Archival Performance of Paper as Affected by Chemical Components: A Review

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For about two millennia, paper has served as a main medium for preservation of people's ideas, stories, contracts, and art. This article reviews what is known about the various components that make up paper from the perspective of their long-term stability under typical storage conditions. Literature evidence is considered relative to the susceptibility of different paper components to embrittlement, acid hydrolysis, microbiological attack, and discoloration, among others. The cellulose that makes up a majority of most paper items is demonstrably stable enough to persist for many hundreds of years on the shelves of archival collections, though it is susceptible to acid-catalyzed hydrolysis, which can be accelerated by byproducts of decomposition. Though less attention has been paid to the archival performance of various minor components of modern paper products, evidence suggests that at least some of them are subject to likely breakdown, embrittlement, or decay in the course of prolonged storage. Based on these considerations, one can envision different categories of paper that can be expected to meet different levels of storage stability: ancient recipes for handmade papermaking, *e.g.* washi and hanji, archival-grade paper products, ordinary modern alkaline paper products, and paper manufactured without concerns for its longevity.

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INTRODUCTION

The premise of this article is that there must be a relationship between the components that are included in a paper specimen and the overall archival performance of that paper material. If one accepts this premise as valid, then it makes sense to consider various possible ingredients of paper in turn, asking what is known about their archival performance. Thus, the present review article has attempted to find out what has been reported regarding a wide range of substances that have been used in the production of paper items. Concerns about the durability of paper items are not new (Johnson 1891; MacAlister 1898). Kantrowitz *et al.* (1940) list approximately 300 annotated articles on the subject of permanence and durability of paper from 1885 to 1939. The two terms permanence and durability have been used variously; often they specify the retention of properties such as strength and color during aging (permanence) as opposed to retention of the physical/mechanical properties during use (durability) (McCrady 1989). The concerns of these writers were not small. For instance, Johnson (1891) regarded inferior paper as a threat to the permanency of literature. Already in 1824 it was suggested that the roots of such problems may lie in the composition of the paper (Murray 1824).

PAPER'S COMPONENTS AND ITS STABILITY

In the context of the present article, the term “paper” will generally refer to typical old or modern grades of printing and writing paper, including xerographic copy paper. In the case of modern printing paper, the components will include cellulosic fibers, mineral particles (most likely calcium carbonate), starch products, and a variety of minor substituents. The focus will skew towards considerations of modern paper (*i.e.* a focus on wood pulp, kraft pulp preparation, and modern fillers, *etc.*), though historic materials and practices will also be considered. This modern focus is because there is obviously less natural aging data available for more recent materials, and, modern papers have increasing quantities of materials other than cellulosic fibers as fractions of their total composition. In principle, a high enough level of degradation in any one of these components of paper – especially the major components – would weaken the structure of the paper as a whole.

Table 1 lists review articles that deal with the storage stability of paper from various perspectives, along with some text indicating their main focus. As shown, many of the articles have focused on (a) mechanisms that can account for the degradation of paper's properties over time as it is being stored, and (b) strategies for slowing down or even reversing the decline in paper properties. Notably, none of the listed articles has as its main focus the archival quality of different components of typical paper.

Most manufactured paper is not intended for long-term storage. Libraries and museums store only a minor fraction of what has been produced. In exceptional cases, where a paper document or artwork is intended to be permanent, there are standards that can be followed with respect to its composition (ANSI 1984; Anon 1993). Further discussion of what constitutes permanent paper can be found in the ISO 20494 and ISO 9706 standards, and in the textbook by Allscher and Haberditzl (2019). Paper products designated as “permanent” will contain a certain amount (*e.g.* 2%) of an alkaline reserve component such as calcium carbonate. The Canadian standard for permanent paper can be regarded as unique due to the fact that it states mechanical and optical aspects of permanence separately (Canadian General Standards Board 2016). The content of lignin in paper is capped by the standard only in cases where the optical properties are of concern. The preparation and properties of permanent or archival papers have been considered in other articles (Clapp 1977; Shahani and McComb 1987; Bird 1999; Basta *et al.* 2006). The present article comes at the topic from a different direction, considering a wide variety of components that are often present in paper products that can be used for printing and writing.

Table 1. Review Articles and Chapters Dealing with Aspects of the Archival Performance of Paper

Main Topics Covered	Citation
Permanence and durability of paper – technical literature	Kantrowitz *et al.* 1940
History of papermaking, including the quality of ancient paper	Hunter 1947
Mechanisms to explain the aging of stored paper	Lindström 1990
Effects of RH, temperature and pollutants on stability of paper	Porck & Teygeler 2000
Practical considerations for minimizing aging in book collections	Smith 2004
Deterioration mechanisms and stabilization strategies for paper	Strlič & Kolar 2005
Deacidification for the conservation and preservation of paper	Baty *et al.* 2010
Natural and accelerated aging of paper	Zervos 2010
Paper aging and degradation	Area & Cheradame 2011
Formation of acetic and formic acid during accelerated aging	Jablonsky *et al.* 2012
Paper conservation methods	Zervos & Alexopoulou 2015
Deacidification with non-aqueous dispersions of alkaline particles	Hubbe *et al.* 2017
Nonaqueous solution deacidification methods for paper	Hubbe *et al.* 2018

Components of Cellulosic Plant Materials

Cellulosic fibers often comprise 70 to 90% of the dry mass of printing paper, a fact that can justify a major focus on what is known about their archival characteristics. This subsection will consider various chemical substances – both major and minor – that make up typical papermaking fibers. A following subsection will consider issues from the perspective of the fiber types derived from different pulping and bleaching methods.

Cellulose

A variety of fibers have been used in papermaking throughout time depending on factors of geography and availability. Currently, however, the majority of machine-made paper is made using wood-derived fibers (Hunter 1947; Collings and Milner 1990; Baker 2010). Plant-derived cellulose can be isolated from wood by conventional pulping and bleaching methods (Dence and Reeve 1996; Sixta 2006; Fardim and Tikka 2011). Bleached kraft fibers, which are widely used in high-quality books, have been processed under conditions that maintain a substantial proportion of hemicellulose, in addition to the cellulose component of the wood. However, the conditions of pulping and bleaching can be adjusted to yield relatively pure cellulose (Chen *et al.* 2016). Such cellulose can be briefly described as a linear polymer of anhydroglucose units (French 2017) in which the units are joined by β-glycosidic bonds. The detailed structure of cellulose (see Fig. 1), having three –OH groups per anhydroglucose unit, is conducive to the development of fibrillar structures, both at the nano-scale and in the macroscopic material. Cellulose from wood or cotton has crystallinity in the range of about 50 to 90, depending on a variety of factors, including the method of assessment (Ahvenainen *et al.* 2016; French 2022).

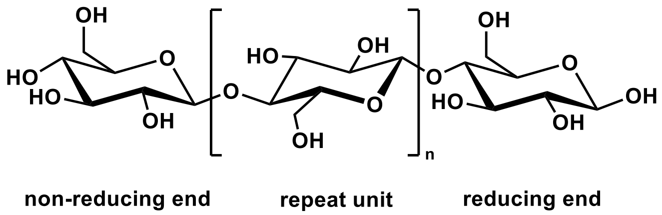


Fig. 1. Features of parts of a cellulose molecular chain having different susceptibility to steps in decomposition (French 2017)

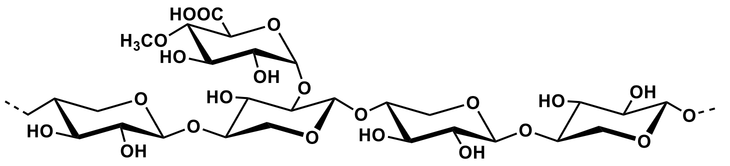
Dry, pure cellulose is relatively stable under ambient conditions. For example, thermogravimetric analysis studies have shown that pure cellulose has a rather narrow range of mass loss at about 295 to 380 °C (Ramiah 1970). The fact that cellulose-based paper items sometimes can last for more than 1000 years (Hunter 1947; Jeong *et al.* 2014b) can be taken as further evidence of the stability of the cellulose itself. Jeong *et al.* (2014b) attributed the exceptionally high storage stability of traditional Hanji paper to an initial high molecular mass of the cellulose and a low rate of chain scissions compared to other paper specimens that were tested. Even more remarkable storage stability has been documented in the case of papyrus samples that had been prepared during Egyptian dynasties. Such specimens, which have cellulose as a main component, have lasted for upwards of 3000 years (Lojewska *et al.* 2017; Bausch *et al.* 2022a,b). Lojewska *et al.* (2017), however, found evidence of substantial degradation of the cellulose in the ancient papyrus. Gel permeation chromatograms show a mean degree of polymerization (DP) of about 2100 in the cellulose obtained from fresh papyrus plants, whereas the ancient material had cellulose with a DP of about 800. Potthast *et al.* (unpublished) measured a DPw of 2000 +/- 400 for historic samples aged 1100 to 2300 years.

A factor that can help account for the relatively high storage stability of cellulose is its notably high density of hydrogen bonding, which occurs within (intra-) and between (inter-) the molecular chains (Wohlert *et al.* 2021). Such bonds, though they are readily reversed in the presence of water, can be expected to constrain the motions of molecular segments, thus making the material less susceptible to chemical degradation than it otherwise might be. The relatively high density and highly regular arrangement in the crystalline domains renders those parts of the cellulose structure especially resistant to various enzymatic or chemical attacks (Meng and Ragauskas 2014; Jerome *et al.* 2016). In addition, as shown by Jeong *et al.* (2014b), the molecular mass may sometimes be as high as 1.4 million g/mol.

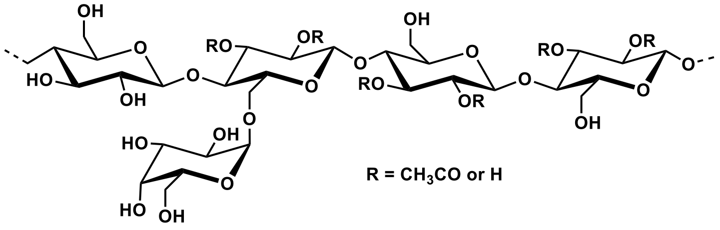
Hemicelluloses

Both the content and the chemical composition of hemicellulose in wood and other plant fibers depend on the species of origin. Though hemicellulose has many similarities to cellulose, it differs in certain respects that can be expected to render it less storage stable. For one thing, the molecular mass is lower, *e.g.* having a weight average of 10,000 to 40,000 g/mole (Bai *et al.* 2012; Krawczyk *et al.* 2013). Figure 2 shows typical hemicellulose structures often present in hardwood xylem (4-*O*-methyl-D-glucurono-D-xylan) and softwood (galactoglucomannan) (Ebringerova *et al*. 2005; Mäki-Arvela *et al.* 2011). In order to maintain a relatively high yield of chemical pulping processes, paper manufacturers have a strong incentive to adjust pulping and bleaching conditions to maintain a relatively high content of the original hemicellulose in most paper grades, including printing papers. In addition, hemicellulose contributes to inter-fiber bonding.

The lower degree of polymerization and the lack of crystallization of hemicellulose may be essential so that it can fulfill its task in helping to bind adjacent cellulosic and lignin-related moieties together (Molin and Teder 2002). Also, it has been found that the presence of hemicellulose tends to make paper items more resistant to hornification, which can be defined as a loss in ability to swell again in water after having been dried (Wan *et al.* 2010).



4-O-methyl-D-glucurono-D-xylan

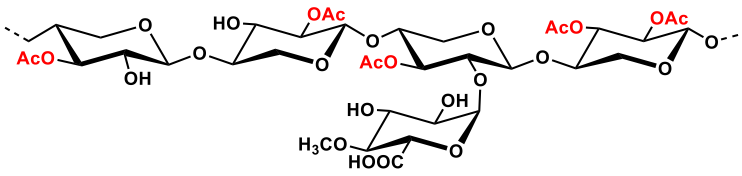


Galactoglucomannan

Fig. 2. Structures of some common hemicellulose types (Figures adapted and redrawn from Ebringerova *et al.* (2005) and Mäki-Arvela *et al.* (2011))

The non-crystalline nature of hemicellulose is known to make it vulnerable to swelling in water (Pere *et al.* 2019). The swollen conditions can make cellulosic materials susceptible to such decomposition mechanisms as acid hydrolysis and enzymatic attack (Zhang *et al.* 2006; Kumar *et al.* 2012). The carboxylic acid groups present on certain hemicellulose molecules (see the first structure in Fig. 2, for instance), can contribute acidity to the material, and therefore to its deterioration (Feller *et al.* 2002). Carboxyls are also responsible for catalyzing the formation of chromophoric groups (Ahn *et al.* 2019). In addition, hydrolysis of acetate ester groups (as in the second example shown in Fig. 2) can release acetic acid in the course of storage (Potthast *et al.* 2022). This mechanism is further shown in Fig 3. In addition, acetic acid is also formed from carbohydrate degradation products in the course of natural aging. Hemicellulose also may be responsible for thermal and photochemical discoloration of paper (Lee and Feller 1986). Under more severe conditions of heating, aqueous suspensions of cellulose have been found to decrease in pH, which can be attributed to the same reaction; such acidity contributes to autohydrolysis during certain treatments of biomass for the production of monomeric sugars and various biofuels (Garrote *et al.* 2001; Nabarlatz *et al.* 2004; Liu *et al.* 2015a; Surek and Buyukkileci 2017).

Questions remain about the extent to which these mechanisms are the same or different under typical dry storage conditions of paper. Though no liquid water is present, typical paper will contain about 4 to 8% water under a wide range of storage conditions. Kramer *et al.* (2015) recommended using an HVAC system to maintain relatively low values of relative humidity in the range of about 35% to 55%, with seasonable adjustments to avoid very large contrasts between the storage conditions and ambient conditions.



Acetylglucuronoxylan (a hardwood hemicellulose)

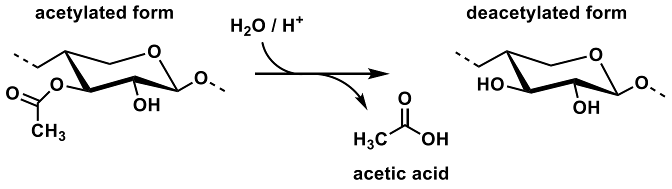


Fig. 3. Acetyl groups in a common hardwood hemicellulose, which can be the source of acetic acid as a result of acid-catalyzed hydrolysis. The acetylglucuronoxylan structure is based on a drawing by Biely *et al.* (2014).

Lignin

When attempting to make high quality paper for printing and writing applications, papermakers through the ages have generally preferred to use fibers that have little or no lignin content.

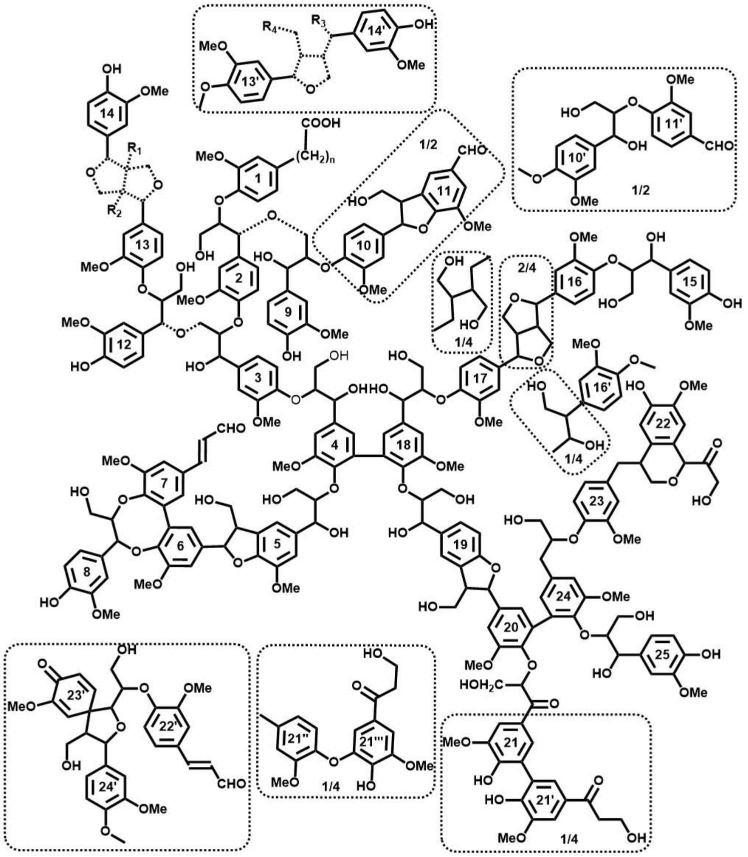


Fig. 4. Some common structures within lignin macromolecules (Adapted from Balakshin *et al.* 2020)

A major reason for that preference is that upon light exposure lignin can be subject to color changes during storage (Wong *et al.* 1995; Bird 1999; Paulsson and Ragauskas 2000; Smith 2012). Lignin also is much more susceptible to oxidation reactions in comparison to cellulose (Malachowska *et al.* 2020). If paper with high brightness stability is needed, the presence of lignin should be avoided. Color change can be deemed acceptable for archival permanence of certain types of (textual) records where it is the information that is important, as long as some contrast between printing/writing and paper surface can be maintained. Optical permanence / brightness stability obviously plays a significant role for other types of cultural records, however (images, art, *etc*.). The situation can become muddy if a record that was intended to be merely useful as an information record turns out to be so significant that someone would like to put it on exhibition. Figure 4 shows common structures and linkages that are present in lignin (Balakshin *et al.* 2020).

An adverse effect of lignin on the storage-stability of paper has been suspected by many authors (Clements 1987; Arnold 1998; Łojewski *et al.* 2010). Bogolitsyna (2011) developed methodology to detect lignin-derived byproducts of the type that may result from the aging of lignocellulosic materials. Dupont *et al.* (2007) observed such aromatic degradation products from lignin in aged papers. However, Zou *et al.* (1993) found that the presence of as much as 28% of lignin in paper fibers did not have a significant accelerating effect on the loss of strength of paper subjected to accelerated aging. Schmidt *et al.* (1995) proposed a sacrificial antioxidant role for lignin after comparing fully-bleached and lignin-containing pulps. Lignin-containing pulps exhibited poor optical permanence, but better retention of paper strength and cellulose DP than their bleached counterparts. One has to keep in mind that lignin cannot be treated as a material with a uniform chemical structure. Thus, the effects on aging highly depend on its origin and the processes involved during pulping and papermaking. One example for a different behavior based on lignin origin during light-induced aging is given by Potthast *et al.* (2004).

Bégin *et al.* (1998) observed that as long as there was sufficient calcium carbonate present, lignin content did not appear to affect the aging behavior of either lab-made handsheets or commercial paper products. They attributed such effects to the buffering of pH to about 7.5 or more. All of the papers tested exhibited substantial loss in tear strength and folding endurance when the extract pH was below 5, but strength was maintained in the case of all sheets having extract pH of neutral or higher. Malachowska *et al.* (2020) likewise found no evidence of faster accelerated aging of paper sheets that contained lignin in the case of specimens prepared at neutral pH.

Clements (1987) mentioned the degradation of lignin as a likely contributing cause of acidification, leading to acid-catalyzed hydrolysis of cellulose. It is worth noting that the presence of lignin is often associated with mechanical pulp grades, and these can be expected to have greater proportions of both hemicellulose and various extractives in comparison to kraft pulps. The acid content of the extractives can lower the extract pH, unless suitably buffered (Verenich *et al.* 2004; Leiviska and Ramo 2008). Hydrolysis of acetyl groups of the hemicellulose is another source of acidity. If “lignin” is being blamed for the poor storage stability of papers that contain higher amounts of extractives and/or hemicellulose, this can be regarded as a kind of guilt-by-association rather than a true effect of the lignin.

Further evidence that lignin does not necessarily contribute to rapid breakdown of paper-like items is apparent from the fact that papyrus specimens, which contain lignin, have lasted for more than 3000 years (Lojewska *et al.* 2017). Natural papyrus is known to contain about 12 to 15% lignin (Bausch *et al.* 2022b). However, these authors suggest that a further contribution to the stability of papyrus may come from its content of natural flavonoids. These compounds, which can act as lignin precursors and not as just extractives, have the potential to serve as internal antioxidants (Rosado *et al.* 2021; Rencoret *et al.* 2022).

Wood extractives

Figure 5 shows the structures of some common wood extractives, which together often make up from 1% to 3% of the dry mass of the wood species most used as the source for papermaking fibers. Among the chemicals related to wood extractives, by far the most research related to the storage stability of paper has been focused on rosin, which is an extractive component present in the wood of pine and other conifers. Many studies have reported relatively poor storage stability of paper that had been manufactured with rosin as a sizing agent (Wilson and Parks 1980; Clements 1987; Shahani *et al.* 1989; El-Saied *et al.* 1998; Basta 2003, 2004; Basta and Fadl 2003; Basta *et al.* 2006; Jacob *et al.* 2017). However, essentially all of the studied rosin-containing papers mentioned in the cited articles had been prepared with papermaker's alum (aluminum sulfate), which is highly acidic. Barrett *et al.* (2016) showed a strong adverse correlation between the alum content of European handmade papers in the period between the 14th and 19th centuries and their permanence characteristics. It is notable that alum was also historically added for purposes other than alum-rosin sizing (Brückle 1993).

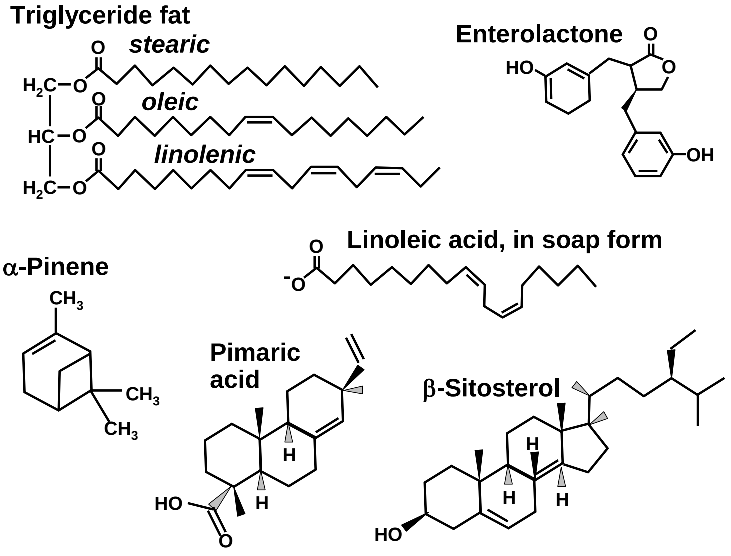


Fig. 5. Chemical structures of some common wood extractives

Bialczak *et al.* (2011) carried out accelerated aging tests on newsprint specimens and focused on the changes in extractives and wetting properties. It was found that the content of extractable material declined very quickly during heating at 60 °C. After two days of such accelerated aging, only 20% of the initial extractives were still capable of being extracted. Results were attributed, at least in part, to polymerization of some of the extractive substances. Evidence also pointed to the oxidation of extractive substances as a likely mechanism leading to lower extractive amounts. It makes logical sense to expect that some portion of the extractives may have been directly volatilized from the paper during the accelerated aging. Another key observation was an increased hydrophobic character of the paper following accelerated aging (Bialczak *et al.* 2011). This is in agreement with earlier research by Swanson and Cordingly (1959). These authors were concerned with mechanisms leading to the self-sizing of paper sheets that contained wood extractives. In other words, the migration of wood extractives to the surface of paper can be a mechanism leading to increased hydrophobicity over time.

Some unique evidence about the chemical stability of certain wood extractives was obtained under more extreme conditions in a study of palm oil fatty acid ester and natural ester as a component for the dielectric fluid within electrical transformers (Tokunaga *et al.* 2016). The synthetic ester was found to have favorable stability in comparison to mineral oil after heating at 170 °C for 20 to 120 days. Likewise, Suzuki *et al.* (2014) found that kraft paper degraded more slowly in a palm fatty acid ester in comparison to when mineral oil was the suspending medium.

Effects of Pulping and Bleaching on Archival Performance

The preceding subsection dealing with the archival performance of cellulose, hemicellulose, lignin, and extractives tells only part of the story. What is missed by such a focus on the individual main chemical components of papermaking fibers is the potentially large effects of such processes as pulping and bleaching. Those aspects will be considered here.

Alkaline pulping and fiber quality

The use of alkaline conditions as a means to obtain long cellulosic fibers from plant materials with a minimum of mechanical damage has been known since ancient times (Hunter 1947; Barrett 2005; Hubbe and Bowden 2009). The lye obtained from wood ash was found to be beneficial in separating the fibers. Such alkaline conditions for the pulping of fibers such as hemp and the bast fibers from the bark of paper mulberry (*Broussonetia papyrifera*) appear to have resulted from the persistent efforts of local artisans to improve their products. The modern alkaline pulping methods, including kraft pulping and soda pulping, thus appear to be rooted in the early cultural history of the technology. Baker (2010) documents the shifts in the western paper-making technology as papermaking was being industrialized in the 19th century. Mizumura *et al.* (2017) show correlations between the amounts of alkali used for preparing Japanese *washi* and the resulting paper qualities. While caustic soda (sodium hydroxide) permits shorter cooking and fiber cleaning times, it also results in shorter fibers and lower quality papers than soda ash (sodium carbonate), and slaked lime (calcium hydroxide). Wood ash (lye/potash) is considered to produce the softest fiber, but it requires the most time and labor during the papermaking period.

Kraft pulp archival performance

Because the kraft process has become the dominant modern pulping method for preparing pulp fibers for paper (exceeding sulfite processes in the 1950s (NAA 2022)), it is worth considering its likely effects on the archival performance of the resulting paper. Kraft pulping differs from the traditional alkaline pretreatment of pulp fibers with respect to such factors as concentration of the alkali, temperature, pressure, and the presence of sodium sulfide as a co-reagent (Fardim and Tikka 2011). For example, the following conditions may be regarded as typical: active alkali 17% to 28%, sulfidity 15% to 28%, and temperature 150 to 170 °C (Mendonça *et al.* 2002; Daniel *et al.* 2003). One of the known consequences of kraft pulping is a decrease in degree of polymerization (DP) of the cellulose. For instance, it was reported that the intrinsic viscosity (a measure of DP) of cellulose solutions decreased from an initial value of about 1300 cm^3/g after kraft pulping to about 950 cm^3/g, depending on the extent of delignification (Tao *et al.* 2011). More severe losses in intrinsic viscosity, at comparable levels of delignification, were observed in cases where kraft pulping had been followed by oxygen delignification. Alkaline conditions are able to catalyze a so-called peeling reaction, starting from the ends of cellulose chains, in addition to random scissions elsewhere in the chains (Fengel and Wegener 1989). The latter, which requires higher temperature, is more of a concern, since they can cause a more drastic drop in DP.

The extent of the peeling reaction is limited due to an alternative pathway, as illustrated in Fig. 6. Note that in this so-called "stopping reaction," the end product is a stable carboxylic acid group at the end of the chain. Once this end group has been established, the peeling reaction no longer proceeds.

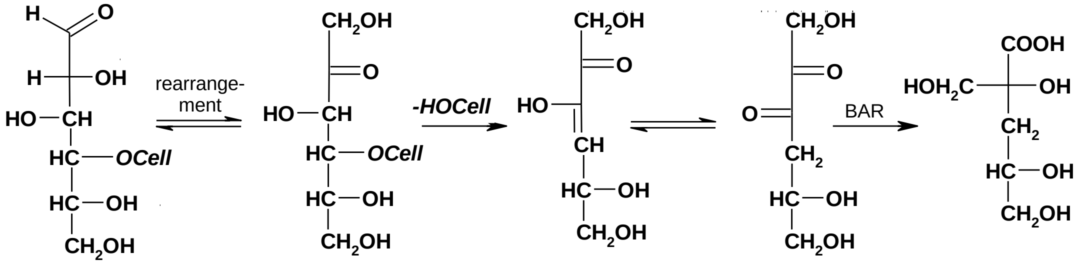


Fig. 6. Mechanism of the peeling reaction. BAR= Benzylic Acid Rearrangement (Fengel and Wegener 1989)

An important consequence of chemical pulping of wood is that the micro-domains once occupied by lignin are converted to mesopores, *i.e.* roughly corresponding to the IUPAC defined range of 2 to 50 nm in diameter (Stone and Scallan 1965, 1968). While the pulp is kept in the wet state, the presence of these mesopores contributes to the conformability of the fibers, especially after the pulp has been mechanically refined (Steadman and Luner 1985). This renders the fibers highly conformable and capable of developing relative bonded area between adjacent fibers upon drying of the paper. But upon drying, many of the pores close up as a result of capillary forces, and a high density of hydrogen bonding can develop between what used to be the adjacent walls of mesopores (Hubbe *et al.* 2007). As a result, the material loses some of its ability to swell again if the paper is placed back in water, an effect that is called hornification (Weise and Paulapuro 1999; Welf *et al.* 2005; Law *et al.* 2006). This is relevant to archival concerns, since hornification contributes to a more brittle nature (Kato and Cameron 1999), as does the aging of paper. Implications of hornification will be further discussed in a later section, "Degraded Conditions of Cellulose in Paper"

Bleaching of kraft pulps

In a broad sense, bleaching treatments of papermaking pulp can be regarded as a continuation of pulping. However, whereas chemical pulping (such as the kraft process) has a primary aim of removing lignin, bleaching processes have an additional goal of either removing or decolorizing chromophoric groups (Engwall *et al.* 1997; Suess 2009). To make matters somewhat more challenging, the residual lignin remaining in the fibers after pulping may be inherently more difficult to break down and remove, in comparison to the lignin already removed (del Rio *et al.* 2001). An ideal bleaching treatment ought to be selective – attacking and solubilizing lignin-related and other chromophoric species with a minimum of damage to cellulose or hemicellulose. However, it is typical for the DP of cellulose after bleaching to be substantially lower than it was at the end of the pulping stage (Pouyet *et al.* 2013).

The cleavage of bonds within the cellulose macromolecule are of greatest concern when they occur close to the middle of the chain, thereby having a large effect on its degree of polymerization. Oxidative processes that are aimed at destruction of residual lignin moieties and chromophores to some extent also affect the cellulose and hemicellulose (Gierer 1997). Ney (1982) proposed a hydrogen abstraction from an anhydroglucose unit as an initial step in the oxidative degradation of cellulose during bleaching of pulp with hydrogen peroxide under alkaline conditions. This was also refined by Gratzl (1992), Zeronian and Inglesby (1995), and Gierer (1997) (see Fig. 7). Hence, the action of reactive oxygen species (hydroxyl radicals, dioxygen, or superoxide radicals among others) in chlorine-free bleaching sequences leads to keto groups along the cellulose chain (Fig. 8). Especially, but not exclusively, under alkaline conditions the glycosidic bond in beta-position to this keto group can easily be cleaved, which results in an immediate drop in DP, depending on the overall position of this keto group (Fig. 9). Based on the model reactions, beta elimination becomes significant above pH 9 (Potthast *et al.* 2006; Hosoya *et al.* 2018).

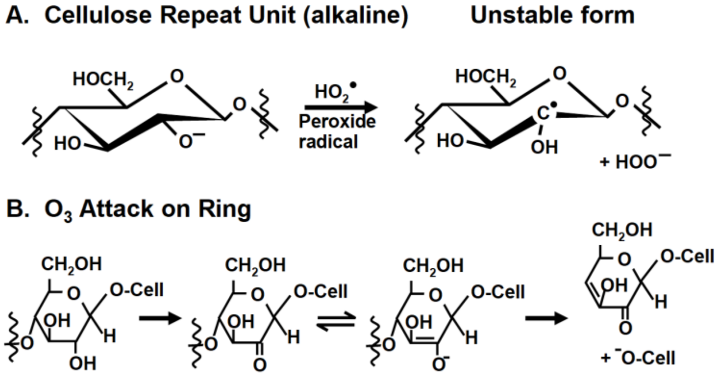


Fig. 7. Mechanisms by which oxidative bleaching may cleave cellulosic chains, thus reducing the degree of polymerization of cellulose in bleached pulps. Structures redrawn

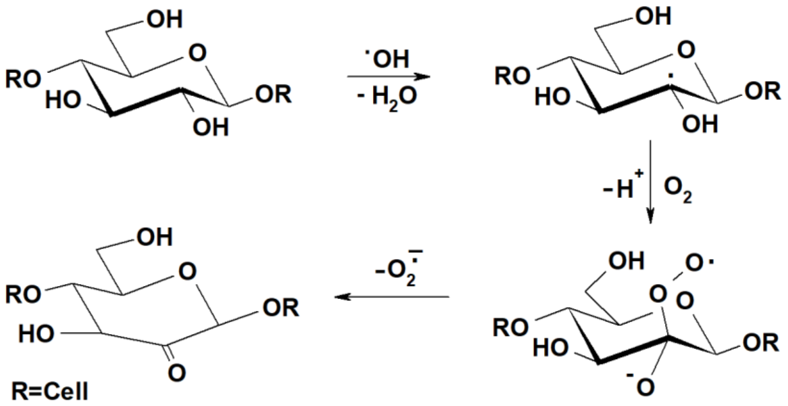


Fig. 8. Formation of carbonyl structures as a consequence of hydrogen abstraction by hydroxyl radicals

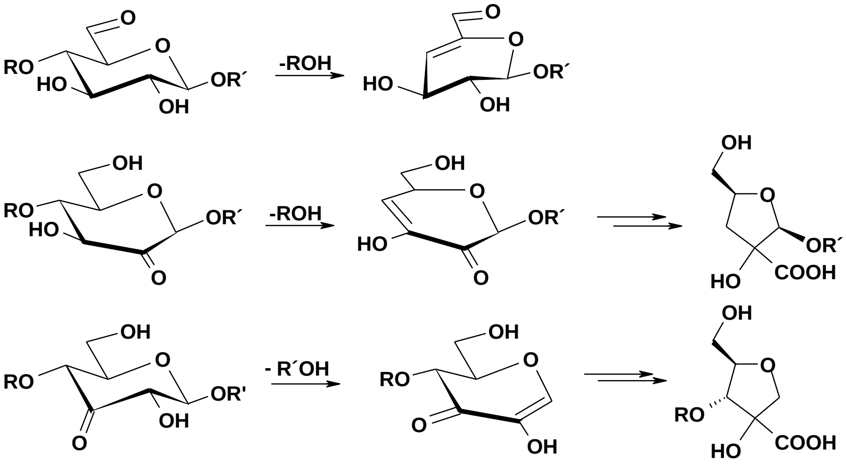


Fig. 9. Cleavage of the glycosidic bond by β-elimination at oxidized structures along the cellulose chain, according to Lewin (1997)

Also ozone bleaching results in the formation of additional keto groups along the cellulose chain (Potthast *et al.* 2003), which results in less stable pulps also with regard to brightness. A study by Lemeune *et al.* (2004) found that oxidation by ozone led to much greater decreases in the degree of polymerization of cellulose, compared to ClO_2. Hypochlorous acid is an example of a bleaching agent that is widely known to be less selective than ClO_2 and therefore generally more damaging to the cellulose. In particular, hypochlorous acid has been shown to bring about oxidative damage to the pulp (Zhou *et al.* 2008; Chenna *et al.* 2013). For details on the effect of different bleaching agents on pulp the reader is referred to the Handbook of Pulp by Sixta (2006).

In modern pulp and paper mills there has been a gradual evolution in bleaching technologies, which generally involve a series of bleaching stages in succession (Dence and Reeve 1996; Hart 2012). For example, a common bleaching sequence in 1970 would include chlorine gas in the first stage, followed by an alkaline (NaOH) extraction stage, and then a couple of stages with sodium hypochlorite as the bleaching agent. However, such practices were shown to generate highly toxic and persistent chlorinated aromatic species in the effluent from such mills (Engwall *et al.* 1997; Axegård 2019). By the 1990s, the chlorine treatment had been replaced mainly by bleaching sequences employing chlorine dioxide (Gellerstedt *et al.* 1995). In a well-run bleaching plant, when relying upon chlorine dioxide, it is possible to reduce the production of chlorinated dioxins and furans to below detectable levels (Axegård 2019). Another shift has been the implementation of an initial oxygen gas bleaching stage in many mills (Tao *et al.* 2011; Hart 2012). Oxygen bleaching is less selective than, for instance, chlorine dioxide as a delignification agent. A consequence of this lower selectivity is a greater tendency to decrease the DP of the cellulose (Pouyet *et al.* 2013; Brännvall and Walter 2020). A few mills, mainly in the Nordic countries, have been running without any chlorine-containing bleaching agents. Such totally chlorine free (TCF) bleaching systems rely heavily on oxygen delignification as an initial stage of bleaching.

Carboxylic acid groups

For carboxyl group determination of pulp and paper specimens, titration approaches are available to measure the overall content (Barbosa *et al.* 2013, TAPPI

Method T237). Also, adsorption of methylene blue is frequently applied (Weber 1955; Philipp *et al.* 1965; Fardim and Holmbom 2003). In some cases a differentiation between C6-carboxyl groups, *e.g.* mainly present in 4-O-methylglucuronic uronic acids of hemicellulose (*cf*. Fig. 3) and C1 carboxyls, *i.e.* an oxidized reducing end group, is desirable. For the first case, the FDAM method can be used. Besides the total content of uronic acids, it also provides their distribution along the molar mass distribution of cellulose and can be used to trace hemicelluloses in a pulp or paper specimen (Bohrn *et al.* 2006). To quantify the C1-Oxidation at cellulose is more difficult. Currently, one approach based on selective fluorescence labeling is being developed (Budischowsky *et al.* 2022).

Relevant data connecting different bleaching methods to the titratable charge demand of cellulosic pulps was reported by Laine (1997). Various oxidizing agents were found to affect the bleaching of kraft pulps, including sequences containing oxygen, ozone, chlorine dioxide, and hydrogen peroxide. A final hydrogen peroxide stage has a greater tendency to convert carbonyls to carboxyl groups, which adds to brightness stability of pulps.

Letnar (2002) considered the question of bleaching or not bleaching relative to the permanence and archival durability of library materials on paper. Pulp was prepared by the kraft and the sulfite processes, such that the kraft fibers were brown in color. Alkaline pH conditions were maintained, due to the presence of calcium carbonate filler. In terms of mechanical properties, good archival performance was observed regardless of whether the pulps had been bleached or not. On the other hand, the unbleached kraft fibers did not have suitable optical properties for graphic papers.

Carbonyl groups

Carbonyl groups in cellulose other than at the reducing end represent a deviation from the perfect cellulose structure and may generate labile spots that affect stability. Although the carbonyl content typically is in the lower µmol/g range, *i.e.* 12 µmol/g, which corresponds to a ratio of approximately one extra carbonyl per 1000 anhydroglucose units, their presence matters with regard to brightness reversion and overall stability, as mentioned before. Hence quantifying carbonyls is a way to judge the effectiveness of a stabilizing treatment as well as the status of a historic paper. The degree of yellowing of a paper may not always give conclusive answers.

If sufficient amounts of material are available, the hydroxylamine method can be performed (Cyrot 1957; Szabolcs 1961; Rehder *et al.* 1965). For smaller sample quantities and for localizing carbonyls in relation to the DP of cellulose, the CCOA method can be applied (Röhrling *et al*. 2002, 2003; Potthast *et al.* 2003). If only aldehyde groups are of interest, mainly in form of reducing end groups, the copper number (TAPPI T-430 om94) or the TTC method (Szabolcs 1961; Horn and Eijsink 2004) can be applied. It has to be kept in mind that both methods operate at strong alkaline conditions; hence, the presence of carbonyls along the cellulose chain may induce chain degradation and new reducing ends.

Mechanical pulp archival performance

So-called high-yield pulps, which typically contain over 90% of the original dry content of the wood, have long come under suspicion as sources of instability of paper (Wong *et al.* 1995; Paulsson and Ragauskas 2000; Seki *et al.* 2005; Bialczak *et al.* 2011; Jablonsky *et al.* 2012). Lignin-containing fibers are known to be susceptible to yellowing, especially when exposed to light (Leary 1994; Yuan *et al.* 2013; Yun and He 2017). As noted by Zervos (2010), the two primary mechanisms of chemical degradation of paper made from high-yield pulps are the same as those for lignin-free paper: acid hydrolysis and oxidation by air. The decomposition of paper made from high-yield pulp during accelerated aging has been tracked by analysis of the volatilized organic compounds (Hrivnak *et al.* 2009b). It has been found that the usage of high-yield pulp, in the presence of calcium carbonate filler particles is able to resist aging (Eggle *et al.* 1984). Likewise, deacidification by spraying aqueous suspensions of magnesium carbonate, an alkaline buffering agent, was found to slow down the aging of such papers. However, paper made from high-yield fibers has been found to be susceptible to yellowing, even after deacidification (Bukovský 1997).

Regenerated cellulose

Though regenerated cellulose, *e.g.* rayon or lyocell fibers, is not ordinarily used for manufacture of paper, its permanence characteristics are likely to interest some readers of this article. In addition, regenerated cellulose is sometimes used indirectly. For instance, rayon fabric has been used as the structural part of a facing to protect fragile archival paper specimens during their repair (Bedenikovic *et al.* 2018a,b). Rayon also has been used for decorative Japanese papers (Japanese Paper Place 2022). Due to the fact that regenerated cellulose has a different crystal structure (cellulose II) compared to native cellulose (cellulose I), it is reasonable to expect there to be differences in such issues as archival performance. One has to keep in mind that different regenerated celluloses are on the market today. Their properties differ in crystallinity, DP, and fiber characteristics. The degree of crystallinity of classical viscose fibers has been reported as lower in comparison to the starting cellulose I materials (Zhang *et al.* 2001; Röder *et al.* 2006a,b; Gao *et al.* 2011; Azubuike *et al.* 2012; Liu *et al.* 2015b). The overall DP of man-made cellulosic fibers is much lower compared to paper pulp, but the high orientation of the fibers gained in the spinning process generates a different type of stability, also due to extra hydrogen bonding, which cannot be directly compared to ordinary pulp. Man-made cellulosic fibers contain much less hemicelluloses compared to paper pulp. Little is known about the aging behavior of man-made celluloses fibers in direct comparison to pulp or paper. This suggests a need for more study before any version of regenerated cellulose would be recommended for archival paper preparation.

Mineral Fillers

Mineral fillers and coatings have been used throughout the history of papermaking to modify the surface properties and opacity, as well as to prepare paper for printing, drawing, and writing media. For example, “prepared” paper surfaces with lead white are described in Cennini's 14th century treatise; in the era of old master metalpoint drawings, a variety of minerals were used to fill/coat/create a smooth drawing surface. The reason for placing mineral fillers second in order of discussion after cellulosic fibers is that a majority of modern printing papers contain about 10% to 25% of mineral content, and sometimes even more (Fairchild 1992; Hubbe 2014a). Mineral particles, especially at higher proportional contents, have a negative impact on the strength properties of paper, but on the other hand they often cost a lot less than the fibers they replace. The strength issue is important, since the aging of paper will result in a further loss of strength. At some point the strength will be insufficient to allow handling of an item without high risk of damage. Though papermakers employ starch and other chemical additives to gain back some of the sacrificed strength (Hubbe 2014a), due to the usage of relatively large amounts of mineral, such practices may just shift the concern to the archival performance of those other additives, and these issues will be considered in subsequent subsections of the article.

An expected debonding and weakening effect of mineral fillers on paper is illustrated in Fig. 10. Item "A" in the figure depicts a typical shape of kaolin clay particles that have been used for many years by papermakers. Item "B" portrays a typical shape of a scalenohedral precipitated calcium carbonate (PCC) particle, which is often called a rosette. Frames "C" and "D" of the figure illustrate an observed "bulking" effect of the rosette particles, in comparison to the clay particles. In either case, the imposition of mineral particles between cellulose fibers impedes the direct development of hydrogen bonding between the cellulosic surfaces.

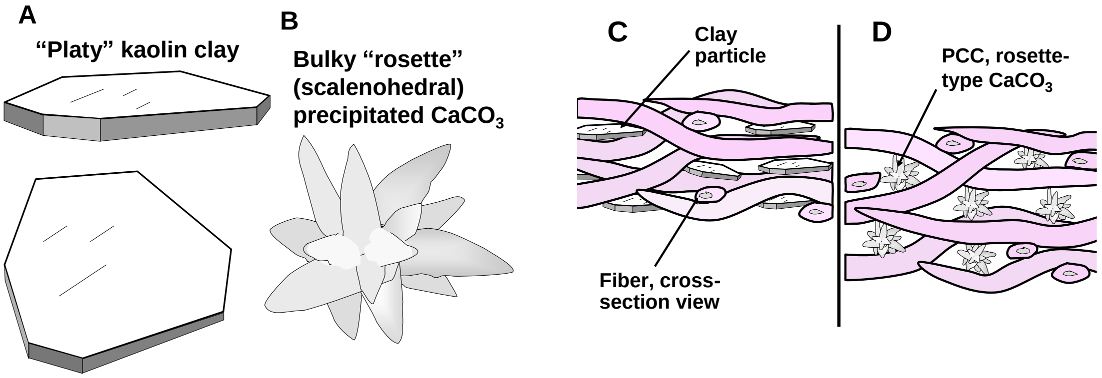


Fig. 10. Schematic depicting likely role of mineral filler particles in preventing close approach of some adjacent fiber surfaces during the formation and drying of paper, thus contributing to lower paper strength

Calcium carbonate

By far the dominant type of mineral used in modern paper is calcium carbonate, and the majority of it that is used in printing paper is PCC (Fairchild 1992; Hubbe and Gill 2016). Commercial usage of calcium carbonate as a filler for paper has been documented back to 1925 (NAA 2022). When a sufficient amount of $CaCO_3$ is placed into aqueous media, it can effectively prevent the pH from remaining below about 7.5. In the presence of acidity, one of the following reactions may take place:

$$CaCO_3 + H_3O^+ \rightarrow Ca^{2+} + HCO_3^- + H_2O \quad (1)$$

$$CaCO_3 + 2H_3O^+ \rightarrow Ca^{2+} + CO_2\uparrow + 3H_2O \quad (2)$$

In addition to consuming the acid, the second reaction can yield carbon dioxide, which will either remain in solution or come out of solution as bubbles. Because the usage of calcium carbonate maintains a non-acidic pH, the use of calcium carbonate in papermaking has been called alkaline papermaking. The usage of calcium carbonate as a filler increased in the 1970s and 1980s, paired with the increasing popularity of alkaline sizing agents (NAA 2022).

Barrow (1974) tracked the relative frequency of paper specimens produced with alum (acidic) or calcium carbonate (alkaline) over the period from 1500 to 1974 and showed a steep rise in the use of alum from 1500 to 1700, with a continuing more gradual rise up to 1974. Barrow attributes a corresponding decrease in pH to this increase in alum. The most recent sets of paper specimens tested by Barrow were over 95% made under acidic conditions. Barrow also showed a strong correlation between acidity and time of production, such that the acidic papermaking conditions seemed to be implicated in the loss of folding endurance. Barrett *et al.* (2016), however, counter this narrative using XRF data to survey nearly 1600 paper samples from the 14th to 20th centuries, showing relatively consistent alum concentrations, but tracking significant decreases in gelatin and calcium that would correlate in the same manner to the decreasing pH. Later, starting in the mid-1980s and continuing through the 1990s, there was a major shift in commercial papermaking practices, such that calcium carbonate displaced clay as the main filler used in printing papers (Hubbe 2005). Because the rosin-alum sizing system does not work effectively under the weakly alkaline pH conditions, papermakers had to turn to other internal sizing agents that do not rely upon the use of alum (see later discussion of ASA and AKD).

Some of the chemistry associated with the production of PCC versions of $CaCO_3$ have the potential to affect the resulting pH, which is a variable that can affect paper permanence in various ways. To minimize the costs of shipping, it is a common practice to convert mined limestone to burnt lime, CaO, at the mine site by strong heating of the $CaCO_3$. Then, after transporting the lime to a satellite facility, usually right beside a paper mill, the following reactions are carried out:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(slaking)} \qquad (3)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{(carbonation)} \qquad (4)$$

The final reaction (the carbonation) is not necessarily carried out to 100% completion. If some of the $Ca(OH)_2$, which is called “milk of lime,” is still present within the resulting PCC, then the paper machine system’s pH may rise to 9 or higher. Though such high pH values are not common in paper mills, various authors have expressed concern that they may later accelerate oxidation of the cellulosic material in the dry paper (Kolar and Novak 1996; Malesič *et al.* 2002).

Titanium dioxide

Titanium oxide can be considered for usage as a filler (or “pigment) in paper products that need to have relatively high opacity, *e.g.* thin paper sheets for religious texts. The high refractive index values of the rutile (2.7) and anatase (2.55) crystal forms of TiO_2 give rise to a high efficiency of light scattering, especially when the particle diameter is optimized at about 0.2 to 0.3 μm (Thiele and French 1998).

The catalytic properties of TiO_2 may raise concern relative to paper permanence. According to Perez *et al.* (1998), TiO_2 undergoes the following reaction in the presence of oxygen and UV light,

$$TiO_2 + e^- + UV \rightarrow TiO_2^{-*} \qquad (5)$$

$$TiO_2^{-*} + O_2 \rightarrow TiO_2 + O_2^{-\cdot} \qquad (6)$$

where TiO_2^{-*} denotes an activated species of titanium dioxide. Photocatalysts have been prepared by adding TiO_2 nanoparticles to clay particle surfaces (Liu and Zhang 2014). Qin *et al.* (2021) recently prepared TiO_2 nanoparticles having junctions between rutile and anatase phases. The heterojunctions between the crystal phases were credited with a high efficiency of creating oxygen radical species upon exposure to UV-containing solar light. In the cited work, this was judged to be a positive outcome, since it conferred an antibacterial effect. However, in addition to killing bacteria, the generated free radical species might be expected to initiate damage to chemical structures within the paper (Perez *et al.* 1998; Campanella *et al.* 2005). It has been shown, for instance, that in the presence of UV light, TiO_2 particles can catalyze the breakdown of lignin (Machado *et al.* 2000). The breakdown appears to involve both degradation of phenolate groups and hydroxylation of aromatic rings. Perez *et al.* (1998) observed relatively minor decreases in the viscosity of cellulose solutions obtained from cellulose pulp that had been exposed to UV light in the presence of TiO_2 and hydrogen peroxide. However, viscosity losses of about the same magnitude were observed in control tests not including the TiO_2. Thus, the main concern is likely to arise in archival paper specimens that contain either lignin or various dyes that have aromatic structures.

Fortunately, there is a way to be able to benefit from the very high light scattering ability of TiO_2 without having to suffer the risk of free-radical-induced degradation pathways. As is commonly done in preparing commercial TiO_2 products for paints, the TiO_2 particles can each be coated with a thin layer of another mineral, such as SiO_2 (van Driel *et al.* 2016).

Kaolin clay

Kaolin clay has been in general usage as a paper filler since the 1780s, with increased usage in the 1870s (NAA 2022). The usage of kaolin clay within the main plies of printing paper products has declined greatly since the early 1980s (Hubbe 2005). However, it is still a major component in many coatings for paper. Kaolin can be generally described as a platy aluminosilicate mineral. Commercial kaolin products mainly are mined from metamorphic deposits that had been formed from the deposition of silt as glacial run-off emptied into ancient oceans (Dill 2016). As would be expected based on such a geologic origin, kaolin particles have a stable and generally unreactive chemistry relative to the concerns of paper's permanence.

In common with other mined products, such as ground limestone calcium carbonate, kaolin products used in the paper industry will contain dispersants, which are usually polyacrylates or their copolymers (Loginov *et al.* 2008). The dispersants render a strong negative charge to the wetted surfaces. The resulting inter-particle repulsion is helpful during the mining, shipping, and storage. Papermakers employ cationic additives such as papermaker's alum and cationic copolymers of acrylamide to retain not only the negatively charged kaolin particles, but also such items as cellulosic fines, PCC particles, and various additives to the papermaking process. The effects of dispersants and other such additives on archival performance do not appear to have been reported.

Other minerals

Some other mineral products are used by papermakers, but generally at lower quantities. Talc, which is a highly platy magnesium silicate mineral, is primarily used as a control agent for pitch and stickies in paper machine systems (Sutman and Nelson 2022). A variety of precipitated silicate and silica products, generally having much higher specific surface areas than ordinary kaolin, can be used in coatings for high-end printing papers, for instance to achieve high resolution ink-jet images (Cawthorne *et al.* 2003). Specialty grades of paper (glossy, coated, filled, *etc*.) historically have contained a variety of inorganic components in addition to those described above, such as zinc sulfide, zinc oxide, lead carbonate, *etc*. (NAA 2022). No information was found in the present literature searching work relative to the archival performance of such products.

Starch Products

Next in order of decreasing amounts in typical modern printing papers are various starch products. Starch has a long history of use in the paper industry as a sizing agent, strengthening agent, or as an adhesive for mineral-based coatings. Hunter (1947) reports use of starch to size paper as early as 700 A.D. Early Persian papermakers employed rice and wheat starches, as well as a variety of plant mucilages to prepare paper for writing (Barkeshli 2003). As papermaking traditions passed from the Middle East to Europe, these materials continued in use. For instance, Anguera (1996) reports that the earliest paper made in Valencia (early 14th century) was sized with “vegetable glue” of rice or wheat origin, or in other words starch. A primary function of these starch products is to confer strength to the paper, either by supplementing the inter-fiber bonding or by applying the starch as a film to the paper surface. In modern papermaking, internal or “wet-end” starch is typically a cationic derivative of starch, and the levels of addition are usually less than about 1.5% on a mass basis (Howard and Jowsey 1989; Jancovicova *et al.* 2012). Cationic starches were introduced to papermaking in the 1950s (NAA 2022). Greater amounts of starch, sometimes comprising 5% of the dry mass of paper, can be applied to the paper surface at a size press (Brouwer 1997; Shirazi *et al.* 2004). Essentially all of the starch that is used in printing papers has first been solubilized by cooking in water before its application (Horie 2010). In paper conservation, it is well known that starch films made from flour sources (*i.e.* gluten protein- and lipid-containing) age much more poorly than purer starch sources. These films stiffen and yellow to a greater degree. The type of starch (*i.e.* amylose to amylopectin ratio / different granule size, *etc*.) also affects how they age – rice *vs.* corn *vs.* potato vs. wheat starch films age differently.

For reasons of minimizing costs, a majority of the starch that is applied to the paper surface during commercial papermaking consists of unmodified starch, which is often called pearl starch. Such starch, when it comes from natural maize, potato, wheat, or tapioca sources, is invariably a mixture of two contrasting molecular forms. The amylopectin form, which has a branch point at each third amylose group on the chain, has some crystallinity in the native state, but it resists recrystallization (retrogradation) when dried from a solution (Gudmundsson 1994; Chang *et al.* 2021). The amylose form, which is linear and has a relatively low molecular mass often near one million g/mole (Ong *et al.* 1994), can adopt various crystalline forms. Figure 11 depicts two forms of structure within starch that can be present during the preparation of paper. Native starch can be in the form of helical structures. Notably, as shown in an end-wide view at the left of the fibers, V-type starch helices have been shown to have a more hydrophobic character toward the inside, making it possible for the starch to serve as a carrier of relatively hydrophobic compounds (Immel and Lichtenthaler 2000; Bildik Dal and Hubbe 2021). Most notably, the V-complex is able to enclose fatty acids or iodine (Tolstoguzov 2003; Putseys *et al.* 2010).

Cooking of the starch, followed by the passage of time in a heated solution, leads to a process called retrogradation (Andersson *et al.* 2008). This effect becomes prominent if an amylose-containing solution is held a long time within a temperature range of about 70 °C or higher, such that the amylose portions of it undergoes irreversible crystallization (Keetels *et al.* 1996). At a molecular scale, this entails formation of the macromolecules into a different form of helix (A-type) and precipitation of clusters of those helices (Conde-Petit *et al.* 2006; Liu *et al.* 2007). Though such changes indicate potential instability in starch structures, it is unclear the extent to which the helical forms and clustered forms of starch might continue to change during the subsequent storage of dried paper.

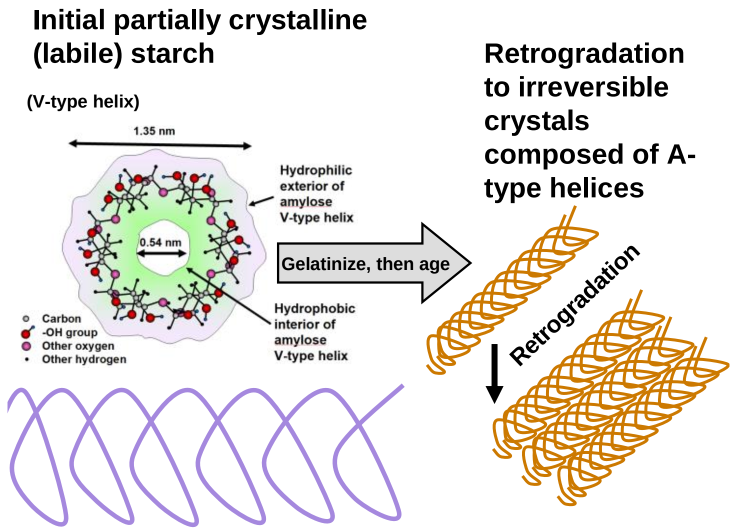


Fig. 11. Representation of a progressive crystallization process within starch, as has been observed in the aging of starch films over relatively short time periods

When starch is used as a binder in aqueous pigment formulations for the coating of paper, the starch type of choice is hydroxyethylated starch (Jauregui *et al.* 1995). Starch that has been hydroxyethylated is noted for its tough, non-brittle films and the absence of retrogradation phenomena. Since an ether bond is formed in the hydroxyethylation process, such products are expected to have good storage stability (Wu *et al.* 2018).

Evaluations of the storage stability of starch invariably have involved time periods very much shorter than those of interest to paper archivists. For instance, Mali *et al.* (2006) reported significant increases in crystallinity of various plasticized starch films during 90 days at room temperature. Fama *et al.* (2007) observed significant increases in crystallinity of starch films that had been plasticized with either glycerol or sorbate within a 4-week test period. Significant decreases in moisture content were apparent after eight weeks of storage. Thirathumthavorn and Charoenrein (2007) showed that the crystallinity of starch films increased during a month of storage. Panaitescu *et al.* (2015) found that nanofibrillated cellulose could be used to form a network within films comprised of starch and polyvinyl alcohol, thus hindering starch crystallization. Because all of these listed changes took place during a relatively short period, relative to the storage of books, one might anticipate more substantial changes to starch in paper over longer periods. In paper conservation, it is empirically known that starch films made from flour sources (*i.e.* gluten protein- and lipid-containing) age much more poorly (*i.e.* stiffen and yellow to a greater degree) than purer starch sources (Wills 1984). The type of starch (*i.e.* amylose to amylopectin ratio / different granule size, *etc.*) also affects how they age, such that rice *vs.* corn *vs.* potato *vs.* wheat starch films age differently (Indictor *et al.* 1978; Van Steene and Masschelein-Kleiner 1980).

Other Natural Polymers

Chitosan

The polysaccharide chitosan, which is depicted in Fig. 12, is remarkably similar to cellulose except that what would have been an –OH group on the C2 carbon of the anhydroglucose unit is an amine group instead. Chitosan can be obtained by treating the shells of shrimp or other crustaceans with strong solutions of NaOH. Various authors have proposed the use of chitosan as an additive for papermaking (Rohi Gal *et al.* 2023). In particular, Basta (2003) evaluated the possible use of chitosan to enhance the aging resistance of paper that had been treated with rosin and alum. It is well known that chitosan is soluble under acidic aqueous conditions, as in the presence of acetic acid. In the cited work, paper specimens were dipped in solutions of 0.4% chitosan and 1% acetic acid, which was followed by treatment with alkaline solutions of sodium hydroxide or sodium silicate as precipitators. The type of precipitating agent was found to be important, with the sodium silicate providing better results. The reported results are generally consistent with what would be expected based on a deacidification treatment (Baty *et al.* 2010).

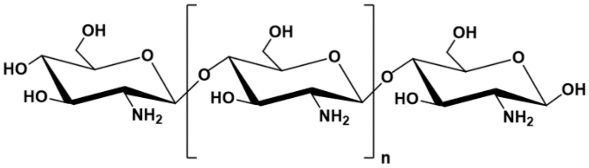


Fig. 12. The structure of chitosan (depicting a fully deacetylated form)

Proteins

Proteins, especially gelatin, have been widely used as sizing agents during the period of hand-papermaking in Europe (Lang *et al.* 1998). As shown in Fig. 13, proteins are products of the formation of peptide bonds between amino acids.

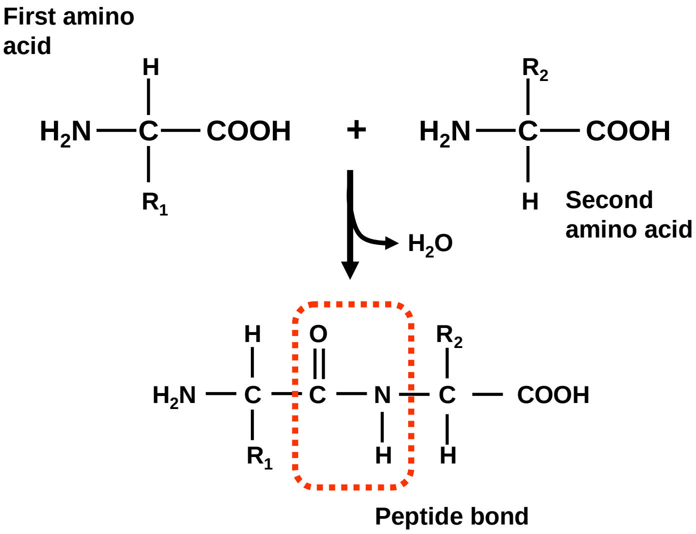


Fig. 13. Peptide bonding structures as the linkages within proteins

It is important to note that alum was not first introduced to the papermaking process for alum-rosin internal sizing, but as an additive during external sizing of paper with the protein gelatin (tub sizing). Potassium aluminum sulfate was introduced by the mid-17th century to assist in hardening the gelatin size, and, in increasing amounts throughout the week to prevent putrefaction of the gelatin solution (Clapp 1972; Baker 2010), such that gelatin use and alum use cannot always be detangled. Chen *et al.* (2003) showed faster degradation of paper that had been sized with a combination of alum and animal glue when subjected to accelerated aging. Gelatin, which is mainly composed of the protein collagen, is also considered as a strengthening agent for the conservation of weakened paper specimens (Basta and Fadl 2003; Hummert 2019). The word “resizing” is used to mean treatment of a paper artifact with solutions of either gelatin or cellulose ethers to increase strength or replace sizing removed during the course of aqueous treatment (Henry 1986; Hummert 2019).

Basta and Fadl (2003) reported that paper specimens strengthened by treatment with solutions of gelatin were subject to rapid loss of strength during accelerated aging. The effects were especially evident when testing paper having a relatively low basis weight. The results were surprising in the light of work reported by Barrett and Mosier (1994), who found a positive correlation between the gelatin content of historic paper specimens and their lightness (L^*) value from color measurements. The observed beneficial effect of the gelatin had been attributed to an alkaline buffering capability of gelatin (Baty and Barrett 2007). Lang *et al.* (1998) reported correlations between the gelatin content of historic paper specimens and several other parameters, including surface pH, fluorescence, sulfur content, and the L^* value. The cited work by Barrett and Mosier (1994) and Lang (1998) did not, however, include any evaluation of strength of the historical papers that were evaluated. It is possible that even if the gelatin treatment had contributed to raising the pH of the historical papers when they were new, that gelatin might have decomposed, in part, during the ensuing years, leading to the strength losses corresponding to those reported by Basta and Fadl (2003). Another possibility is that the gelatin material or the procedures employed by Bast and Fadl (2003) were significantly different from those that had been employed in originally preparing the historical specimens studied by Barrett and Mosier (1994). Further testing is needed to resolve such issues.

Gelatin has also been shown to have stabilizing effects on the oxidative and hydrolytic damage that can be caused by iron gall inks, either as initial sizing material, or as re-sizing applied during a conservation treatment (Kolbe 2004; Poggi *et al.* 2016; Gimat *et al.* 2021). Gimat *et al.* (2021) demonstrated that in gelatin sized or re-sized samples there is less iron to be found inside the cellulosic fiber.

Other proteins, such as animal glue and casein, and later soy proteins have been used as coating adhesives (NAA 2022).

Synthetic Water-soluble Polymers

In modern papermaking a variety of petroleum-derived chemical additives are used. Water-soluble polyelectrolytes widely used by papermakers include acrylamide copolymers, glyoxylated polyacrylamide, polyvinyl alcohol, and polyamidoamine-epichlorohydrin, among others. An example is shown in Fig. 14. No accounts of accelerating aging tests were found corresponding to the acrylamide products mentioned.

Perhaps because it is widely used in paper conservation, several studies have considered the permanence characteristics of polyvinyl alcohol (PVOH). Bicchieri *et al.* (1993) found that treatment of paper with low-mass PVOH for restoration purposes was effective for restoration of strength. Selected accelerated aging tests were carried out on a paper prepared by the authors, treated by immersion in PVOH, and then subjected to the hot conditions for specified time periods. The beneficial effect of the PVOH on paper properties did not deteriorate as a function of accelerated aging time. The PVOH treatment also appeared to resist biological attack according to sources cited by those authors.

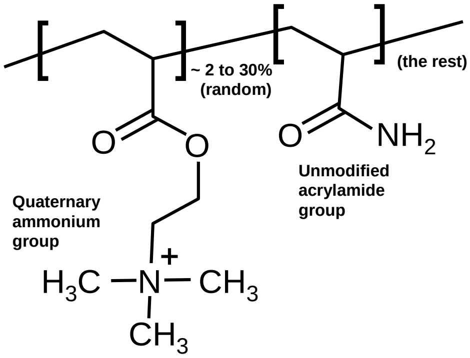


Fig. 14. Chemical structure of an acrylamide copolymer using in papermaking

Basta (2004) prepared a mixture of PVOH with or without borax. The best results, with respect to paper treatment, were with a PVOH treatment level of 0.5%. Borax treatment, as a supplement to the PVOH treatment, led to slight further improvements at low levels of PVOH. Notably, by adding borax, the beneficial effects of PVOH did not fall off even when the PVOH level was increased to 0.75% or higher. Because borax has an alkaline pH, it might be expected that the beneficial effect on the paper was related to maintaining an alkaline pH in the paper.

Hydrophobic Sizing Agents

Due to contrasting sets of issues, the following discussion regarding hydrophobic internal sizing agents will be divided into four main topic areas: rosin-alum sizing, alkaline sizing, surface-application of hydrophobic copolymers, and the use of wax-like materials. Gelatin, starch, and plant mucilages applied as external sizing agents have been discussed in other sections of this paper.

Rosin sizing agents

There are many reports documenting the adverse effects of rosin-alum sizing on the permanence of paper (Clements 1987; El-Saied *et al.* 1998; Baty and Sinnott 2004; Area and Cheradame 2011).

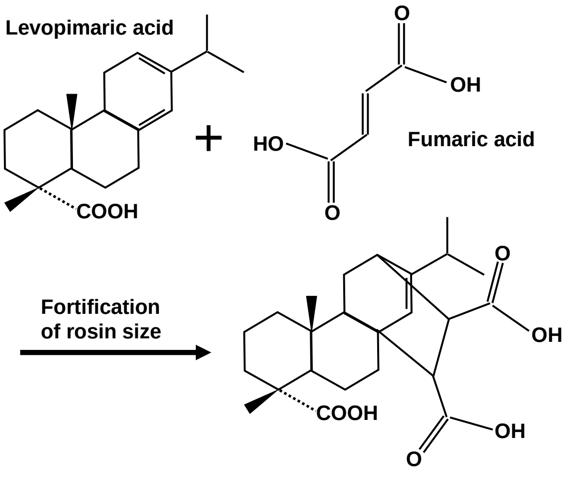


Fig. 15. Preparation of fortified rosin from levopimaric acid (a rosin component) and maleic anhydride

Kim *et al.* (1988) reported degradation of rosin by UV illumination, leading to discoloration of paper. El-Saied *et al.* (1998) found that paper that had been sized with rosin and alum also had a lower thermal decomposition temperature, which can be taken as evidence of some molecular breakdown having occurred before the testing. Figure 15 illustrates the preparation of fortified rosin, which is a main component of most rosin products currently used by papermakers.

There are two main approaches that papermakers employ to render paper hydrophobic with usage of rosin products. The oldest technology is based on the saponification of rosin with alkali, which converts the carboxylic acids to their soap form. After adding the soap to a papermaking fiber suspension, the rosin is set (precipitated onto the fiber surfaces) by addition of aluminum sulfate (Ehrhardt and Leckey 2020). This reaction is largely accomplished in the aqueous phase, even before the resulting paper sheet is dried. The second approach is to heat up the rosin mixture (including fortified rosin) to its melting point and prepare an emulsion in the presence of a stabilizing polymer, such as cationic starch or polyamidoamine-epichlorohydrin. When such an emulsion is added to a paper machine furnish, the emulsified droplets coated by the cationic polymer are retained onto fiber surfaces, but the rosin does not become molecularly spread and anchored onto the fiber surfaces until the paper is being dried (Ehrhardt and Leckey 2020).

A recent review article by Jablonsky *et al.* (2020) suggests that the aluminum has a more dominant effect on paper degradation, in comparison to the rosin. In addition to the well-known effects of low pH, the cited authors provided evidence of involvement of aluminum species in redox radical oxidation of cellulose carboxyl or carbonyl groups. Because alum has a high buffering capacity, at a given pH in the range of about 4 to 5.5, the titratable acidity in the presence of alum will be significantly higher than in a solution of a strong acid such as sulfuric acid. Notably, it has been reported that deacidification treatments do not necessarily remove the adverse effects of aluminum compounds on paper permanence (Jablonsky *et al.* 2020). The cited authors suggested that such effects may be due to non-uniformity of the chemical compounds, such that acidic regions may still persist.

Because rosin compounds such as abietic acid and levopimaric acid are carboxylic acids, one can expect that they too might contribute to the acidity of paper. The fallacy in that argument is that the pH of the added rosin product added during papermaking can be very different, depending on the type of rosin product that is employed. The traditional rosin-alum system, going back to the invention by Illig (1807), employed the soap form of rosin, which has an alkaline pH. Rosin free-acid emulsion sizing agents, which have become increasingly popular in recent years, have an inherently acidic pH, but they tend to be employed in papermaking processes at a somewhat higher value of pH (*e.g.* 4.5 to 5.5) than the traditional rosin soap sizing agents (*e.g.* 4 to 4.5) (Ehrhardt and Leckey 2020).

Another factor worth considering is the effect of the rosin sizing on the strength of the original paper, even before being subject to the effects of time. Recent work by Korpela *et al.* (2021) showed that sizing with rosin and alum decreased the initial strength of paper handsheets. The effects were consistent with the rosin having become spread over the fiber surfaces before formation of inter-fiber bonding. No strength loss was observed in cases where the sizing was carried out using alkylketene dimer (AKD) as the sizing agent. Those results are consistent with a mechanism in which an emulsified sizing agent does not spread until the paper has become substantially dry and the bonded areas have become established (Hubbe 2014b).

Alkaline sizing agents

When paper is manufactured in the presence of calcium carbonate filler, it is common to employ the hydrophobic sizing agent alkylketene dimer (AKD) or alkenylsuccinic anhydride (ASA). Introduced in the 1950s and 1970s, respectively (NAA 2022), both of these products need to be emulsified using some form of polymer, such as cationic starch or a cationic synthetic polymer. Because the latter are likely to benefit the strength of the paper, once again there can be uncertainty regarding the direct effects of the AKD or ASA on archival properties. Perhaps more importantly, the calcium carbonate (as discussed earlier) will have controlled the pH to be higher than 7.5 and more likely to be between 8 and 8.5. Thus, it is not surprising that Basta *et al.* (2006) found that AKD-sized paper had much higher tolerance of accelerated aging in comparison to paper than had been sized with rosin and alum. This is consistent with the earlier finding of El-Saied *et al.* (1998) and Basta and Fadl (2003) that handsheets prepared at neutral pH were stronger than those prepared at acid pH with rosin and alum. A search of the literature did not reveal any work having been done relative to effects of ASA on the archival properties of paper. Figure 16 represents the reactions associated with paper sizing with ASA and AKD.

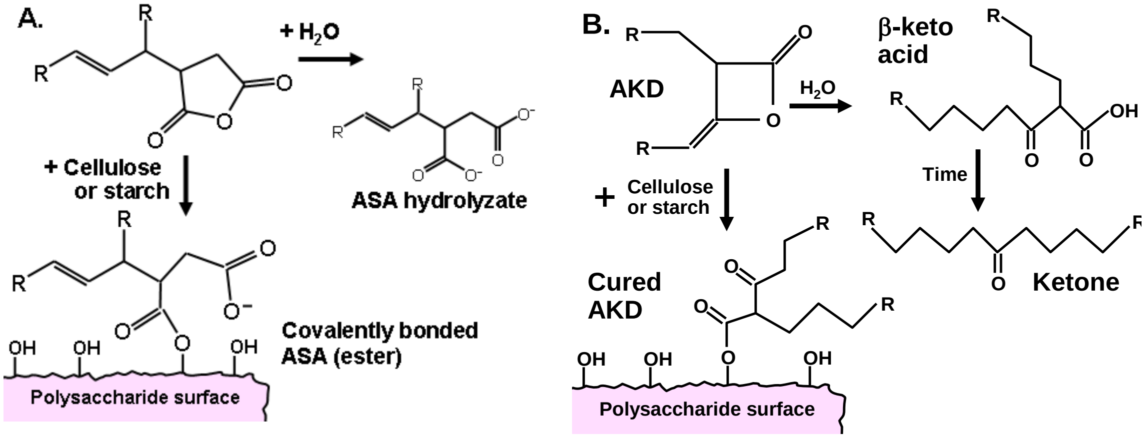


Fig. 16. Hydrophobic sizing systems based on treatments with alkenylsuccinic anhydride (ASA) and alkylketene dimer (AKD)

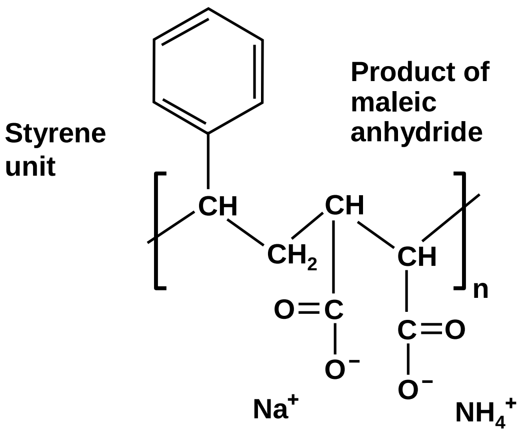


Fig. 17. Chemical structure of styrenemaleic anhydride (SMA) and a representation of its tendency to orient itself so that the styrene groups face outwards toward the atmosphere at a paper surface during the drying process

Surface-applied hydrophobic copolymers

Hydrophobic copolymer agents applied at the size press of a paper machine were considered in a review article (Bildik Dal and Hubbe 2021). As shown in Fig. 17, a representative of this type of agent is styrenemaleic anhydride (SMA) copolymer. Due to the content of maleic acid functional groups, it is reasonable to expect some formation of ester bonds, depending on the temperature and time of curing as the paper is being dried. Effects relative to the archival performance of paper do not appear to have been considered in published literature.

Waxes

Surface treatment or impregnation with wax can be used for making wax paper or preparing a barrier coating for food packaging (Spence *et al.* 2011). Figure 18 shows representative structures for waxes derived from natural sources or from petroleum. The direct effect on paper properties may be hard to predict, since one might expect that a hydrophobic material such as wax would interfere with the formation of hydrogen bonding between the adjacent fibers. However, Renee *et al.* (2004) observed that treatment of kraft bagasse pulp fibers with a petroleum wax emulsion resulted in higher strength of the resulting handsheet paper. The authors concluded that the wax was able to cover the surfaces of individual fibers, creating a hydrophobic surface. The fact that a hydrophobic, waxy surface sometimes can contribute to bonding is consistent with the results of Bildik *et al.* (2016), who treated blotter paper with solutions of waxy AKD sizing agent in heptane. It was proposed in that work that the AKD was functioning as the matrix phase of a composite structure.

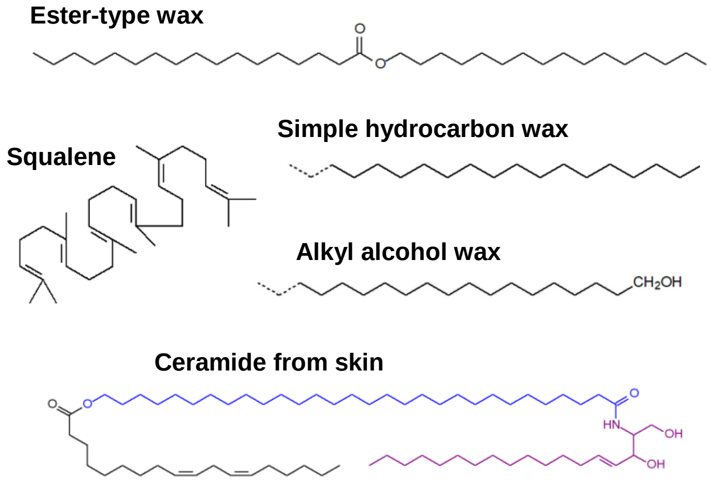


Fig. 18. Chemical structures of typical wax components from natural sources (adapted from Christie 2022)

With respect to archival performance related to wax, interesting results were presented by Jeong *et al.* (2014b), who evaluated Hanji paper from the Annals of King Sejong from about year 1300 that had been coated with beeswax. These specimens had suffered a much more severe loss in degree of polymerization in comparison to a conventional Hanji paper specimen. In this case, the reason for degradation was not the wax or components thereof and also not degradation products that could have increased the acidity of the wax-coated papers, but the microorganisms growing on the wax secreting cellulolytic enzymes that caused severe hydrolysis. The presence of citric acid, not a degradation product of cellulose/paper, but a classical metabolite from microorganisms, provided the evidence. Natural waxes are known to be comprised of fatty acids (Tulloch and Hoffman 1972), such that their hydrolytic breakdown would give rise to carboxylic acids. This concept is consistent with the findings of Regert *et al.* (2001), who found that the heating of beeswax yielded palmitic acid, among other compounds. However, their p*K*a is less detrimental compared to the action of a hydrolytic enzyme in the splitting of a glycosidic bond. Barrow (1953) reported instances in which paper sheets appeared to be damaged due to their location adjacent to natural material. In that case, groundwood material was identified as the source of acid substances. The damaging effects were attributed to migration of acid-containing material into an adjacent structure composed of delignified fibers.

Inorganic Coagulants and Iron Gall Ink

The topic of coagulants deserves to be considered more deeply, in light of the importance of alum, which is not only a coagulant but also an important source of acidity that affects the permanence of paper items. Another important inorganic coagulant is polyaluminum chloride (PAC). Some examples of coagulants are shown in Fig. 19. Iron salts also would fall in the same category, but due to their rust-like color, they seldom are intentionally used by papermakers.

A potential contributing problem associated with the usage of inorganic coagulants, in addition to their acidity, would be their tendency to reduce the swelling of cellulosic materials (Nedeltschewa 1977; Kato *et al.* 2000). As shown by Kato *et al.* (2000) the presence of aluminum compounds in pulp reduced the water retention value of carboxymethylcellulose (CMC) powders that had been dried at either 20 or 105 °C. This implies partial and irreversible loss of swelling ability occurring in the course of drying of the material. In other words, the aluminum treatment may have promoted hornification of the fibers during the drying process. This is a concern in the light of the previously mentioned relationship between hornification and the accelerated aging of paper (Kato and Cameron 1999). It is worth noting, however, that CMC it quite different from the cellulose fibers present in paper documents.

The topic of inorganic coagulants appears to bear a relationship to the widely studied problems associated with the use of iron gall inks on certain archival documents (Kolar *et al.* 2006; Potthast *et al.* 2008; Melo *et al.* 2022). Iron gall and carbon black inks were the most commonly used black inks in early European manuscripts because of their durability. The main ingredients of iron gall ink are gallic acid, iron source ($FeSO_4$), gum arabic, and water (Stijnmann 2004; Çakar and Akyol 2022). Kolar *et al.* (2006) found strong correlations between the width of an ink line, decreasing pH, and decreasing basis weight of the paper on the likelihood of apparent damage to historical documents upon which iron gall inks had been applied. When copper salts are present as either an ingredient or a trace contaminant in iron salts, increased oxidation has been observed, but the same amount of hydrolysis (Kanngießer *et al.* 2004; Potthast *et al.* 2008). Neevel (1995) found that documents could be protected by treating them with natural complexing agents, such as calcium phytate or calcium hydrogen carbonate in aqueous solution. Presumably these agents were able to complex with iron species. Follow-up work by Henniges *et al.* (2008) showed that treatment with a mixture of calcium phytate and calcium hydrogen carbonate inhibited further hydrolysis and oxidation. Importantly, this stability is demonstrated both in areas of paper carrying ink, but also in regions of un-inked paper. Tse *et al.* (2010) used micro-fading to show that the combined calcium phytate and calcium hydrogen carbonate treatment also serves to make iron gall inks less sensitive to change with light exposure. Research by Rouchon *et al.* (2011) also supported oxidation as a main mechanistic pathway for damage of paper due to the presence of iron gall inks. The cited authors suggested that the mechanism may be promoted by the ability of gallic acid, a tannin component, to reduce iron (III) to iron (II).

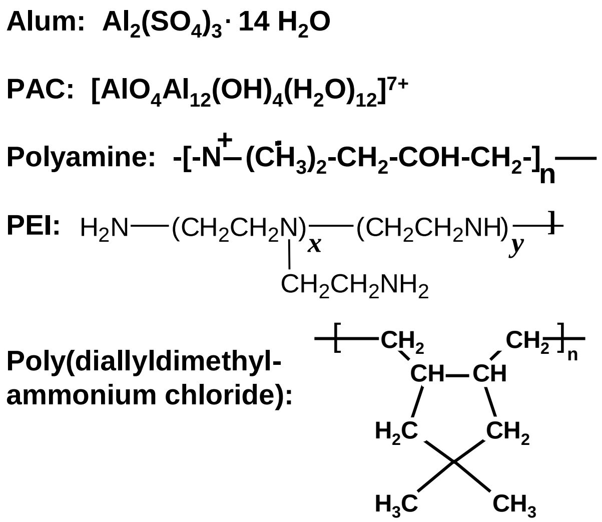


Fig. 19. Some inorganic coagulants (papermaker's alum and polyaluminum chloride (PAC)), as well as chemical structures of the high-charge cationic organic polymers dimethylamine-epichlorohydrin, poly(ethyleneimine), and poly-(diallyldimethylammonium chloride)

Organic Coagulants

The organic coagulants employed in modern papermaking can be described as intermediate molecular mass polyamines having a high density of cationic charge. Examples include poly(dimethylamine epichlorohydrin), poly(diallyldimethylammonium chloride), poly(ethyleneimine), and in recent years poly(vinylamine). Some biocexamples are shown in the lower part of Fig. 19. There does not appear to have been research attention focused on the effects of such additives on permanence characteristics of paper. However, a relevant effect, analogous to what has been reported for treatment with aluminum species (Kato *et al.* 2000), has been reported. Zhang *et al.* (2002) reported that treatment of never-dried unbleached kraft pulp with poly(dimethylamine epichlorohydrin) before drying at 105 °C led to relatively large losses in the strength of paper made from the same fibers after they had been reslurried in water. The observations were consistent with the hornification mechanism already discussed. It follows that treatment of fiber suspensions with sufficient amounts of such coagulants might be expected to embrittle paper, though further testing would be needed to confirm such a mechanism.

Dyes and Fluorescent Whitening Agents

Dyes may represent a point of vulnerability of archival papers. Dyes necessarily absorb the energy of light in order to perform their function, and such absorbed energy has the potential to break down various chemical structures, depending on their susceptibility

(Colombini *et al.* 2007; Gervais *et al.* 2014). There is a wide range of color-fastness relative to light exposure among different dyestuffs used in papermaking (Lips 1981).

According to one report, certain dyes can affect the storage stability of paper items (Anon 1957). It was reported that direct dyes can have a protective effect on paper, whereas acid dyes can be harmful. Anthraquinoid dyes were said to have a "photo-rendering" effect on cellulose (El-Saied and Basta 1998). When such paper samples were treated with non-aqueous antioxidant and deacidification solution along with a natural dye, there were decreases in the rate of loss of the degree of polymerization and decreasing pH of the papers (Çakar and Akyol 2022).

Fluorescent whitening agents, which have chemical and structural aspects similar to those of some direct dyes, have been noted for their tendency to lose their fluorescent whitening ability during long exposure to light (He *et al.* 2015). The mechanism of energy absorption of ultraviolet light, partial dissipation as heat, followed by emission of visible light, is illustrated in Fig. 20. Such a mechanism suggests that the molecule may be susceptible to decomposition when it is in its activated state, while an electron is in an antibonding orbit. Several authors have explored the history and deterioration of these "optical brighteners" in cultural heritage materials, confirming their light-sensitivity (Leclerc and Flieder 1992; Mustalish 2000, Connors-Rowe *et al.* 2007). Mustalish (2000) notes additional pH and heat sensitivities and identifies that their deterioration may alter appearances not only by a quenching of their emitted fluorescence, but possibly also by a darkening of yellowing of the degraded dye compound, along with any adverse interactions between degrading dye and other paper materials. Conservators are becoming increasingly aware that optical brighteners may be moved or removed by aqueous treatments (Wetzel 2005; Engelke 2023).

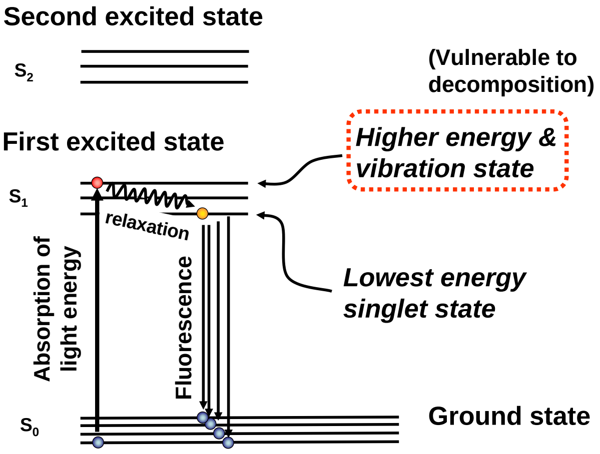


Fig. 20. Light-induced fading of dyes (especially fluorescent whitening agents) represented as an energy of activation phenomenon

UNINTENDED INGREDIENTS IN PAPER

Degraded Conditions of Cellulose in Paper

Pulping and bleaching, in addition to other steps in the process of pulp and paper production, can be regarded as ways in which various defects can be inserted into the structures of paper's components. In that light, a meaningful question to consider is the extent to which specific types of damage might be expected to render a paper-based item susceptible to such issues as embrittlement or discoloration during storage.

Degree of polymerization

Losses of degree of polymerization of the cellulose can be regarded as a result of the aging degradation of paper items, as already mentioned. A consequence of such decreases in DP is an increase the proportion of end groups of cellulose chains (Calvini and Gorassini 2006; Calvini *et al.* 2008). Products of chain scissions can include both oxidized groups and their reduced forms. In most cases the end groups are present as new aldehydes (REGs) or acids after oxidation, peeling/stopping depending on the history of the pulp. The carboxyl groups stabilize the chain ends of cellulose. Depending on the prevailing pH, the acids are present also as the corresponding lactone moiety (for details see Potthast *et al*. 2006). Degradation of paper is always accompanied by the formation of very different volatile organic compounds (VOCs). Their presence and overall concentration affect how paper aging proceeds.

Of special concern is the concentration of acetic acid. There is interest in how it accelerates the overall degradation speed and whether autocatalytic effects play a role. The latter effects have been ruled out lately for the aging of cellulose acetate (Knight 2014), but they are still under discussion for aging of paper in sealed systems. In such a case, the rate of cellulose decomposition will increase. The mechanisms are consistent with the findings of Jeong *et al.* (2014b), who detected lower rates of cellulose degradation in the case of Hanji paper, which had a higher molecular mass of the cellulose in comparison to other specimens tested. Higher degrees of cellulose crystallinity have also been correlated with more endothermic reaction activity prior to oxidative decomposition (Júnior 2000). For more details on VOCs and cellulose the reader is referred to the pertinent literature (Lattuati-Derieux *et al.* 2006; Strlič *et al.* 2011; Tétreault *et al.* 2013; Becker *et al.* 2016).

Contents of degradation products

The products of degradation can be regarded as late-arriving components of paper. Such compounds can include aliphatic carboxylic acids, which generally might be expected to originate from degradation of the polysaccharide components of paper (Bogolitsyna *et al.* 2011). Hrivnak *et al.* (2009a,b), Jablonsky *et al.* (2012), Becker *et al.* (2016), and Cabalova *et al.* (2017) quantified the amounts of acetic acid and furfural in the gas phase within enclosed stacks of papers of aged old books or artificially aged paper specimens. Other detected peaks in chromatograms were identified as acetone, methyl acetate, 2,3-butanedione, methyl propanoate, 2,3-pentanedione, pentanal, toluene, octane, hexanal, decane, 2-pentylfuran, alpha-terpinene, limonene, benzoic acid, and tridecane to name a few (Hrivnak *et al.* 2009a,b). Dupont *et al.* (2007) detected formic, acetic, glycolic, succinic, and lactic acids and attributed these compounds to the degradation of cellulose or hemicellulose. Erhardt and Tumosa (2005) tracked the concentration of soluble sugars, including xylose and glucose, in papers dating back as far as 500 years. Notably, higher levels of simple sugars were found in relatively young paper specimens that had been manufactured under acidic conditions. A notable feature of the combined diverse list is that many of the compounds found in aged papers, or in the adjacent headspace, are carboxylic acids, which would contribute to general acidity. Thus, acid-catalyzed hydrolysis of glycosidic bonds is a degradation pathway of concern (Overend *et al.* 1962).

Various aromatic compounds present in old paper might be attributed to the breakdown of lignin (Bogolitsyna *et al.* 2011). In the case of lignin-containing paper specimens, Dupont *et al.* (2007) found that the degradation products also included acetosyringone, 4-hydroxyacetophenone, 4-hydroxybenzaldehyde, vanillin, vanillic acid, furoic acid, and 4-hydroxybenzoic acid.

State of oxidation

The presence of oxidized groups, *e.g.* carboxylic acids and aldehydes, within cellulosic fibers of paper may be expected to promote more rapid degradation of paper during storage (Lindström 1990; Ahn *et al.* 2012b). To begin, the polar nature of the oxidized groups will tend to increase the equilibrium moisture content (Hatakeyama and Hatakeyama 1998). As noted by Berthold *et al.* (1994), moisture uptake by such materials at various levels of relative humidity also can be affected by the type of counter-ion associated with the anionic groups. Oxidized groups can be increased by atmospheric oxidation (Arney and Jacobs 1979). Other oxidized groups may be the consequence of oxidative bleaching agents or related treatments (Whitmore and Bogaard 1994). Baranski *et al.* (2003) found that after paper had been subjected to accelerated aging, it was then susceptible to a catastrophic rate of subsequent degradation. This susceptibility was attributed to the formation of oxidized groups during the accelerated aging treatment.

The presence of oxidized groups also can make the material susceptible to β-elimination reactions under alkaline conditions (Kolar and Novak 1996; Malesič *et al.* 2002; Hosoya *et al.* 2018). The first two sets of cited authors found that the effects were more rapid when the counterion was Mg rather than Ca. Shahani and Harrison (2002) noted that the two mechanisms of oxidation and acid hydrolysis can reinforce each other, leading to a progressive acceleration in the decomposition rate. Ahn *et al.* (2012b) found that chemical oxidation of pulp fibers makes them susceptible to loss of molecular mass of the cellulose component. This susceptibility was much greater in the case of freshly prepared fibers than that of old library book paper, despite similar contents of acidic groups. Follow-up work caused these researchers to conclude that the benefits of appropriate alkaline treatment of old paper relative to their permanence far outweighed any problems related to the β-elimination reaction, particularly as the β-elimination occurring in naturally aged book papers occurs at cellulose chain ends and less in the middle of the polymer backbone of cellulose. Daniels (1996) likewise considered the possibility of storage of library resources in oxygen-free environments and decided that such practices would not be worth the effort. Tse *et al.* (2002) summarize a series of eight studies designed to investigate alkaline sensitivity of cellulose in paper and textiles during aqueous washing and deacidification treatments. They found no clear evidence of alkaline sensitivity with most naturally aged rag, peroxide-treated, lignin-free or lignin containing papers, with one 800-year-old cotton textile perhaps displaying some evidence of deterioration in alkaline conditions. Stephens *et al.* (2009) found that degradation due to the presence of oxidized groups could be minimized by avoiding excessively high-pH conditions during deacidification treatments.

In an effort to circumvent the further oxidation of aged paper materials, Jancovicova *et al.* (2012) included KI as a reducing agent. The treatment with KI, in the presence of magnesium and calcium bicarbonates, was found to be effective in the case of newsprint paper, which is known to contain a high proportion of high-yield cellulosic fibers (Strlič *et al.* 2005). Treatments with KI and other halides such as NaCl, NaBr, and tetrabutylammonium bromide, sometimes together with $NaBH_4$, have been found to be helpful in mitigating damage from acidic iron gall inks (Kolar and Malesič 2005; Malesič *et al.* 2005; Rouchon *et al.* 2013). Both in these instances, and where methods have been sought to stabilize copper-based pigments such as verdigris (Ahn *et al.* 2014; Malašič *et al.* 2015), the halide-based reagents are described as antioxidants to help ameliorate the effects of transition-metal-based catalysis of cellulose degradation; specifically, the halides are described as being peroxide decomposers.

Initial acidity and acidity that develops during storage

The effects of acidity on paper's archival performance also can be discussed in terms of its extract pH. Methods are available for such assessment (Kohler and Hall 1925; Liers 1999; TAPPI Methods T 435; T 509; T 529). The results of such tests might be seen as a way to quantify a condition of the paper that is related to its likely rate of decomposition during storage (Clements 1987; Zou *et al.* 1994; Bégin *et al.* 1998; Area and Cheradame 2011). Notably, Wilson and Parks (1980) reported a strong correlation between the permanence characteristics of archival paper specimens and their cold extract pH values. Sources of acidity originally within the paper before any aging has taken place will include the acid components of wood extractives (Back and Allen 2000). It will also include aluminum-based additives, especially papermaker's alum (aluminum sulfate). As was shown earlier in Fig. 3, the acid-catalyzed hydrolysis of acetate ester groups associated with some hemicellulose structures can be an important source of further acidification with the passage of time (Maloney *et al.* 1985; Kapu *et al.* 2016).

Most of the acetyl groups in hemicellulose are cleaved during pulping and bleaching. A minor amount may still be present, but the majority is generated directly by the aging itself (Potthast *et al*. 2022). The acids that develop during aging of paper, as already mentioned, can be regarded as an additional portion of the acidity that becomes evident in measurements of extract pH. It has been shown that air pollution also can contribute to the acidity of stored paper items (Mochizuki *et al.* 2020). Because such acids can build up over time, they can continue to lower the extract pH and speed up the rates of acid-catalyzed hydrolysis (Shahani *et al.* 1989; Zervos 2007, 2010). Tétreault *et al.* (2019) attempted to model the effects of these increasing acid levels (from both internal and external sources) in different relative humidity storage environments.

Hornification

The fact that paper material can become stiffer, in addition to weaker in the course of aging has not received enough attention. Each time that kraft (or other delignified) fibers are dried, either in the course of making paper the first time or when making paper from recycled fibers, mesopores within the well wall structure will close up, and such closure is only partly reversible (Stone and Scallan 1966; Hubbe *et al.* 2003, 2007). As was discussed under pulping, such changes have been called hornification, and they result in a decreased ability of the fibers to swell and become conformable when they are placed back into water (Weise and Paulapuro 1999; Welf *et al.* 2005; Law *et al.* 2006). The general mechanism by which this process may take place is shown in Fig. 21. As shown, very strong capillary forces tend to draw cellulosic surfaces together during the evaporation of water. Once those surfaces are in molecular contact, hydrogen bonds can form directly between the surfaces, which may be comprised not only of cellulose, but also of hemicellulose and starch. Based on a review of the literature, Kato and Cameron (1999) drew a parallel between the processes of hornification and what happens during thermally accelerated aging of paper. They proposed that hard-to-reverse hydrogen bonding within the fiber structure takes place during the accelerated aging. It is an unresolved question as to whether the same process happens, probably at a much lower rate, when paper is stored for years on library shelves. A mechanism of increased brittleness, due to the gradual development of crystal-like patterns of hydrogen bonding within the nanostructure of cellulosic paper, is consistent with the relatively large drops in folding endurance due to the aging of paper (Bicchieri *et al.* 1993; Zervos 2007; Horst *et al.* 2020). Hornification also becomes relevant to the conservation of chemical wood pulp papers that exhibit hornification, as the rehydration and swelling of papers during aqueous treatments (from humidification through to washing) can be expected to be both slower, and less complete than is possible for papers of other manufacture (Keller 2018).

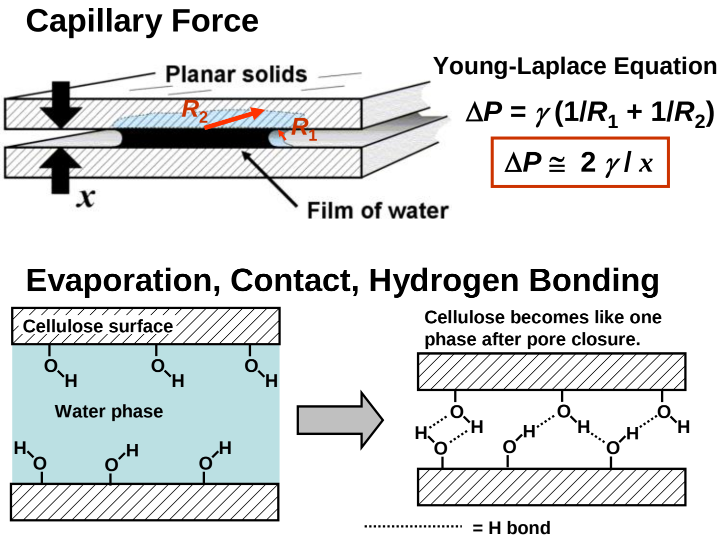


Fig. 21. Hypothetical role of capillary forces and hydrogen bonding in the hornification of cellulosic materials that are subjected to wetting and drying

Biodegradation

Microbial attack, including mold, can be a serious threat to stored books, especially under conditions of high humidity (Area and Cheradame 2011; Sequeira *et al.* 2014). It is well known that various natural bacteria and fungi produce enzymes, certain of which can speed up the hydrolysis of lignocellulosic material, as long as sufficient moisture is present (Alvira *et al.* 2010; Yang *et al.* 2011). The greatest extent of damage, as quantified by the loss of cellulose DP, can be expected from the action of endoglucanases; these cellulase components act to cleave cellulose chains at random points (Asztalos *et al.* 2012; Jalak *et al.* 2012). The endoglucanases in particular are expected to act on the amorphous parts of the chains (Jalak *et al.* 2012). The endoglucanases work in concert with exoglucanases, which start at chain ends. The exoglucanases have been reported to work in a layer-layer fashion, generally remaining on the accessible exterior parts of the cellulose, including crystalline zones (Zhang *et al.* 2011). Jalak *et al.* (2012) noted a tendency for the exoglucanases to become stuck when reaching an amorphous region, which helps to explain the strong synergy between the two kinds of cellulase. Though these mechanisms are well known, they are not often studied in the context of archival items. It is uncertain whether or not stored paper items will contain sufficient moisture to allow the same processes that are evident in pulp.

Zyska (1997) provides a literature review of molds found on a broad range of library materials, while Zerek (2006) reported on mold isolated specifically from paper-based historical items. In addition to decreasing the strength of papers, the discoloration caused by mold is another aspect of decreased archival performance. Sequeira *et al.* (2018) and Melo *et al.* (2019) link mold species to the colored stains that result from their growth on and in paper substrates. Jacob *et al.* (2017) quantified the amounts of viable bacteria present in old paper-based maps.

Traditional papermakers have long utilized a practice called retting to render raw bast fibers more suitable for sheetmaking (Hubbe and Bowden 2009). Retting, which continues to be widely used for the treatment of bast fibers for textile applications, involves immersion in water for about two to four weeks, during which time pectic substances, gums, hemicellulose, and some of the lignin break down (Tahir *et al.* 2011). As noted by Barrett (2016), papermakers in pre-industrial Europe took advantage of natural enzymatic degradation in order to convert waste cloth material into papermaking fibers. In principle, the same results can be achieved in a shorter time by the intentional usage of specific enzyme treatments (Djemiel *et al.* 2020; Lee *et al.* 2020; Hossain *et al.* 2021). Indeed, modern papermakers can use a similar approach, but with much greater control, to reduce the amount of energy needed to refine kraft fibers (Przybysz Buzala *et al.* 2016), rendering them sufficiently conformable to enhance inter-fiber bonding and meet various strength specifications.

From the perspective of archival quality, the retting practices just described may raise some concerns. Due to the expected action of natural cellulases during such retting processes, the molecular weight of the cellulose present can be expected to fall due to its enzymatic hydrolysis (Mooney *et al.* 2001). In addition, the loss of hemicellulose in the course of retting (Tahir *et al.* 2011; Djemiel *et al.* 2020; Lee *et al.* 2020) can be expected to render the resulting paper less well bonded and possibly more susceptible to brittle failure (Molin and Teder 2002). These effects and concerns are suggested in Fig. 22.

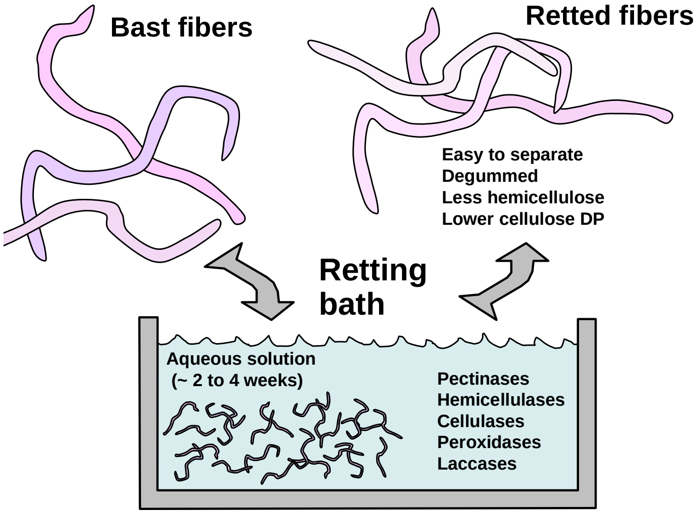


Fig. 22. Key features of a retting process from the perspective of cellulosic fiber archival quality

Though the citations listed above provide evidence that paper items would be susceptible to microbial enzymes under certain conditions, they leave open the question of whether past microbial attack renders the archival materials more susceptible to future microbial attack. The answer may lie in such issues as whether spores and other fungal structures survive in a state of inactivity or dormancy and can be reactivated again given the proper growth conditions (namely, access to sufficient moisture). Sequeira *et al.* (2016) compare interventive and preventive conservation treatments for mould on paper, concluding that after initial colonization, even if samples are thoroughly cleaned, regrowth is both faster and more intense than initial colonization.

Certain components of paper have the potential to render it more resistant to various microbial attacks. For instance, the terpenoid components of high-yield softwood pulps are known for their antimicrobial action (Cowan 1999). As noted by Borrego *et al.* (2016) and Mikala *et al.* 2016), the essential oils of plant materials can help protect paper against microbes. Such effects of essential oils have been reviewed (de Oliveira *et al.* 2022). Antimicrobial agents also are added during the manufacture of paper (Woodward and Stoner 2018); however, the purpose of these additives is to control levels of slime during the manufacturing process, not during storage and use of the product. It is not known whether such agents have significant effects on microbes after the product has been made. On the other hand, Sequeira *et al.* (2012) have reviewed the intentional applications of antifungal treatments during conservation of paper items.

Pollutants

Acidic gases

Not to leave out something potentially important, pollutants coming from the air, either as external sources or released by the aging of paper itself, may be regarded as an additional class of components of stored paper (Smith 2004). Some of these are depicted in Fig. 23. Acetic acid, hydrogen sulfide, nitrogen dioxide, ozone, sulfur dioxide, fine particles, and water vapor are airborne pollutants that can adversely affect cultural heritage collections (Tétreault, n.d.). Some of the most persuasive evidence of the effects of airborne substances was shown by Mochizuki *et al.* (2020). It was shown in that work that the pH at the edges of stored alkaline paper sheets tended to decline, whereas in the case of acidic papers, the edges tended to have a higher extract pH. The latter effects can be understood in terms of the more ready volatilization of acidic compounds such as acetic and formic acids (Shahani and Harrison 2002; Dupont *et al.* 2007; Jablonsky *et al.* 2011, 2012; Becker *et al.* 2016; Cabalova *et al.* 2017) near to the exposed edges of blocks of paper. The results observed in the case of alkaline papers might be understood in terms of the acidity provided by carbonic acid, which is the expected product of adding carbon dioxide from the air to water. Such a mechanism may depend on the capillary condensation effects discussed earlier (Hubbe *et al.* 2017). Tétreault *et al.* (2013) found formic acid to be much more aggressively destructive than acetic acid, and that it penetrates more deeply into stacks of paper than either acetic acid or hydrogen peroxide vapors. Commonly studied pollutants include sulfur dioxide and nitrogen dioxide. Sulfur dioxide, which is released in automotive exhaust, can be easily oxidized to form sulfur trioxide, which can react with sheet moisture to form sulfuric acid. Sulfur dioxide uptake is significantly higher at higher temperatures and in the presence of metal ions. The presence of rosin and alum has also been linked to higher sulfur dioxide absorption (Zou and Gurnagul 1994).

Bégin *et al.* (1999) demonstrated that calcium carbonate can be used as a buffering agent to significantly minimize the impact of air pollution on the stability of aging of lignin-containing and lignin-free papers. In conditions of nitrogen dioxide exposure, neutral-sized pulp and paper was demonstrated to have no significant reduction in mechanical or optical properties, while acid-sized pulp and paper deteriorated quickly. This was similarly attributed to the presence of calcium carbonate (Williams and Grosjean 1992). Further study of the effects of nitrogen oxides on the chemical structures and surface properties of stored air-dry cellulose pulp were reported by Milichovský *et al.* (2007) and Hajek *et al.* (2016).

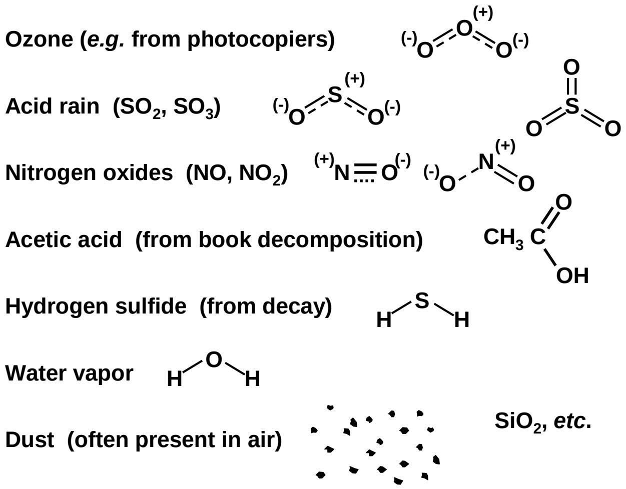


Fig. 23. Chemistry of various gaseous species that may be expected to affect the storage stability of cellulosic items

Dust, as another source of pollutants (being comprise of organic aerosols, elemental carbon, crystal elements, and ammonium, sulfate, and nitrite ions), had been shown to be a contributing factor in the decrease of degree of polymerization of pure cellulosic paper (Bartl *et al.* 2016). The smaller particulate matter (PM1) was stated to be particularly deleterious.

The Role of Moisture in Paper

Though it is often overlooked in lists of the ingredients of paper products, water is always present. Paper's physical properties are determined by its moisture content, which plays an essential role in its chemical reactivity. Furthermore, it allows for the hydrolysis of glycosidic bonds with free protons and the production of active oxygen species (superoxide, hydrogen peroxide, and hydroxyl radicals) (Corsaro *et al.* 2016). This hydrolytic scission makes cellulose much more susceptible to degradation by water than most other commercially used hydrocarbon polymers (Scheirs *et al.* 2001). Water often comprises about 4 to 7% of the mass of paper under intermediate conditions of relative humidity (Berthold *et al.* 1994). That amount is equivalent to about one-half a water molecule per anhydroglucose repeat unit in the cellulose. Figure 24 is drawn to represent such water as being a non-equilibrium cellulose hydrate (Joubert *et al.* 1959). The cited authors based their hypothesis on the fact that up to about 10% of water adsorbed onto cellulose had no effect on measured contact angles. Because of the high polarity of cellulose, water within the fiber is hydrogen bonded to cellulose chains. Under high temperatures, (> ~130 °C), hydrothermal degradation of cellulose has been found to be greatly exacerbated due to the loss of acetalic chain-ends (Scheirs *et al.* 2001).

Some of the important mechanisms associated with the aging of paper appear to involve water. As supporting evidence, it has been shown that the inclusion of moisture during the accelerated aging of paper can greatly increase the rate of loss of paper strength properties (Wilson and Parks 1980; Zou *et al.* 1996; Hajji *et al.* 2016; Malachowska *et al.* 2021). In response to such findings, relatively low relative humidity conditions have been recommended for library and museum collections (Michalski 2000; Menart *et al.* 2011; Atkinson 2014; Lucchi 2018). Relative humidity has been standardized on the basis that it has a significant impact on the physical and mechanical properties of paper (TAPPI Method T402). In addition, Lin *et al.* (2007) showed that "modified atmosphere and humidity agents" incorporated into packaging were able to reduce levels of relative humidity and decrease the aging of paper items kept within the packages. Malachowska *et al.* (2021) evaluated cellulosic pinewood paper sheets at two different aging conditions: a dry atmosphere and a wet atmosphere (RH- 59%). The temperature was 90 °C in both cases. Different chromatographic and spectroscopic analysis methods were used to measure the structural changes of cellulose and lignin by artificial aging.

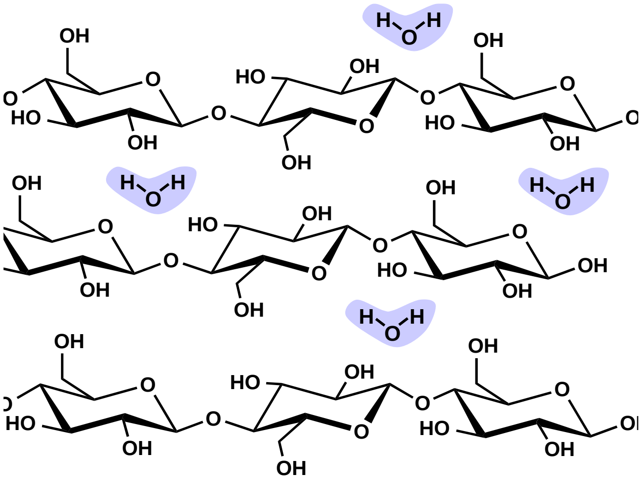


Fig. 24. Representation of the approximate amount of equilibrium water within cellulose behaving as a non-stoichiometric cellulose hydrate structure

The equilibrium moisture content of paper is a strong function of the relative humidity (Shahani *et al.* 1989; Zou *et al.* 1996; Zervos 2010). Shahani *et al.* (1989) observed that intermittent increases in relative humidity achieved equally harmful effects compared to steady conditions at a higher level of humidity. Thus, the cycling of humidity appeared to contribute to the effects. Such effects might be understood based on the mechanism of capillary condensation (Bocquet *et al.* 1998; Hubbe *et al.* 2015, 2017). As was illustrated earlier in Fig. 11, according to the Kelvin equation, tiny menisci of water can condense within the nanostructure of paper at levels of relative humidity below 100%. However, at levels of humidity likely to be encountered in the shelves of libraries and museums, only the narrowest nano-sized junctions between adjacent cellulosic surfaces will be the sites of such condensation. Nevertheless, cycles of changing relative humidity would have the potential to repeatedly lead to concentration of the aqueous solution within such nano-lenses of water. A possible repeated outcome of cyclic humidity changes could be the development of increased acidity at points of contact between solids. The concern is that repeated events of this type could be expected to weaken the inter-fiber bonded regions within a paper specimen. Oscillations in atmospheric relative humidity, and by association paper moisture content, can have a significant impact on fiber properties (Bogarrd and Whitmore 2002). Also swelling and deswelling of cellulose in the humidity cycles may induce mechanical stress to the polymer backbone that can result in loss of DP.

IMPACT OF PRESERVATION AND CONSERVATION EFFORTS

When paper conservators and restorers treat archival paper-based items, often a priority is placed upon strengthening and preventing further harm. An additional issue that can be considered is the archival performance of different substances that are introduced during such procedures. These will be discussed here according to the categories of deacidification effects and conservation treatment components. This section will primarily focus on treatments aimed at stabilization, rather than at aesthetic improvement (*e.g.* stain reduction or removal of discoloration) of paper-based heritage objects.

Deacidification Effects

The two main goals of deacidification may be expressed as neutralization of acidic groups within the paper and deposition of sufficient alkaline reserve within the paper so as to compensate for future ongoing processes contributing to acidity. Indeed, studies have confirmed the increases in alkaline reserve within paper that has been deacidified (Ahn *et al.* 2012a, 2013).

Deacidification treatments may be carried out on bunches of whole books (mass deacidification) or on individual pages (Baty *et al.* 2010; Ahn *et al.* 2012b; Hubbe *et al.* 2017, 2018; Horst *et al.* 2020; Malesič *et al.* 2022). In general terms, such procedures can be categorized as either aqueous based, non-aqueous solutions-based, and non-aqueous dispersion-based. This third category, based on dispersions of MgO particles in a non-aqueous solvent, has been relatedly shown to be ineffective (Potthast and Ahn 2017; Hubbe *et al.* 2017; Malesič *et al.* 2022), so the main emphasis here will be on the other methods.

Concern has been raised relative to whether or not chemical damage to paper items may occur in the course of mass deacidification procedures. Studies searching for alkaline deterioration of oxidized cellulose in cultural heritage contexts have been described earlier in this paper. Baty *et al.* (2010) discuss the range of mass deacidification treatments that have been employed. Instances are outlined in which media solubility or migration, darkening of paper after treatment, uneven distribution and/or surface deposition of inorganic compounds, residual odor, changes in paper wettability, and other side-effects have been observed.

Effects of moistening

Hey (1979) emphasizes the importance of complete wetting of paper in instances where aqueous deacidification is to be employed, in order to fully remove soluble acids and neutralize acidic groups in the paper structure. However, in cases where deacidification processes involve wetting of the pages to be treated, concerns have been raised regarding whether there will be lasting harm to strength and other properties.

Expected effects of water immersion, relative to conservation practices, have been considered in various studies (Moropoulou and Zervos 2003; Banik and Brückle 2012). As noted by Bristow (1971), one of the prominent effects of such wetting is the swelling of the paper. Such swelling can be regarded as a consequence of water being able to loosen hydrogen bonding within the cellulosic nanostructure as water fills the pores. Moropoulou and Zervos (2003) reported a significant decrease in the tensile strength of Whatman filter paper and four out of five historical paper samples upon wetting and redrying of paper specimens. Carr *et al.* (2006) demonstrated that the effects of aqueous treatments on the mechanical properties of paper depend on the paper type (*i.e.* handmade *vs.* machine made). A likely explanation of such effects may include the application of lower levels of pressing before the final re-drying of such paper specimens. This situation is illustrated in Fig. 25. In commercial papermaking practices, the wet paper web typically passes through two or three high-pressure press nips before being dried. It is unlikely that such high pressures would be applied in a paper conservation facility.

A number of authors have considered the influence of unrestrained and restrained drying on the resulting properties of paper after either humidification or wet conservation treatment (Keyes 1984; Vitale 1992; Sugarman and Vitale 1992; Nielsen and Priest 1997; Munoz-Vinas 2009; Neufeld 2014; Kato and Kimishima 2017). Lipponen *et al.* (2008) and Sugarman and Vitale (1992) discuss the various factors that can lead to potentially irreversible cockling or planar deformation in unrestrained paper drying.

The formation of wet-dry interfaces, sometimes called tidelines, either during a local conservation treatment or during an unintentional wetting during use, or in a disaster such as a water leak, has been demonstrated to cause enhanced oxidation at, and on either side of the interface (Eusman 1995; Dupont 1996a,b; Jeong *et al.* 2012, 2014a). Oxidizing species have been identified, with Jeong *et al.* (2012 and 2014a) tracing the formation of both hydroperoxides and hydroxyl radicals. The enhanced deterioration at these interfaces points to the need for caution in the local wetting of paper during conservation treatments.

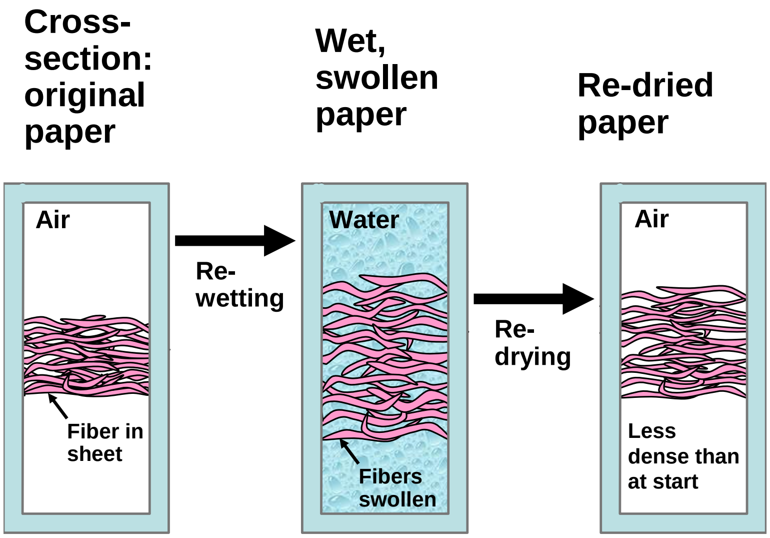


Fig. 25. An expected decrease in paper's density and bondedness when wetted and redried without application of squeezing pressure in the damp state

Trapped liquid water

Small domains of liquid water present within the nanostructure of solid materials have the potential to affect the storage stability of paper. The Kelvin equation predicts the existence of lenses of water developing in nano-scale pores at sufficiently high relative humidity (Mitropoulos 2008). High variations in humidity during storage of paper can be expected to repeatedly change the sizes of such menisci, thereby providing a mechanism by which degradative agents, such as acidity, could become concentrated (Hubbe *et al.* 2017). As explained by Geffert *et al.* (2017), such processes, involving cyclic humidity changes, also can be expected to lead to hornification effects in stored paper items.

The presence of nano-scale liquid water domains within paper articles implies that various self-assembly processes can be involved in the changes that occur over time during storage. For example, Milichovský (2022) described how surface-active compounds can be expected to organize themselves into bilayers. Water confined within nanospaces is proposed to participate in a process whereby bilayers and multilayers of amphiphilic compounds arrange themselves over the course of time. The resulting colloidal-scale structures can be expected to depend on the detailed chemical structures of the monomers. The participation of such self-assembly processes during the manufacturing of paper products has been reviewed (Hubbe *et al.* 2020, 2023). More research is needed to determine the extent of such potential changes in the case of stored paper items. Such concepts are most relevant for grades of paper made from high-yield pulps, such that they contain substantial quantities of fatty acids, resin acids, and other amphiphilic compounds (Cesek and Milichovský 1996). Because the extractives components of woody materials are generally monomeric, it is reasonable to expect continuing migration or reorganization of those molecules within stored paper items (Barrow 1953; Swanson and Cordingly 1959).

Magnesium-specific effects

Jablonsky *et al.* (2012) presented evidence that the magnesium ion, which is enriched in paper in certain deacidification processes, can promote formation of organic acids, which tend to work against the goals of deacidification. In that study, paper was treated with mixtures including MgO particles or methylmethoxy magnesium carbonate (MMMC). Addition of either type of alkaline agent was observed to increase the subsequent production of acetic and formic acid during subsequent accelerated aging. However, the paper specimens appeared to be protected from such acidity due to the alkaline reserve matter present in the paper.

A number of studies have found enhanced yellowing when magnesium-based deacidification treatments are employed (Lienardy and van Damme 1990; Bukovský1997; Bansa 1998). Strlič and Kolar (2005), however, did not find any difference between the yellowing of papers treated with either calcium or magnesium bicarbonates when aged at room temperature. Using both an aqueous and a non-aqueous magnesium-based deacidification treatment, Kolar and Novak (1996) demonstrate that different paper pulps behaved in different manners: bleached sulfate pulps showed no negative effects from the magnesium reagents, while sulfite and magnefite magnesium-treated pulps were destabilized relative to the untreated controls.

Conservation Treatment Additives

Though a review of all materials used in the conservation of paper-based heritage is beyond the scope of this paper, there are various substances that have been widely used in the conservation and repair of paper-based items that continue to age with the artifacts over time (Clapp 1977; Zervos and Moropoulou 2006; Zervos and Alexopoulou 2015). In most cases, residues of treatment reagents (such as enzymes, chelating agents, reducing agents, oxidative bleaches, *etc.*) or delivery mechanisms (such as gels or poultice materials used to localize treatment or control dwell times) are minimized to the greatest extent possible at the end of treatment by subsequent rinsing or clearing steps. In addition to the deacidification agents already discussed, these materials intentionally left at the end of conservation treatment include thin layers of paper, water-soluble polymeric strengthening agents, fixatives for colorants, antioxidants, and adhesives such as starch (predominantly wheat or rice starch paste), cellulose ethers, gelatin, and various synthetic polymers. Antioxidants for stabilization of transition metal catalysis in paper deterioration, such as halides and calcium phytate, have already been discussed in earlier sections of this paper.

Cellulose

Fragile paper artifacts are often strengthened by adding supplementary layers of paper – sometimes called secondary supports. Through the history of conservation and restoration, there have been non-cellulose based secondary supports such as silk or cellulose acetate films, but these materials have all been demonstrated to age more rapidly than the historic paper they are meant to support (Wang and Wong 2019; McGath *et al.* 2015). Secondary support methods include localized mending (often called tear repair), overall lining (adhering a sheet of paper to the back of the artifact), laminating (adhering the artifact between two thin layers of paper), paper splitting (splitting the artifact in two, and inserting a central paper core), or a process called leafcasting (forming a thin mat of pulp fibers either over the entire sheet, or concentrating the pulp deposition to infill areas of loss) (Bansa and Ishii 1997; Hajji *et al.* 2016; Santos *et al.* 2016; Bedenikovic *et al.* 2018a; BPG Lining 2022). While Western papers and tissues (such as lens tissue) were used as cellulosic secondary supports historically, since the mid- 1960s, lining has most often been carried out using thin, strong sheets of Japanese paper (*washi*). In recent years Korean *hanji* papers are also being used. Figure 26 illustrates the process of using a leafcasting device (*i.e.* a device that uses one or more vacuum pumps to aid in the distribution of pulp) during lamination or pulp infill treatment. Commonly used Japanese paper secondary supports are prepared from kozo (also called paper mulberry) bast fibers (Santos *et al.* 2016), which are well known for their strength. The kozo can be delignified by alkaline pulping with various agents (Mun *et al.* 1998; Uyeda *et al.* 1999). Uyeda *et al.* (1999) showed that the milder alkali species, such as wood ash and sodium carbonate, yielded the most stable paper. Follow-up work showed that the milder alkaline agents resulted in delignified kozo fibers having a higher degree of polymerization of the cellulose (Inaba *et al.* 2002). Evidence of the high archival performance of these fibers is provided by the work of Jeong *et al.* (2014b), who carried out accelerated aging tests. The degradation of the cellulose was two to three times slower in comparison to the historical rag paper that was manufactured before the rise of mechanized papermaking in Europe.

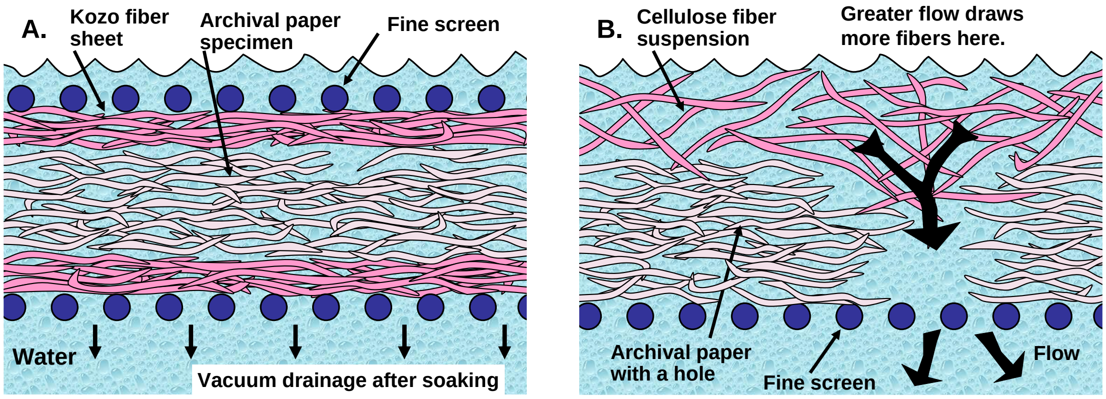


Fig. 26. Examples of possible paper conservation methods of strengthening and repairing weak and damaged specimens using a leafcasting device. A: laminating with specimen with top and bottom thin layers of kozo (*washi* or *hanji*) paper; B: leafcasting with a suspension of papermaking fibers

Either as a supplement or as an alternative to kozo fibers, it has been proposed to employ highly fibrillated cellulose (*i.e.* nanocellulose) as a paper conservation treatment (Völkel *et al.* 2017). The cited authors evaluated bacterial cellulose and nanofibrillated cellulose. Strength improvements were observed. There are two issues of concern when using such a strategy for leafcasting treatments of archival specimens. First, it is well known that highly fibrillated cellulose suspensions are slow to dewater. Second, one might expect dimensional stability problems of the resulting paper. In particular, curling of the paper might occur if the nanocellulose is unevenly distributed relative to the sides of the paper and there are large changes in relative humidity (Anderson 1991).

Materials used for repair

Lining and tear repair adhesives are commonly aqueous: starch, cellulose ethers (such as methyl cellulose, sodium carboxymethyl cellulose, or for a non-aqueous option, hydroxypropyl cellulose (*e.g*. Klucel G in ethanol)), gelatin, or sometimes synthetic adhesives such as acrylic emulsions or poly(vinyl) acetates or alcohols. Recent methods have included application of nanocellulose suspensions to consolidate paper damage, close cracks, and coat small areas of material loss (Völkel *et al.* 2017). For a non-aqueous options, hydroxypropyl cellulose (*e.g*. Klucel G) may be employed in alcohol or by the synthetic adhesives listed above can be applied as dried films activated by pressure or heat.

It is significant to note that while conservators choose to apply a narrow range of adhesives to paper that are expected to age as well as possible, collections contain a wide range of poorly aged adhesives. For instance, focusing just on a fifty-year span from 1870 to 1920, Cannon (2010) identified 695 recipes for commercial or make-at-home adhesives advertised in newspapers, magazines, and trade journals marketed for use on paper-based materials that now reside in collections – containing materials not yet mentioned in this review article such as drying oils (triglycerides), resins (terpenes), pitch (cyclic hydrocarbon), and more. Many of the materials in these recipes or formulations are found to be difficult to reverse or remove in time (Cannon 2015). A literature review by Müller *et al.* (2022) tracks the challenges of the removal of poorly-aged pressure sensitive tape carriers and adhesives from paper-based collections.

Strengthening agents

Either as a supplement or as an alternative to repair of the application of a secondary support, the strength of archival paper can be strengthened by sizing (wet application) of water-soluble polymers. Though a variety of agents are employed by book and paper conservators, the most common include gelatin and methylcellulose. For non-aqueous application, hydroxypropyl cellulose in ethanol may be used. Gelatin was already considered under the subsection titled Proteins. Methylcellulose, which is widely used in paper restoration as a strengthening agent, is shown in Fig. 27.

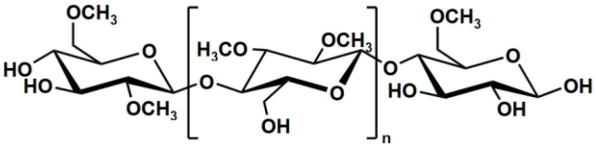


Fig. 27. Molecular structure of a methylcellulose molecule with a degree of substitution below 2

A remarkable feature of methylcellulose is that treatment of the water-insoluble cellulose molecule with methyl groups, replacing many of the –OH groups by $–OCH_3$, gives rise to a water-soluble polymer. The likely explanation is that the methylcellulose has side groups that interrupt many of the hydroxyl groups sites on the polymer chain, such that the methylcellulose does not crystallize. As a water-soluble, amorphous polymer, it is then well suited for serving as a bonding agent among papermaking fibers. It seems likely that the lowered content of –OH groups in the methylcellulose decreases the density of hydrogen bonding within the paper structure, and this would be expected to lead to greater flexibility. The following studies reported promising results when using methylcellulose to strengthen brittle paper specimens (Hanus 1994; Strnadova and Durović 1994; Sundholm and Tahvanainen 2003; Zervos 2007; Seki *et al.* 2005, 2010). Notably, Hanus (1994) reported substantial increases in tensile strength and elongation to breakage of deacidified paper sheets following the methylcellulose surface treatment. Methylcellulose was found to be more effective than gelatin. Seki *et al.* (2010) compared the effects of methylcellulose with several other related chemicals and found it to give the best effects. Though the polymeric treatments did not prevent the loss of strength of paper sheets subsequently subjected to accelerated aging, it did appear to slow down the strength loss. Sundholm and Tahvanainen (2003, 2004) found evidence that degradation of the methylcellulose itself appeared to contribute to strength losses during accelerated aging of the strengthened paper. However, the alkaline reserve in the treated (also deacidified) papers limited the strength losses. Zervos (2007) likewise carried out accelerated aging of paper that had been strengthened with methylcellulose, but the main conclusion was that effective ventilation of paper is an effective strategy for minimizing the detrimental effects of the buildup of acids during paper storage.

Sulaeva *et al.* (2018) evaluated the permanence attributes of several cellulose-based ether adhesives mixtures that had been utilized for the conservation of archival paper items that had been partly damaged in a fire. Specimens were subjected to accelerated aging. Gel permeation chromatography (GPC) was used to sense any changes in molecular mass of the additives. Neutral ethers of cellulose were observed to undergo loss of molecular mass, which might be attributed to formation of hydroperoxides during the accelerated aging (Feller and Wilt 1991). However, there was evidence that the cellulose ethers were functioning as sacrificial components, thus decreasing the extent of depolymerization of the cellulose within the paper that had been subjected to accelerated aging (Sulaeva *et al.* 2018). Carboxymethyl cellulose showed a different change upon accelerated aging: an increase in molecular mass, which was attributed to a cross-linking reaction.

Bleaching treatments

In addition to the bleaching of fibers before the manufacture of paper, bleaching treatments also have been used for conservation and repair of paper-based items (Burgess 1988; Henniges and Potthast 2009; Brückle 2009, 2012; Smith 2012). Smith (2012) emphasized the importance of maintaining a sufficiently high pH (above 9) during bleaching with hypochlorite, for instance, in order to minimize the formation of carbonyl groups, which is highest at pH 7 (Lewin and Epstein 1962). Though chlorine dioxide was described as a highly favorable type of treatment for the industrial preparation of paper, it was not recommended for routine paper conservation due to concerns about health and safety. Henniges and Potthast (2009) studied several alternative bleaching chemicals used in conservation workshops, including both oxidizing agents and reducing agents. The oxidizing beaching agents, including calcium hypochlorite, hydrogen peroxide, and potassium permanganate, tended to increase the oxidized functionalities in the cellulosic material. By contrast, the reducing agents tended to stabilize the material by decreasing the amounts of carbonyl groups. In particular, sodium borohydride was judged to be an effective reducing agent for both bleaching the fibers and rendering them less susceptible to degradation during storage. Oxidizing agents such as hydrogen peroxide can be particularly damaging to cellulose in the presence of iron ions in historic papers and can result in brightness reversion after aging. These risks have traditionally been mitigated by raising the pH prior to treatment (Burgess 1988). However, Niehus *et al.* (2012) demonstrate that combining deacidification with iron removal or complexation can provide enhanced stability for papers containing a high level of iron. Henniges *et al.* (2021) successfully masked the metal ions by a phytate treatment prior to bleaching.

Fixatives and their removal

Conservators sometimes need to work with paper specimens printed with dyes that are too soluble for certain potential treatments. The word fixative denotes additives that are intended to stabilize such specimens, such that a dye (or other substance) is held in place as an aqueous (or other) conservation treatment is being done. Once the conservation treatments have been applied, the fixative then may be removed, at least in part. Paper conservators may use temporary fixatives such as cyclododecane (a wax that sublimates slowly at room temperature and pressure) or Paraloid B-72 (a synthetic resin that can be applied and later removed with organic solvents). Papermakers employ fixing agents (usually moderately high cationic charge polymers) when applying acid dyes or highly soluble direct dyes to the fiber suspension in a paper machine system. Conservators have, with varying success, adapted some of these ionic fixatives as treatment tools. Porto and Shugar (2008) tested two cationic fixatives for use with dye-based inkjet inks, encountering a permanent change in the inks, as well as insufficient fixing for aqueous treatment. Havlinova *et al.* (2005) describe the usage of a fixing agent to treat paper that had been colored with a variety of dyes. Though the results were diverse, in several cases the treatment with the fixative appeared to prevent the loss of coloration in the course of deacidification. Roller *et al.* (2015) showed that fixatives can be removed by a series of three 10-minute rinses with water. Notably, a counterstatement from the company providing the conservation systems (Zinn 2016) disputed some problems described by Roller *et al.* (2015) in their article, indicating that the published research had deviated from the commercially sold system. However, the main findings of the study were not disputed. To summarize the work cited above related to fixatives, it appears likely that some of the fixative typically will remain within a paper specimen after the conservation work has been finished. Thus, future studies might probe the archival performance of the fixatives themselves.

CONCLUDING STATEMENTS

This review article has attempted to report and discuss what is known about the archival performance of individual components that make up old and new specimens of paper. Though much information was found during the search of the published literature, there are clearly many aspects that are in need of further research efforts focused on bringing fuller understanding. The present review particle was only able to depict an incomplete account of the archival performance of different components and additives of paper. The authors hope that the foundation prepared in the present work will inspire others to make further gains in the coming years.

As a general statement, the detailed findings discussed in this review suggest that the useful lifetime of paper products can be adjusted upwards, within reasonable limits, by judicious selection and processing of fibers, by the usage of alkaline papermaking practices, and by usage of a variety of chemical additives to optimize the papermaking processes and product attributes. The goal of papermaking usually is not to achieve something that will last forever; but on the other hand, one can strive to manufacture printed items on paper that will last for many hundreds of years under suitable conditions of storage. Technology will continue to undergo rapid change, but paper appears to be deeply rooted in our culture as a means of communication.

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