulp series (E–G), each containing celluloses with an increasing amounts of carbonyl groups. Each pulp in series E contained 45 µmol/g COOH (acid form), each pulp in series F had 45 µmol/g COONa (salt form) and each pulp in set G had 45 µmol/g COOMe (ester form)

dependence on the yellowing rate. Interestingly, this rate was identical (within the accuracy of measurement) for all carboxyl-free starting celluloses used. This means that the yellowing rate was independent of the type of pulp, that is, independent of whether bacterial cellulose, cotton linters, or hardwood dissolving pulps were the starting cellulosic matrix. As such, it can be stated as a finding that yellowing in celluloses is (largely) independent of their morphological features but strongly depends on the carbonyl functions, which are the minimal fundamental structural prerequisite for chromophore formation.

A similar observation regarding the yellowing rate of cellulose was made for the three other pulps with a carboxyl content larger than zero (series B–D in Fig. 2). Within every pulp series (at constant carboxyl contents), the yellowing/chromophore formation rate strictly depended linearly on the amount of carbonyl groups with regression factor values better than $R^2 = 0.995$, showing a clear linear dependence. With increasing carboxyl content, the slope of the linear regression lines increased significantly. At a given carbonyl content, the pulp with the lowest carboxyl content showed the lowest yellowing tendency and the pulp with the most COOH the fastest yellowing. Together, this leads to the second conclusion: The yellowing of cellulosic pulps is linearly dependent on the carbonyl content of the pulp at a given constant carboxyl group content. Furthermore, the chromophore formation reactions of the carbonyl groups (which can be seen for the pulps without COOH) are evidently accelerated by the presence of carboxyl groups, see the slopes of the graphs A–D that increase with increasing carboxyl contents in Fig. 2.

The effect of carboxyl groups

Based on the results so far, it was assumed that the promoting activity of the carboxyl groups was a catalytic effect of the COOH groups' acidity. For instance, chromophore formation reactions from carbonyl groups in celluloses are condensation reactions involving both elimination processes (loss of water) and aldol-type condensations (Rosenau et al. 2017; Korntner et al. 2015). These reactions are catalyzed by acids (see, for instance, Schwetlick 2015). If the carboxyl groups only acted by their acidity, their promoting effect should disappear when the carboxyl groups are neutralized and present in the form of their salts. So, in one experimental set, the pH of the model pulps was kept at 8.5 during the aging to make sure that all carboxyl groups were, in fact, present as carboxylates (sodium salts). This way, any acid-catalysis effect of the carboxyls was excluded.

Nevertheless, the effect of the carboxyl groups was still clearly seen, and the slope of the linear regression lines increased with increasing carboxylate (carboxyl salt) content (series G vs. series E, Fig. 3).

Based on these results, it was likely that carboxyl groups—in addition to the acidity effect—exert electronic effects, which would promote the reactions of the carbonyls. For example, carboxyl groups are known to have a mild activating effect on the methylene activity of α-carbons in aldol-type processes (see, for instance, Schwetlick 2015). If this activation towards (aldol-type) condensation reactions is the reason for the observed carboxylate activity, then ester functionalities (instead of carboxylates) should greatly increase the effect on the methylene activity, because esters (–COOR) strongly increase the methylene activity of the neighboring carbon atoms (the α-carbons) and enable them to undergo all types of condensation reactions (e.g., aldol-type, Knoevenagel, and Claisen). For this reason, the pulps were treated with trimethylsilyldiazomethane (TMS-DAM), as TMS-DAM is a reliable method to convert any carboxyl group in pulps into their corresponding methyl esters (Tot et al. 2009). The methylation reaction requires the carboxyl group to be present in its protonated form, which is why the standard pulps—and not the pulps with slightly alkaline pH—had to be used as starting material. The slopes of the regression line (i.e., the yellowing rates) increased significantly after methylation (series F, Fig. 3), providing strong evidence of an electronic effect of the carboxyl/ester groups. Based on these findings, it can be concluded that the promoting effect of carboxyls in pulp on the color formation from carbonyls is due to both its acidic-catalytic and electronic nature.

In the last set of experimental tests, three pulp series with no carbonyl groups present and different carboxyl group contents were employed. During the first hour of accelerated aging, no color formation was observed (Fig. 4). The initial phase was much longer in the case of dry aging than in the case of wet aging: up to 8 h without any color generation. The buffered pulps (pH 8) exhibited such a long initial period until the onset of color formation also upon humid/wet aging. For all cases, this first phase was followed by a short phase of exponential increase in UV absorption (Fig. 4) until the yellowing kinetics eventually entered a linear course such as the ones shown in Fig. 2. A mathematical fitting of the exponential phases and their relation to kinetics was not attempted since the system

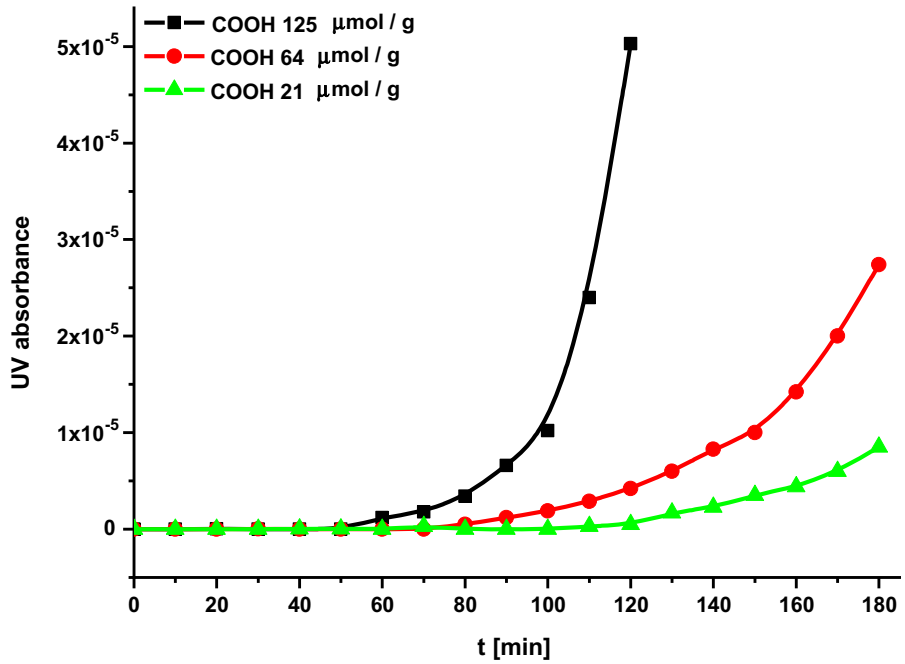


Fig. 4 Chromophore formation from three pulp series with constant carboxyl contents of 21, 64, and 125 µmol/g with no initial carbonyl contents

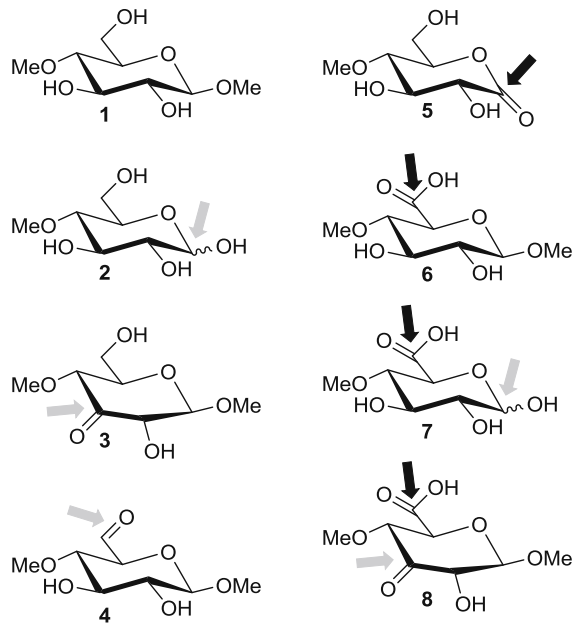
appeared to be too complex to produce meaningful results. In these experiments, carboxyl groups alone (i.e., in the absence of carbonyl groups) did not cause yellowing. Only when acidic hydrolysis reactions (or to a smaller extent thermal stress) cause chain cleavage—and thus the generation of new reducing ends (= carbonyl functions)—the yellowing commences. A higher carboxyl content would both cause faster hydrolysis (shorter yellowing-free induction periods) and higher yellowing rates through the above-discussed catalytic carboxyl effect (Fig. 3). It should be noted that only in a special case, such as carbonyl-free model pulps, the neutralization of the carboxyl groups is an effective approach to avoid acidic chain cleavage, and therefore, the onset of chromophore generation. For real-world pulps, alkaline media would trigger both beta-elimination reactions from the carbonyl groups, causing fast chain degradation and alkali-induced condensation reactions that could possibly overcompensate the beneficial effect of carboxyl inactivation.

The final part of the pulp experiments allowed the conclusion that carboxyl group per se are unrelated to chromophore generation. Carboxyl groups in the absence of carbonyl groups do not cause the yellowing effects. However, in the presence of carbonyl functions—and almost all real-world pulps contain carbonyl groups or develop carbonyl contents by aging processes—carboxyl groups promote and catalyze the color-forming condensation reactions of the carbonyl groups.

Model compound studies

With the above results, it was still not possible to adequately answer whether additional hitherto unknown contributions of polymeric or macromolecular features contribute to the yellowing tendency or whether the yellowing effects are indeed solely determined by the presence of oxidized groups and their local chemistry in degradation and condensation reactions. If the latter was true and no macromolecular effects were active, then the same previous effects of cellulose should be observable when working with model compounds representing the (oxidized) anhydroglucose units of cellulose. In this regard, it is important to note that the literature offers abundant examples of chromophore generation studies that use low-molecular-weight carbohydrates (e.g., Perrin et al. 2014), but only a few of these model compounds represent cellulose sufficiently. Here, a 4-*O*-substituent is imperative to resemble the chemical behavior of the β-1,4-glycosidically linked glucopyranose units in cellulose closely. This is not only true in regard to the solid-state structure, where the hydrogen bond network of 4-*O*-methylated methyl glucopyranoside derivatives is similar to cellulose (cellulose II allomorph), while that of derivatives with the free 4-OH group is rather different from celluloses (Röhrling et al. 2002c, Mackie et al. 2002), but also with regard to general reactivity. Under alkaline conditions, the keto group of C1 (or a keto group introduced by oxidation) can migrate along the whole C_6-chain (Adorjan et al. 2004a), which can be seen by complete isomerization of all carbons. However, when the 4-hydroxyl group is not free, the isomerization is limited to C1 to C3.

The cellulose model compounds in Scheme 1 were available from previous studies, and their syntheses have been described previously (Röhrling et al. 2001, 2002c, Adorjan et al. 2004b, Bohrn et al. 2005; Krainz et al. 2010b). All of these compounds contain a 4-*O*-methyl group that mimics the truncated β-1,4-glucan chain in cellulose. Here, C1 is either free



Scheme 1 Model compounds mimicking genuine and oxidized anhydroglucose units of (oxidatively damaged) cellulose. The grey arrows indicate free or masked carbonyl functionalities and the black arrows free or masked carboxyl groups

in the form of a hemiacetal as in **2** or **7** (corresponding to the reducing end in cellulose), present as glucoside (compounds **1**, **3**, **4**, **6**, and **8**, corresponding to a non-terminal anhydroglucose unit in cellulose), or oxidized to a carboxylic acid/lactone (compound **5**, paralleling oxidized reducing ends in cellulose). In addition, carbonyl functions in different positions and/or carboxyl functions are present. Furthermore, oxidized positions are present at C3 (keto, compounds **3** and **8**) and C6 (aldehyde as in compound **4** or carboxyl as in compounds **6**, **7**, and **8**). Please note, that in an aqueous solution, the aldehyde function in compound **4**, the keto function in compound **3**, and the ketoacid in compound **8** are in equilibrium with their corresponding aldehyde hydrate ($-CH(OH)_2$), ketohydrate ($> C(OH)_2$), and intramolecular lactal ($-C(OH)-OOC-$), respectively. The latter is formed between the 6-carboxyl group and the hydrate of the 3-keto function.

The cellulose model compounds were thermally treated at 100 °C as 0.1 mM aqueous solutions, and the color generation was followed directly by UV spectroscopy (pressurized vessel with a quartz window). In parallel, some runs were repeated in aqueous solutions with the pH buffered to either acidic or alkaline levels. Inorganic buffer systems (dihydrogenphosphate/monohydrogenphosphate and hydrogencarbonate/carbonate) were used to exclude any possible participation of the buffer in chromophore-forming reactions. Also, the model compounds were heated as neat solids triturated with sea sand. Aliquots were taken and suspended in distilled water after different periods of time, and the filtrates were subjected to UV measurements. The results for these solid-state aging experiments were identical with those of the aqueous solution and therefore not separately discussed further.

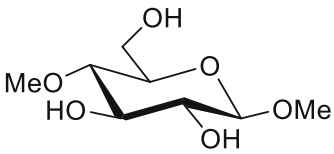
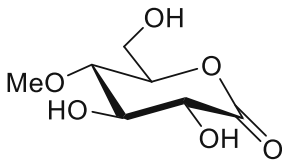
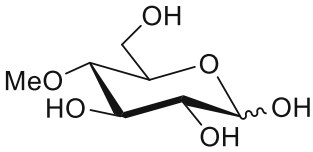
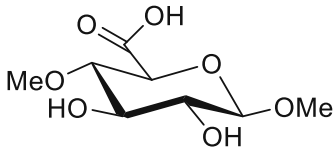
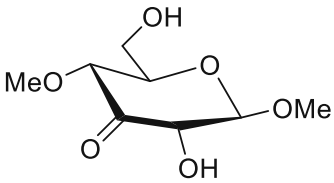
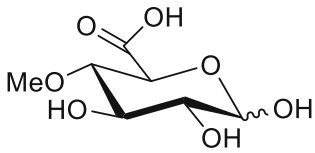
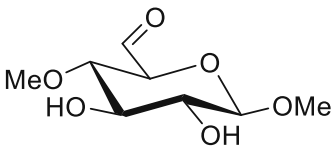
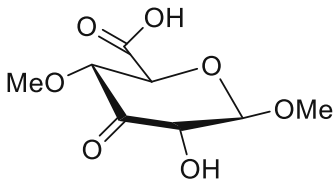
It should be noted that the "degree of substitution" of oxidized groups (DS_{CO} and DS_{COOH}) in the model compound case is several orders of magnitude higher than that in the oxidized pulps discussed in pulp section. For the model compounds, the DS of the oxidized groups is 1 ($DS_{CO} = 1$ for compounds **2**, **3**, **4**, **7**, and **8**, and $DS_{COOH} = 1$ for compounds **5**, **6**, **7**, and **8** [Scheme 1]), because every anhydroglucose unit carries an oxidized functionality. For cellulosic pulp with a carbonyl content of 25 μmol/g, the DS_{CO} is 0.00405 ($M_{AGU} = 162$ g/mol). In other words, only about every 250th AGU is oxidized. As such, the model compound experiments can be imagined as a procedure to "zoom out" the behavior of the oxidized AGUs while disregarding the "dilution effect" of regular, non-oxidized AGUs. Indeed, this simplifying view has been shown to be valid thanks to an experiment that compared the chromophore formation rate of a pulp with a carbonyl content of 25 μmol/g to a 1:250 molar mixture of the 3-keto-AGU model compound **3** and the non-oxidized model compound **1** and showed they were identical (within the error of measurement).

The high concentration of oxidized groups in the model compounds (DS = 1), on the other hand, means much faster chromophore formation. Depending on the type of compound and the respective conditions, the chromophore generation, as seen by UV at 457 nm, was linear for at least 45 min. The slope of the respective regression line was taken as the rate for the respective model compound. Only in some cases was the chromophore formation too fast (see below) and the extinction exceeded the reliable measurement range after 20 min. In these cases, the regression was only done within this shorter period.

Model compound **1**, representing a regular, non-oxidized AGU in cellulose, was taken as the blank. And both for the neutral aqueous solution and for the solid state no thermal chromophore generation was observed over a period of 1 h. This compound was therefore taken as a gauge, and for the reason of comparability, the yellowing rates of the other model compounds are listed relative to compound **1** in the following (Table 1).

In contrast to model compound **1**, compound **2** possesses a reducing end, that is, a masked aldehyde functionality in the form of a hemiacetal, and compound **3** possesses a keto carbonyl group. Chromophore formation of compound **2** was about 100 times faster than that from compound **1**, whereas the yellowing of the ketosugar compound **3** was about 100 times faster than that of compound **2** (i.e., about 10,000 times faster in respect to compound **1**). These results confirm impressively the conclusion drawn from the previous pulp experiments—where a carbonyl group was shown to be the minimum structural unit to generate chromophores. Also in the model compound case, one carbonyl function per AGU, as present in compounds **2** and **3**, was a sufficient structural prerequisite for color generation. As such, the absence of any "polymer effect," that is, a

Table 1 Numbers represent the relative chromophore formation rates from the model compounds **1** to **8**, monitored by UV spectrometry (457 nm)

Structure	A	B	Structure	A	B
1 	1	1	5 	0.08	0.65
2 	124	96	6 	1.4	1.8
3 	10,249	12,632	7 	1482	1588
4 	2674	10,542	8 	> 32,000	> 36,000

Column A shows the 0.1 mM aqueous solution, and column B the 0.1 mM solution in *N*-methylmorpholine-*N*-oxide monohydrate, both at 100 °C (heated pressurized cuvette)

macromolecular influence beyond the mere effect of carbonyl groups, has been clearly demonstrated by the above experiment, which showed that the same chromophore formation rates were found for a pulp with a carbonyl content of 25 μmol/g and a 1:250 molar mixture of the 3-keto-AGU compound **3** and the non-oxidized compound **1**. Overall, the chromophore formation rate was only dependent on the amount of carbonyl groups and not on their monomeric or polymeric chemical environment.

In contrast to the yellowing-active carbonyl groups, carboxyl groups did not cause chromophore generation, independent whether present in their protected form of a lactone (the gluconolactone derivative **5**) or as a free acid (the glucopyranosiduronic acid derivative **7**), see Table 1. In both cases, the initial chromophore formation rate was close to zero. Interestingly, chromophore formation from compound **7** started after an induction period similar to the carboxyl-only pulps, indicating acidic hydrolysis of the methyl glucoside (the protected reducing end) and the onset of chromophore generation immediately when free reducing ends (hydrolyzed glucosides) are present (data not shown). Also, these results further confirmed the conclusion from the cellulose work, namely that carboxyl groups per se (i.e., in the absence of carbonyl groups) are innocent in regard to the color generation.

Compounds **6** and **8** illustrate the promoting effect of carboxyl groups on the chromophore formation from carbonyl groups. Compared to compound **2**, compound **7** possesses a free reducing end group as

well, but an additional carboxyl functionality, which increased the chromophore formation by a factor of approximately 15. A similar but even more drastic effect was seen for the compound couple of the ketosugar **3** and the ketoacid **8**, both distinguished by the additional carboxyl group of the latter. The chromophore formation rate from compound **8** was increased by a factor of approximately three relative to compound **3** and was too fast for a reliable quantification by UV measurement. The accelerating effect of the carboxyl groups also remained when the sodium salts of compounds **7** and **8** were employed. The yellowing rate from the sodium salt of compound **7** was 6.5 times faster than that of compound **2** (vs. an increase of 15 times for compound **7** containing a free carboxylic acid), and the sodium salt of compound **8** was 1.8 times faster than that the ketosugar **3** (vs. an increase of three times for compound **8** containing a free carboxylic acid). Together, these results of the model compound work confirmed the results of the pulp experiments, where carboxyl groups were shown to promote the chromophore-forming reactions from carbonyl motifs. The COOH groups do not only act via acidic catalysis but also exert electronic effects that increase the reactivity in condensation reactions.

The yellowing studies of the model compounds are summarized in Table 1, which includes the relative chromophore formation rates from the model compounds (slope of the linear regression lines of the initial reaction rates). Based on the results, it can be stated that the major effects—the chromophore formation from carbonyls, the promoting effect of carboxyls, and the innocence of carboxyls in the absence of carbonyls—were largely independent of the reaction conditions. The individual reaction rates varied, yet the general effects were always similar. In Table 1, column A shows the result for a 0.1 mM aqueous solution, and column B for a 0.1 mM solution in *N*-methylmorpholine-*N*-oxide monohydrate (NMMO), the solvent for cellulose in Lyocell fiber-making processes. The data for aqueous solutions buffered at pH 4 or pH 10 and for the heated neat solid provided similar trends but are not shown.

Conclusions

The combination of model compound experiments and studies on special pulps allowed a clear definition of the factors causing yellowing of celluloses. In both model compounds and pulps, the effects of carbonyl (aldehyde and keto) and carboxyl groups could be separated so that their influence could be studied without superposition effects. Carbonyl functionalities in pulps are the fundamental precursor for later color generation/brightness reversion. This is true, independently of their structure (aldehyde/keto functions), and also applies to forms that are in equilibrium with the free carbonyl motifs (i.e., hydrates, hemiacetals, and hemiketals). Stable masked forms, such as acetals in glycosidic bonds, do not cause chromophore formation as long as the acetal is not hydrolyzed, and thus converted into a reducing end. Carboxyl groups, when present in addition to carbonyls, enhance the chromophore generation rate by both acidic catalysis and electronic activation effects. However, when carboxyl groups are alone, without the presence of carbonyls, they are unrelated to the yellowing. However, carboxyl groups might exert acidic hydrolysis effects, causing chain cleavage, and therefore, the generation of new reducing ends (carbonyl groups). As soon as those carbonyl groups are generated, the COOH groups catalyze their condensation reactions to chromophores.

In real-world pulps, CO and COOH groups are always present together, and their effects superimpose each other, which explains why the literature has been so contradictory about this topic. Nevertheless, the present study allows an unambiguous answer to the title question. Carbonyl groups are the culprit of chromophore formation in celluloses. They are the "bad guys" in regard to yellowing and brightness reversion. Carboxyl groups alone are "harmless" but promotive when occurring together with carbonyl groups. Metaphorically speaking, carboxyl groups are therefore somewhat "shady characters" and are in nature benign, but they are easily influenced and turned "bad" by the example of their carbonyl "mates".

Overall, we hope that this study will contribute to a better understanding of the oxidation chemistry of celluloses, which is not only of scientific interest but also of an economic one with tangible implications, considering the importance of industrial pulp bleaching.

Materials and methods

General All used chemicals and solvents were purchased from commercial suppliers and of the highest purity. All aqueous solutions and washing treatments were performed with distilled water.

Starting celluloses Four cellulose samples were used. The first three included the following: (A) a bleached beech sulfite pulp (kappa number 0.22, brightness 91.2% ISO, viscosity [cuen] 565 mL/g, pentosan 0.93%, DCM extract 0.18%, ash 0.05%); (B) a bleached Eucalyptus pre-hydrolysis kraft pulp (kappa number 0.37, brightness 90.9% ISO, viscosity [cuen] 530 mL/g, pentosan 1.73%, DCM extract 0.13%, ash 0.05%); and C) a cotton linters sample (kappa number 0.12, brightness 92% ISO). These three samples were thoroughly washed with HPLC-grade acetone (to remove extractives) and then with distilled water, followed by air-drying. The fourth sample D was a bacterial cellulose (BC) obtained from Lohmann & Rauscher GmbH & Co. KG, Neuwied, Germany. The BC sheets from cultivation were treated with aqueous NaOH (3–5%) for 1 h at 80–95 °C, then washed to neutrality with distilled water, followed by treatment with 0.5% hydrogen peroxide at pH 10 (NaOH) for another hour at 50 °C. This was finalized with another wash with distilled water until the washing solution was neutral and free of H_2O_2. The hydrogel samples underwent solvent exchange to ethanol and acetone before being air-dried. Initial brightness of the dry samples was 94% ISO.

GPC measurements The gel permeation chromatography system consisted of multi-angle laser light scattering (MALLS), refractive index (RI) and fluorescence detectors with automatic injection and four serial columns. DMAc/LiCl (0.9%, m/V) was used as the eluant. Molecular weight distribution and related polymer-relevant parameters were calculated by the corresponding software programs, based on a refractive index increment of 0.140 mL/g for cellulose in DMAc/LiCl (0.9%, m/V). Following general GPC parameters were used: eluant: DMAc/LiCl (0.9%, m/V); flow: 1.00 mL/min; columns: four PL gel, mixedA, ALS, 20 µm, 7.5 × 300 mm plus pre-column; fluorescence detection: excitation: 286 nm, emission: 330 nm (for CCOA) and excitation: 252 nm, emission: 323 nm (for FDAM); injection volume: 100 µl; run time: 45 min.

Activation of pulp samples To achieve cellulose solubility, i.e., dissolution in DMAc/LiCl (9%, m/V) at room temperature overnight, the pulp samples had to be activated, no matter if genuine or redox-treated pulp had to be dissolved. The pulp samples were activated by solvent exchange (H_2O to ethanol to DMAc) followed by agitating in DMAc overnight and filtration, which produces efficiently activated, i.e., readily soluble samples.

General procedure for the determination of carbonyls in pulp by heterogeneous fluorescence labeling (CCOA method) The detailed procedure is given in: Röhrling et al. (2002a, b) and Potthast et al. (2003). In short, a CCOA stock solution was prepared by dissolving the fluorescence label (62.50 mg) in 50 mL of 20 mM zinc acetate buffer (pH 4.0). Wet pulp (corresponding to 20–25 mg of dry pulp) was suspended in the acetate buffer containing the label (4 mL). The suspension was agitated in a water bath for 168 h at 40 °C. The pulp was removed by filtration, then activated and dissolved in 2 mL of DMAc/LiCl (9%, m/V) overnight at room temperature. Then, the samples were diluted with DMAc, filtered through 0.45 µm filters, and analyzed by GPC. Calibration of the system was done with the pure CCOA label and by means of reference pulps, as described previously. For the determination of the overall carbonyl content, the carbonyl peak area was normalized with regard to the injected mass.

General procedure for the determination of carboxyls in pulp by heterogeneous fluorescence labeling (FDAM method) For a detailed procedure, see Bohrn et al. (2006). Briefly, for pulp conditioning, 20 mg of dry pulp was suspended in 0.1 M HCl and agitated for 20 s in a mixer. The pulp was washed with 0.1 M HCl, ethanol 96%, and DMAc, excess DMAc was removed by filtration followed by the transfer of pulp into a 4 mL vial. The pulp was resuspended in 3 mL of DMAc for derivatization together with 1 ml of FDAM solution (0.125 mol/L in DMAc). The suspension was agitated in a shaking bath at 40 °C for 7 d. The pulp was then filtered off, washed with DMAc, and transferred into a dry vial. For dissolution of the cellulose, 1.6 mL of DMAc/LiCl 9% (m/v) was added. Finally, after complete dissolution, the sample was diluted and filtered through 0.45 µm filters.

Hypochlorite oxidation The sodium hypochlorite (HOCl) oxidation was performed with 2 g of dry pulp in total. To improve accessibility, the pulp was

suspended in water and shortly disintegrated. The excess of water was removed by vacuum filtration and the wet pulp transferred into a 2 L beaker to suspend it in a sodium acetate buffer (1 L, 1 M, adjustment with glacial acetic acid to pH 6.5). The suspension of pulp in the buffer was continuously stirred with a magnetic stirrer. Next, different volumes (between 1 and 120 ml) of HOCl (active chlorine 10–13%, Sigma Aldrich, Schnelldorf, Germany) were added to effect the oxidation. The oxidation was stopped after 45 min by addition of ethanol and was followed by thorough washing with water.

TEMPO oxidation The oxidation was performed with 2 g of dry pulp in total. The pulp was suspended in water and shortly disintegrated to improve accessibility. The excess water was removed by vacuum filtration and the wet pulp transferred into a 2 L beaker containing 1 L of water. This pulp suspension was continuously stirred with a magnetic stirrer. The pH was adjusted to 10.8 by slowly adding NaOH (0.4 M). Then, 20 mg of TEMPO was dissolved in 500 µL of absolute ethanol and added to the pulp suspension, followed by 1.9 g of sodium bromide and different volumes (between 1 and 65 mL) of sodium hypochlorite (active chlorine 10–13%, Sigma Aldrich). The pH was continuously controlled and stabilized at 11.2. The reaction was stopped after 25 min by addition of ethanol and followed by thorough washing with water.

Periodate oxidation To the cellulose sample (2 g suspended in 100 mL of distilled water), different volumes (between 1 and 150 mL) of 0.2 M aqueous sodium metaperiodate ($NaIO_4$) solutions were added. The suspension was stirred at room temperature for 30 min, filtered, and then resuspended in 100 mL of distilled water. A total of 5 mL glycol was added, and the stirring continued for 1 h. The pulp was separated by filtration and washed thoroughly on a Büchner funnel. Details of the experimental setup and reaction conditions can be found in Siller et al. (2015).

$NaBH_4$ reduction The sodium borohydride treatment of all oxidized pulp modifications ($NaIO_4$, HOCl, Swern, and TEMPO) was performed at two different concentrations (0.25 M and 1 M) in a phosphate-buffered solution at a pH of 8 at room temperature, and over five different time intervals: 5, 10, 30, 60, and 120 min. Exhaustive reduction employed a 1 M solution at pH 8 over 6 h at a slightly elevated temperature of 35 °C. $NaBH_4$ (Sigma Aldrich) was dissolved in demineralized water at the chosen concentrations. The reaction was performed in closed glass vials with a pressure outlet (H_2 gas evolution) containing 200 mg of wet oxidized pulp and 20 mL of the $NaBH_4$ solution. The reaction was stopped after the designated time intervals by washing with distilled water, 1 M acetic acid, and again with distilled water.

TBAB reduction The *tert*-butylaminoborane (TBAB) reduction treatment of all oxidized pulp modifications ($NaIO_4$, HOCl, Swern, and TEMPO) was performed at two different concentrations (0.2 M and 0.4 M) at a pH value of 7 (phosphate buffer) at room temperature and over different time intervals: 60, 120, 180, 240, and 480 min. Exhaustive reduction employed a 0.4 M solution at pH 7 over 24 h at a slightly elevated temperature of 35 °C. TBAB pellets (98% pure, Sigma Aldrich) were dissolved in demineralized water while being mildly heated to accelerate the dissolution process (60–70 °C). The reaction was performed in closed glass vials with a pressure outlet (H_2 gas evolution) containing 200 mg of wet oxidized pulp and 40 mL of the TBAB solution. The reaction was stopped by washing with distilled water, washing with hydrochloric acid (1 mM), and another washing repetition with distilled water.

Aging Handsheets were prepared from 2 g of pulp suspended in distilled water (500 mL) on a Büchner funnel, followed by pressing. In some experiments, the pH of the water was modified using either sulfuric acid (1 mM) or sodium hydroxide (1 mM). The handsheets were dried at 92 °C for 5 min. Brightness was measured before and after aging according to ISO 2470 (2009), following the remission of UV light at 457 nm. Aging was carried out continuously under dry conditions following the TAPPI method UM 200 (105 °C, 40% humidity), and under humid conditions according to Paptac E.4P (100 °C, 100% humidity). The progress was continuously followed by UV (brightness reversion) measurements to record the kinetics of chromophore formation.

Acknowledgments Open access funding provided by University of Natural Resources and Life Sciences Vienna (BOKU). The contributions of all former and current lab members and students working in the field of cellulose yellowing and chromophore chemistry are thankfully acknowledged. We would like to thank Dr. H. U. Suess (formerly Degussa-Evonik, Hanau, Germany), as well as Prof. J. Colodette (Universidade Federal de Viçosa, Brazil) for their inspiring and fruitful discussions.

References

Achwal WB, Murali R (1986) Characterization of acidic groups in oxycelluloses IV. Effect of accelerated aging on yellowing as well as carboxyl groups and lactones in pulp. J Appl Polym Sci 32(3):3913–3917

Adorjan I, Sjöberg J, Rosenau T, Sixta H, Kosma P (2004a) Kinetic and chemical studies on the isomerization of monosaccharides in *N*-methylmorpholine-*N*-oxide (NMMO) under Lyocell conditions. Carbohydr Res 339(11):1899–1906

Adorjan I, Mereiter K, Pauli J, Jäger C, Rosenau T, Potthast A, Kosma P (2004b) Crystal and Molecular structure of methyl 4-*O*-methyl-*β*-*D*-ribo-hex-3-ulopyranoside. Carbohydr Res 339(4):795–799

Ahn K, Rosenau T, Potthast A (2013) The influence of alkaline reserve on the aging behavior of book papers. Cellulose 20(4):1989–2001

Area MC, Cheradame H (2011) Paper aging and degradation: recent findings and research methods. BioResources 6(4):5307–5337

Arney JS, Chapdelaine AH (1981) Kinetic study of the influence of acidity on the accelerated aging of paper. Adv Chem Ser 193:189–204

Barbosa LCA, Maltha CRA, Demuner AJ, Cazal CM, Reis EL, Colodette JL (2013) A rapid method for quantification of carboxyl groups in cellulose pulp. BioResources 8(1):1043–1054

Beyer M, Koch H, Fischer K (2006) Role of hemicelluloses in the formation of chromophores during heat treatment of bleached chemical pulps. Macromol Symp 232:98–106

Bohrn R, Potthast A, Rosenau T, Sixta H, Kosma P (2005) Synthesis and testing of a novel fluorescence label for carboxyls in carbohydrates and cellulosics. Synlett 20:3087–3090

Bohrn R, Potthast A, Schiehser S, Rosenau T, Sixta H, Kosma P (2006) A novel method for the determination of carboxyl profiles in cellulosics by fluorescence labeling. Method development. Biomacromolecules 7:1743–1750

Chirat C, De La Chapelle V, Lachenal D (2000) Heat-induced brightness reversin of certain bleached chemical pulps. Rev. ATIP 54(2):34–39

Eiras KMM, Colodette JL, Silva VL (2009) The role of bound chlorine in the brightness reversion of bleached hardwood kraft pulp. Quim Nova 32(1):51–55

Henniges U, Kostic M, Borgards A, Rosenau T, Potthast A (2011) Dissolution behaviour of different celluloses. Biomacromol 12(4):871–879

Henniges U, Vejdovszky P, Siller M, Jeong MJ, Rosenau T, Potthast A (2014) Finally dissolved! Activation procedures to dissolve cellulose in DMAc/LiCl prior to size exclusion chromatography analysis—a review. Curr. Chromatogr. 1(1):52–68

ISO 2470-1 (2009) Measurement of diffuse blue reflectance factor—part 1: indoor daylight conditions (ISO brightness). International Organization for Standardization, Geneva

Jääskeläinen AS, Toikka K, Lähdetie A, Liitiä T, Vuorinen T (2009) Reactions of aromatic structures in brightness reversion of fully-bleached eucalyptus kraft pulps. Holzforschung 63(3):278–281

Korntner P, Hosoya T, Dietz T, Eibinger K, Reiter H, Spitzbart M, Röder T, Borgards A, Kreiner W, Mahler AK, Winter H, French AD, Henniges U, Potthast A, Rosenau T (2015) Chromophores in lignin-free cellulosic materials belong to three compound classes. Chromophores in cellulosics. XII. Cellulose 22(2):1053–1062

Krainz K, Rosenau T, Potthast A, Suess HU, Dietz T, Mereiter K, French A (2010a). Mechanistic studies on aging and chromophore formation in celluloses. In: Abstracts of papers, 239th ACS national meeting, San Francisco, CA, USA, March 21–25, 2010; American Chemical Society, CELL-179

Krainz K, Hofinger A, Dietz T, Suess HU, Potthast A, Rosenau T (2010b) Synthesis of methyl 4-*O*-methyl-beta-D-ribo-hex-3-ulopyranoside-1-^{13}C and methyl 4-*O*-methyl-beta-D-ribo-hex-3-ulopyranoside-3-^{13}C as fragment analogues of oxidized cellulose units. Lett Org Chem 7:186–190

Lewin M (1965) The yellowing of cotton cellulose—part III: on the mechanism of yellowing upon aging and alkaline extraction. Text Res J 35:979–986

Lewin M (1997) Oxidation and aging of cellulose. Macromol Symp 118:715–724

Lewin M, Epstein JA (1962) Functional groups and degradation of cotton oxidized by hypochlorite. J. Polym. Sci. 58:1023–1037

Mackie ID, Röhrling J, Gould RO, Walkinshaw M, Potthast A, Rosenau T, Kosma P (2002) Crystal and molecular structure of methyl 4-*O*-methyl-*β*-*D*-glucopyranosyl-(1 → 4)-*β*-*D*-glucopyranoside. Carbohydr Res 337:161–166 **(Corrigendum: Carbohydr Res 337:1065)**

Mosca Conte A, Pulci O, Del Sole R, Knapik A, Bagniuk J, Lojewska J, Teodonio L, Missori M (2012a) Experimental and theoretical study of the yellowing of ancient paper. E-Journal Surf Sci. Nanotechnol. 10:569–574

Mosca Conte A, Pulci O, Knapik A, Bagniuk J, Del Sole R, Lojewska J, Missori M (2012b) Role of cellulose oxidation in the yellowing of ancient paper. Phys Rev Lett 108(15):1–5

Perrin J, Pouyet F, Chirat C, Lachenal D (2014) Formation of carbonyl and carboxyl grups on cellulosic pulps: effect on alkali resistance. BioResources 9(4):7299–7319

Potthast A, Röhrling J, Rosenau T, Borgards A, Sixta H, Kosma P (2003) A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 3. Monitoring oxidative processes. Biomacromol 4(3):743–749

Potthast A, Rosenau T, Kosma P (2006) Analysis of oxidized functionalities in cellulose. In: Klemm D (ed) Polysaccharides II. Advances in polymer science, vol 205. Springer, Heidelberg

Potthast A, Rosenau T, Kosma P (2007) Carbonyl and carboxyl profiles as two novel parameters in advanced cellulose analytics. In: Argyropoulos D (ed) Materials, chemicals and energy from forest biomass materials, chemicals and energy from forest biomass ACS book series, vol 954. American Chemical Society, Washington, pp 513–530

Potthast A, Rosenau T, Henniges U, Schiehser S, Kosma P, Saake B, Lebioda S, Radosta S, Vorwerg W, Wetzel H, Koschella A, Heinze T, Strobin G, Sixta H, Strlic M, Isogai A (2015) Round robin test on gel permeation chromatography of cellulose: coming closer to a standard protocol. Cellulose 22(3):1591–1613

Pouyet F, Chirat C, Potthast A, Lachenal D (2014) Formation of carbonyl groups on cellulose during ozone treatment of pulp: consequences for pulp bleaching. Carbohydr Polym 109:85–91

Röhrling J, Potthast A, Rosenau T, Lange T, Borgards A, Sixta H, Kosma P (2001) Synthesis and testing of a novel fluorescence label for carbonyls in carbohydrates and cellulosics. Synlett 5:682–684

Röhrling J, Potthast A, Rosenau T, Lange T, Ebner G, Sixta H, Kosma P (2002a) A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development. Biomacromol 3:959–968

Röhrling J, Potthast A, Rosenau T, Lange T, Borgards A, Sixta H, Kosma P (2002b) A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 2. Validation and applications. Biomacromol 3:969–975

Röhrling J, Potthast A, Rosenau T, Adorjan I, Hofinger A, Kosma P (2002c) Synthesis of methyl *β-D*-glucopyranosides and methyl *β-D*-glucopyranosyl-(1 → 4)-*β-D*-glucopyranosides as substrates for fluorescence labeling reactions. Carbohydr Res 337:691–700

Rosenau T, Potthast A, Milacher W, Hofinger A, Kosma P (2004) Isolation and identification of residual chromophores in cellulosic materials. Polymer 45(19):6437–6443

Rosenau T, Potthast A, Kosma P, Saariaho AM, Vuorinen T, Sixta H (2005) On the nature of carbonyl groups in cellulosic pulps. Cellulose 12(1):43–50

Rosenau T, Potthast A, Krainz K, Yoneda Y, Dietz T, Shields ZPI, French AD (2011) Chromophores in cellulosics VI First isolation and identification of residual chromophores from aged cotton linters. Cellulose 18(6):1623–1633

Rosenau T, Potthast A, Kosma P, Hosoya T, Henniges U, Mereiter M, French AD (2017) 2,4′:2′,4 Dianhydride of 3-keto-glucoside, a precursor to chromophores of aged, yellow cellulose, and its weak interactions. Cellulose 24(3):1227–1234

Schwetlick K (2015) Organikum, 24th edn. Wiley-VCH, Weinheim. ISBN 978-3-527-33968-6

Sevastyanova O, Li J, Gellerstedt G (2006) On the reaction mechanism of the thermal yellowing of the thermal yellowing of bleached chemical pulps. Nord Pulp Pap Res J 21(2):188–192

Siller M, Ahn K, Pircher N, Rosenau T, Potthast A (2014) Dissolution of rayon fibres for size exclusion chromatography: a challenge. Cellulose 21(5):3291–3301

Siller M, Amer H, Bacher M, Rosenau T, Potthast A (2015) Effects of periodate oxidation on cellulose polymorphs. Cellulose 22(4):2245–2261

Smith AW (2012) Bleaching in paper conservation. Restaurator 33(3–4):223–248

Suess HU (2010) Pulp bleaching today. DeGruyter, Berlin

Suess HU, Filho CL (2003). How to improve brightness stability ofeucalyptus kraft pulp. In: Proceeding of 36th ABTCP, SaoPaulo, Brazil

Tot I, Müller Y, Werner C, Rosenau T, Potthast A (2009) A novel, mild and selective methylation of carboxyl groups in cellulosic pulps. Holzforschung 63(6):657–664

Virkola NE, Hentola Y, Sihtola H (1958) The yellowing of pulp. III. Carboxyl groups and cations as factors affecting the yellowing of cellulose. Pap Ja Puu 40:627–631

Vuorinen T, Fagerstrom P, Buchert J, Tenkanen M, Teleman A (1999) Selective hydrolysis of hexeneuronic acid groups and its application in ECF and TCF bleaching of kraft pulps. J Pulp Pap Sci 25(5):155–162

Wilson WK, Parks EJ (1979) An analysis of the aging of paper: possible reactions and their effects on measurable properties. Restaurator 3(1–2):37–62

Zhou Z, Jääskeläinen AS, Adorjan I, Potthast A, Kosma P, Vuorinen T (2011) Brightness reversion of eucalyptus kraft pulp: effect of carbonyl groups generated by hypochlorous acid oxidation. Holzforschung 65(3):289–294