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# Thermal stability of cellulose insulation in electrical power transformers – A review

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## ABSTRACT

Cellulosic pulp has been processed into insulation paper since the earliest days of electrical engineering. This polymer synthesized by nature has proved to be competitive to man-made plastics throughout the last century and is still widely used in electrical power transformers. The high working temperatures prevailing in such apparatuses and the desired lifespans of up to 40 years shifted the thermal stability of cellulose to the center of attention of many researchers. In this literature review, a summary of theories and recent insights regarding the processes upon thermal degradation of cellulose in the temperature range relevant for electrical power transformers is given, followed by an overview of strategies to improve the thermal stability of cellulosic insulators. Special emphasis is placed on the discussion of additives and modification agents and their action modes, and on the understanding how successful upgrading of cellulose towards high thermal stability is achieved.

## 1. Introduction

Carbohydrates exposed to hot oil are associated by most people rather with the preparation of junk food than with assuring the electricity supply for our societies. Nonetheless, cellulose fulfils a crucial role as insulator wrapped around the copper windings and as material for structural support in oil-filled electrical power transformers. Cellulosic paper has been used as insulator since the earliest days of electrical engineering. In the beginning of the 20th century, before synthetic plastics emerged at large scale, paper had been the standard insulator in all kind of electrical cables, capacitors, coils, and electrical devices like. Nowadays it is still used in high-voltage power cables and electrical power transformers. Due to the high availability combined with low price, excellent insulation performance in dry state, and satisfying mechanical properties at elevated temperatures in comparison to synthetic materials, cellulose is unparalleled for this purpose, and worldwide several million tons of pulp are processed into insulating materials for the electrical power industry (Emsley and Stevens, 1994, Prevost and Oommen, 2006), making it a smaller, but continuously important business field of the pulp and paper industries.

A general problem that comes along with the technical utilization of celluloses and papers is the complexity of chemical processes upon their degradation. This holds especially true for the applications of paper insulators and paper elements for structural support in oil-filled power transformers, where longevity and predictable lifespans of the insulating system are crucial for a reliable electricity supply (cf. Fig. 1). A transformer is a static machine that either increases alternating current (AC) and decreases voltages in the case of a step-down transformer or acts oppositely in the case of a step-up transformer. For example, when electricity is transported from a power station to a city, at first the voltage is increased by means of a step-up transformer for minimizing the losses in the long transmission cables, but subsequently for safe utilization of electricity the voltage must be reduced again by means of a step-down transformer in local transformer stations. In the most basic form this is achieved by two copper coils with different numbers of turns, wound around the same magnetic core. If the secondary winding (load circuit, e.g. city) has less turns than the primary winding (supply circuit, e.g. power plant) the voltage induced in the secondary winding is lower than in the primary winding (step-down transformer). Considering the high voltages used, a good insulation between all elements is

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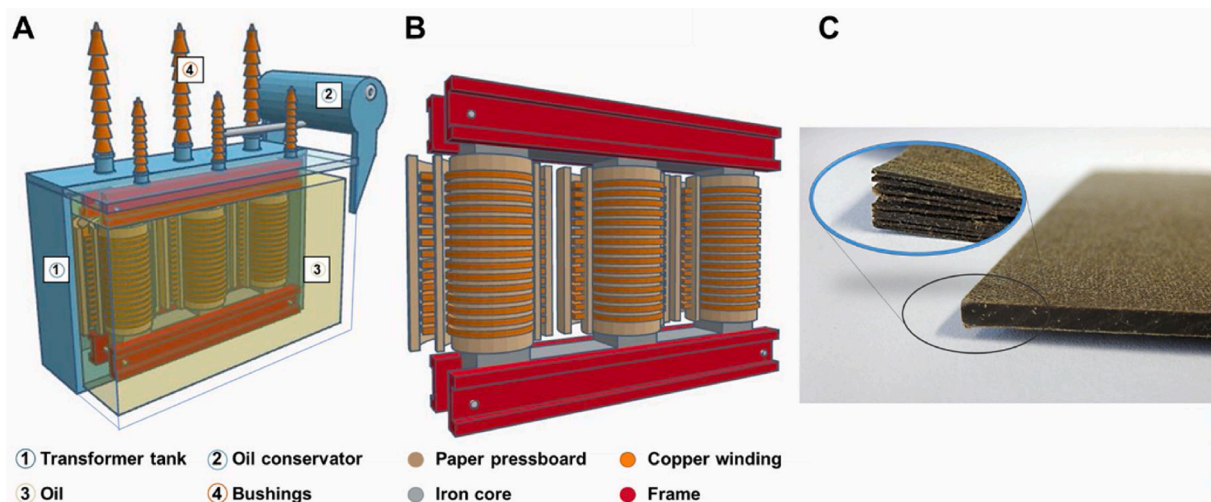


Fig. 1. Sketch of an electrical power transformer (three phases, core type) (A) and an electrical power transformer core (section view through copper windings and paper pressboard) (B). Laboratory-aged paper pressboard insulation consisting of several layers of compressed Kraft paper (C).

essential for an efficient and safe transformer operation. For this purpose, electrical coils are wrapped with paper insulation (mostly Kraft paper) and mechanically supported by compressed paperboards, which then are submersed in thermo-oils in closed systems that – ideally – are supposed to work and remain unchanged without replacement for years and even decades.

Such power transformers feature working temperatures of 60 °C–90 °C (Levchik et al., 1998) under normal conditions combined with locally restricted temperatures of up to around 100 °C, the so-called hot spot temperature. This equals or already exceeds the conditions of accelerated aging tests of paper in material and conservation science (Ahn et al., 2013; Luner, 1988; Potthast et al., 2008). Apart from cooling the system, enhancing heat dissipation and improving insulation properties, the respective oils in these transformers also protect the paper by excluding water and oxygen to a significant extent, which would have a detrimental effect on cellulose stability at elevated temperatures (Shroff & Stannett, 1985; Zou et al., 1994). Under heavy loads or even overloads, the inherent temperature of oil-filled transformers can easily surpass 100 °C and reach up to several hundreds of degrees Celsius in severe cases. Such temperatures will inevitably lead to degradation of the oil-impregnated cellulosic insulation boards as well as to slow decomposition of the oil, especially when considering the desired service life of up to 40 years (Levchik et al., 1998; Shroff and Stannett, 1985). The commonly accepted end-of-life criterion is reached when the degree of polymerization (DP) of cellulose falls below a value of 200, which approximately corresponds to 20 % of residual tensile strength of the paper (Jalbert et al., 2007; Levchik et al., 1998; Lundgaard et al., 2004). Beyond that level of deterioration, a fatal short circuit is extremely likely to happen.

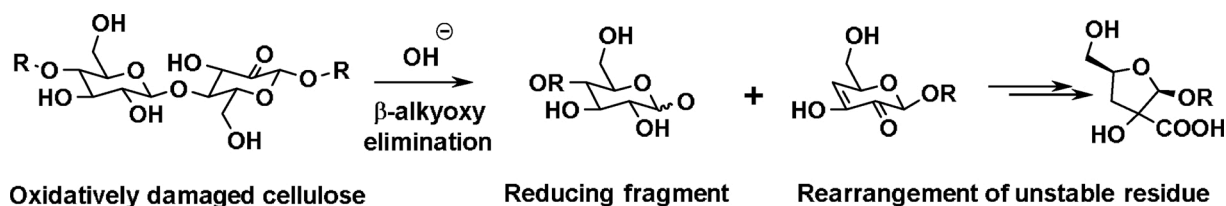
In this literature review we will discuss thermal degradation of celluloses with a focus on power transformer applications as well as existing strategies to thermally upgrade paper pressboard insulation to cope with such extreme conditions and life spans of up to 40 years. How pulping conditions, origin and composition of the raw material, structure of the paper as well as fiber characteristics, such as cellulose chain length and crystallinity, affect the ageing performance of paper was already discussed elsewhere (Emsley and Stevens, 1994; Gurnagul et al., 1993; Luner, 1988; Poletto et al., 2014; Poletto et al., 2012; Zou et al., 1993; Zou et al., 1994). This article will focus on the chemical modification of cellulose as well as additives enhancing the thermal stability of paper insulation in electrical power transformers. In order to discuss the interplay of the respective modifications and improvement measures

with the ongoing degradation processes, an overview on cellulose / paper degradation under the relevant temperatures will be given first.

## 2. Cellulose degradation in power transformers

The typical raw material for paper insulation in power transformers is electrical grade softwood Kraft pulp consisting of approximately 85 % cellulose, 10 % hemicelluloses, and 5 % residual lignin. The lignin content of the papers could well be higher if no bleaching at all would be applied. Avoiding bleaching steps generally better preserves cellulose integrity. Additionally, it has been observed that lignin *per se* seems to have a beneficial effect on the thermal resilience of Kraft paper (Vänskä et al., 2016). It has been demonstrated that the stability of lignins during thermal decomposition can be attributed to the ability of lignin to form more highly condensed structures with increasing temperature (Ando et al., 2019). Although higher lignin contents would be beneficial from the viewpoints of thermal endurance, pulps for insulation papers are not specially produced in most cases, but are derived from conventional Kraft paper grades, such as packaging papers, so that their composition is the same as in those grades. However, one critical requirement of insulator paper pulps is a very low content of main and transition metal ions to assure low conductivity, *i.e.*, good insulation properties, as well as satisfying aging performance under elevated temperatures. Transition metal ions are more critical than main group metal ions, because they are known to trigger oxidative cellulose degradation by catalyzing the formation of hydroxyl radicals, other reactive oxygen species and hydroxyl anions in the presence of oxygen and water (Kolar, 1997; Lundgaard et al., 2004; Šelih et al., 2007). Even though engineers do their utmost to exclude water, oxygen, and metal ions from the system, these players will always be present in traces ready to start the vicious circle of paper degradation.

Oxidation of cellulose causes introduction of carbonyl groups (keto groups: C2, C3, aldehyde function: C6) and carboxyl groups (C6) along the cellulose chain (Potthast et al., 2005) which can be traced very well throughout paper ageing experiments by means of Fourier transformed infrared spectroscopy and ultraviolet-visible spectroscopy (Bagniak et al., 2019). The keto groups entail decreased thermal stability because they render the structure more prone to aldol-type condensation reactions. Most importantly, they introduce a pronounced instability towards alkali (hydroxyl anions) and constitute “hot spots” along the cellulose chain where cleavage is to occur. Small amounts of such oxidized groups are found well distributed over the cellulose polymer



**Scheme 1.** Alkali-triggered oxidative cellulose degradation according to a  $\beta$ -alkoxy elimination mechanism, starting from a single oxidized hydroxyl group (C2 carbonyl in the example) along the cellulose chain (Hosoya et al., 2018; Potthast et al., 2006), R = cellulose residue.

introduced by pulping processes or due to thermally induced partial dehydration (cf. Scheme 3A). The first step of an alkali-induced degradation is the nucleophile attack of the hydroxide ion ( $\text{HO}^-$ ) at the carbonyl carbon (low electron density), i.e. at C2 position in Scheme 1), initiating  $\beta$ -alkoxy elimination, which causes cleavage of the cellulose backbone already at low alkalinity (pH 9 and above) and promoted by increased temperature (Hosoya et al., 2018; Potthast et al., 2006). This chain breakage as illustrated case in Scheme 1 results in a new reducing end group and an unstable counterpart that rearranges to stable products, mostly of the saccharinic acid type. In this way, a second chain end with a carboxylic acid group is formed. The  $\beta$ -alkoxy elimination mechanism becomes active independently of whether the carbonyl group is found at C2, C3 or C6 position. In general, oxidative cellulose decomposition does not contribute much to the absolute degradation of oil impregnated cellulose insulation (Lundgaard et al., 2004; Zou et al., 1994) when oxidative factors (oxygen, transition metals) are reliably excluded, but it can become an important influence in the case of oxidatively pre-damaged (overbleached) celluloses. This alkali-promoted degradation pathway is self-inhibiting, as the respective degradation products acidify the system (cf. Scheme 1) and hence, counteract the progress of oxidative cellulose decomposition. The actual danger of oxidative degradation lies in the slow but steady generation of organic acids (carboxylic acid groups) which cause an acidification of the system in the presence of water, which paves the way for subsequent acid-catalyzed hydrolysis of cellulose. This reaction, which would cause only “normal” chain shortening by hydrolytic cleavage of a glycosidic bond (Oberlerchner et al., 2015), can cause production of additional acids under thermal conditions and thus become an autocatalytic process (Scheme 2). Furthermore, the respective oils for transformer application themselves acidify when

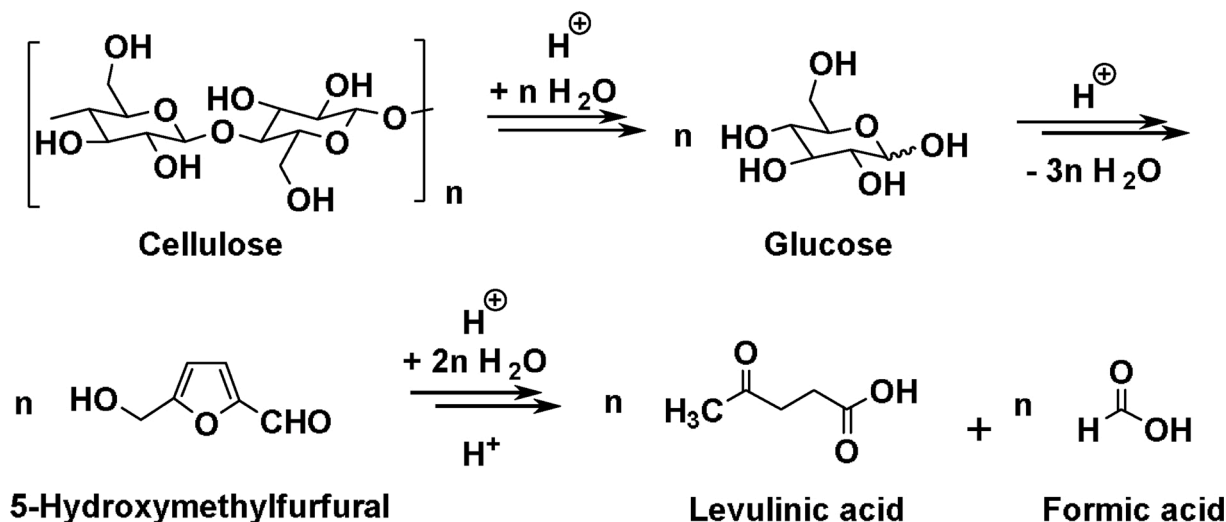
**Table 1**

Summary of advantages and disadvantages of established measures to thermally upgrade paper.

	Chemical modification	Incorporation of additives
<b>Advantages</b>	Effective enhancement of thermal stability of paper	Effective enhancement of thermal stability of paper Easy integration in existing industrial processes (application of additive solution on paper machine)
	–	Cheap
<b>Disadvantages</b>	Requires vast amounts of hazardous and toxic reactants	Possible release of corrosive ammonia
	Requires separate industrial process after pulping	–
	Reduction of mechanical properties of paper due to substitution of hydroxyl groups	–

subjected to accelerated ageing conditions (Wang et al., 2019). Although usually a side effect, also the general change of the pH (increase of acidity) with temperature is well relevant for the power transformer systems: while pure water has a pH of 7 at room temperature, the neutral pH value at 100 °C is about 6, meaning that water dissociation and hydronium ion concentration are increased by a factor of 10 (Table 1).

In contrast to alkali-promoted oxidative degradation ( $\beta$ -alkoxy elimination), acid-catalyzed hydrolysis is not suppressed by its own degradation products. On the contrary, in the presence of water and



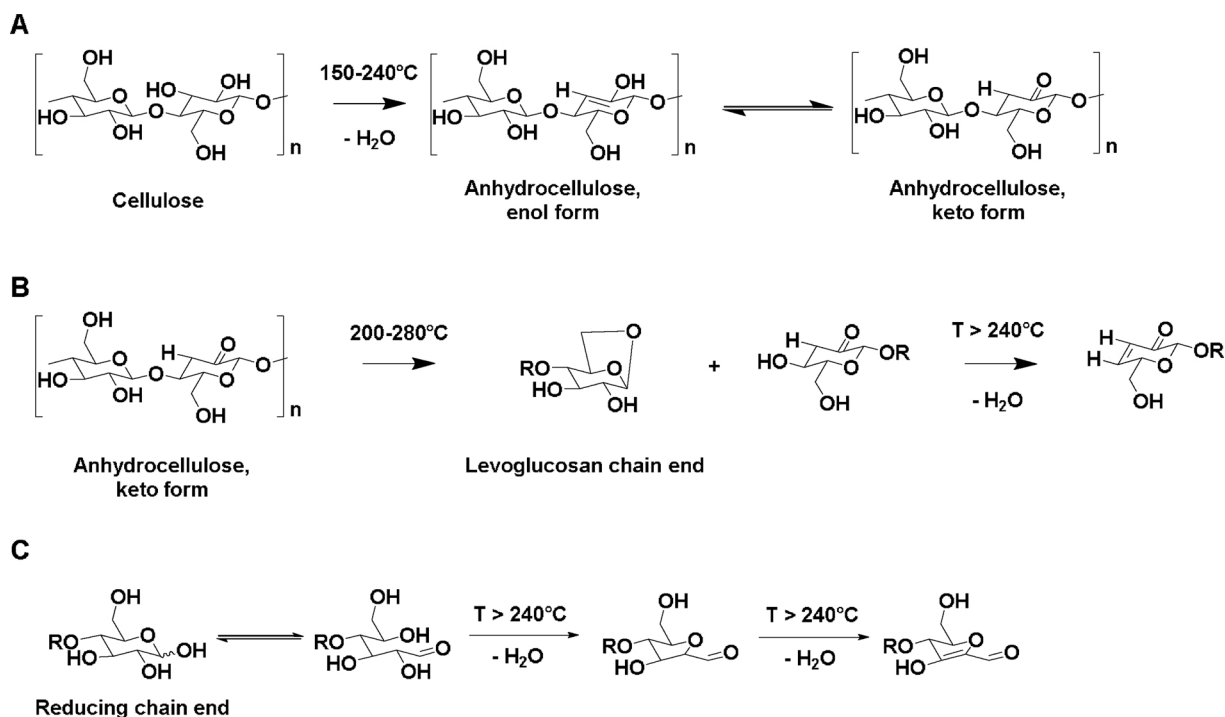
**Scheme 2.** Acid-catalyzed hydrolysis of cellulose under thermal stress, causing additionally condensation, fragmentation and acid generation from the primary hydrolysis products (Girisuta et al., 2007; Klemm et al., 1998a; Sixta et al., 2006). Note that, according to theory, every glucopyranose unit liberated generates two equivalents of carboxylic acid. While the net water consumption/generation is zero for the overall reaction, more water is generated than consumed if the reaction stops at the 5-hydroxymethylfurfural stage.

within the normal working temperature range of a power transformer, the carboxylic acids eventually formed by cellulose hydrolysis (cf. Scheme 2) will further accelerate chain scission (Girisuta et al., 2007; Lundgaard et al., 2004), rendering the process autocatalytic. The hydrolytic chain scission is initiated by the protonation of either the oxygen of any  $\beta$ -(1-4)-glycosidic bond along the cellulose backbone or by protonation of the ring-oxygen of any pyranose (Klemm et al., 1998a; Sixta et al., 2006). As a result, the  $\beta$ -(1-4)-glycosidic bridge is heterolytically cleaved and a new reducing end is formed by consuming one water molecule. The catalytically active proton is always regenerated and not consumed. In principle, this mechanism continues until only glucose monomers are present. In acidic environment ( $H^+$ ) and especially under thermal stress, glucose is transformed into 5-hydroxymethylfurfural, which also is rather unstable under the given conditions (Girisuta et al., 2007). Each formation of 5-hydroxymethylfurfural from glucose is accompanied by the release of 3 water molecules (cf. Scheme 2). Ultimately, this unstable compound is converted into levulinic acid and formic acid through the consumption of 2 molecules of water. It is noteworthy that - apart from catalyzing hydrolysis of carbohydrates - acidic paper degradation products also trigger corrosion of copper windings (Gao et al., 2017). The corrosive dibenzyl disulfide present in traces in most insulation oils corrodes copper conductors with formation of copper sulfide ( $Cu_2S$ ) in acidic environment. Overall, the rate of acid catalyzed hydrolysis of cellulose depends on the inherent temperature of the system, the concentration of protons ( $H^+$ ) and on the availability of  $H_2O$  molecules facilitating the dissociation of carboxylic acids (Klemm et al., 1998a). Consequently, a regular removal of water from the insulating system of electrical power transformers is essential in order to assure the stability of the system and the integrity of the cellulosic insulation throughout the desired life span (Oommen and Prevost, 2006).

Certainly, to keep the system as free of water as possible is challenging since thermal degradation of cellulose releases considerable amounts of water, in particular from the amorphous cellulose fraction. This type of degradation, which is not triggered by alkaline or acidic

catalysts, but by elevated temperatures above approx. 150 °C, proceeds via a levoglucosan intermediate, which requires a cellulosic  $\beta$ -glucopyranose unit to adopt  ${}^4C_1$  conformation instead of the usual  ${}^1C_4$  conformation. The spatial freedom for this conformational change is only given in the amorphous and thus relatively flexible cellulose areas, not in the highly order crystalline ones. The degradation results in a random cleavage of the cellulose chain and a release of water. The dehydration pathways depicted in Scheme 3 correspond to well investigated and commonly accepted routes of water release from cellulose prevailing at temperatures which occur, at least temporarily, in electrical power transformers. Schemes 3 visualizes the threat that a temperature rise in a power transformer poses to the integrity of the paper insulation. One aspect is the direct thermal degradation of the cellulose, another one the production of water that enforces further hydrolytic degradation. Of course, the actual insulation system does not only consist of cellulose. In fact, hemicelluloses are even less stable under thermal conditions than pure cellulose or Kraft paper (Shen et al., 2010; Soares et al., 1995), with the dehydration mechanisms being similar (Patwardhan et al., 2011). Therefore, it is logical to assume that water release and thermal degradation starts with the hemicellulose part, but is in later stages dominated by cellulose which is the main component, present in much larger amounts.

Even though cellulose is thermally more stable than hemicelluloses, at temperatures close to the hotspot temperatures in power transformers water is released from the backbone of amorphous cellulose chains (cf. Scheme 3A) (Scheirs et al., 2001). Further temperature increase (200–280 °C) additionally causes chain scission in non-crystalline cellulose regions resulting in a levoglucosan chain end formed and a non-reducing chain end in an thermally induced deglycosylation reaction (cf. Scheme 3B) (Hosoya and Sakaki, 2013). In this high-temperature range, all chain ends, both the non-reducing chain ends (cf. Scheme 3B) as well as reducing chain ends (cf. Scheme 3B and Scheme 3C) are prone to easy dehydration (Collard and Blin, 2014; Scheirs et al., 2001). For pyrolysis of cellulose under vacuum conditions, a maximum water release was found in the range of 300–350 °C (Julien et al., 1991). These



**Scheme 3.** Thermal dehydration of amorphous cellulose in the temperature range from 150 °C to 400 °C (Scheirs et al., 2001, Klemm et al., 1998a, Hosoya and Sakaki, 2013), causing random chain cleavage and release of water (A,B). Thermal dehydration of reducing end of celluloses (Collard and Blin, 2014; Scheirs et al., 2001) (C). R = cellulose residue.

temperatures are significantly higher than those expected in electrical power transformers under normal operation conditions. Nevertheless, once an electrical fault or short circuit causes a severe temperature rise, a dangerous amount of water will be accumulated in the system. Recent research showed that partial discharges in transformers additionally cause locally restricted thermally induced decomposition and dehydration of the paper pressboard (Li et al., 2020). Water molecules derived from cellulose dehydration eventually lead to an increased moisture content of insulation paper and pressboard parts that may exceed 5 wt% after several years of use (Żukowski et al., 2015). Typical initial moisture levels in insulation paper are approx. 0.8 wt%. Żukowski et al. (2015) revealed that the formed water is preferentially found as nanodrops of an average diameter of 2.3 nm evenly dispersed within the paper rather than in the hydrophobic oil. In a subsequent study, Żukowski et al. (2016) demonstrated that the frequency-dependent and temperature-dependent relative (dielectric) permittivity, formerly known as dielectric constant, is heavily affected by the papers' moisture content. Consequently, the water released in the course of paper degradation does not only accelerate hydrolysis of carbohydrates, it directly deteriorates the insulation properties of the system.

It is noteworthy that dehydration of cellulose polymers presumably does not only occur in an intramolecular way as illustrated in Scheme 3, but could also take place intermolecularly, leading to crosslinked structures (Kilzer and Broido, 1965). However, crosslinking could also be a result of interactions of carboxyl groups with hydroxyl groups of neighboring chains in formal esterification reactions, especially when considering the abundance of such oxidized groups in thermally damaged systems (Kato and Cameron, 1999), see Schemes 2 and 3.

In summary, as long as the moisture content in the insulation system is still low and the paper is free of acidity, degradation appears to be initiated by and limited to oxidative cellulose damage (Lundgaard et al., 2004). Local alkalinity might induce  $\beta$ -alkoxy elimination leading to cellulose chain cleavage. The resulting degradation products, in particular acids and water, increasingly enable acid-catalyzed hydrolysis. Hydrolytic degradation apparently is the main mechanism acting on the destruction of cellulose at given temperatures as it is of autocatalytic nature (Jalbert et al., 2007; Lundgaard et al., 2004; Zou et al., 1994). The progress of hydrolytic cellulose decomposition is further accelerated by water deriving from thermal dehydration reactions facilitating the dissociation of carboxylic acids formed as degradation products. Thermal degradation, causing chain cleavage and water release according to several dehydration pathways, is relatively slow under normal operation conditions, but may become dominant in the case of thermal events caused by short circuits. Generally, it has been observed that in thermally aged commercially available continuously transposed conductors (CTC) the extent of deterioration of insulation paper wrapped around copper conductors was more strongly pronounced for the inner paper layers than for the outer ones (Oria et al., 2020). The vicious circle of cellulose degradation, water formation and autocatalytic acidic processes is hard to break – still it is possible to improve the thermal resilience of paper and improve its application properties and life span in power transformers.

### 3. Paper insulation of enhanced thermal stability in electrical power transformers

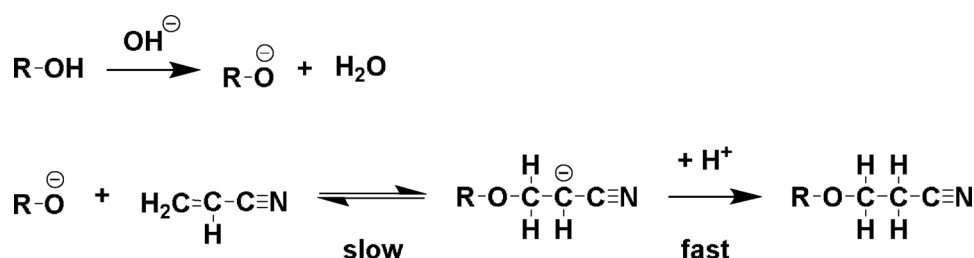
Since the 1950ies material scientists have been looking for measures to obtain cellulosic paper with optimized thermal properties for the application as insulators in electrical power transformers (Prevost, 2005). The definition of thermally upgraded insulation paper by the IEEE Standards Association specifies that either covalent cellulose modifications (i.e. cyanoethylation) or incorporation of stabilizing agents (i.e. amine derivatives, such as dicyandiamide) are applied to reduce the rate of paper decomposition (IEEE Std. C57.12.80-2010). In this overview, we only discuss measures to improve the thermal stability of cellulose/paper for which sufficient evidence for a satisfactory large-scale applicability has been presented. All the strategies presented within this article have been used or are still used in commercial products, confirmed by a systematic screening of patents and scientific literature dealing with this topic. The two general strategies are discussed in the following sections placing special emphasis on the molecular interactions of possible treatments with cellulose upon thermal decomposition.

#### 3.1. Chemical modification of cellulose

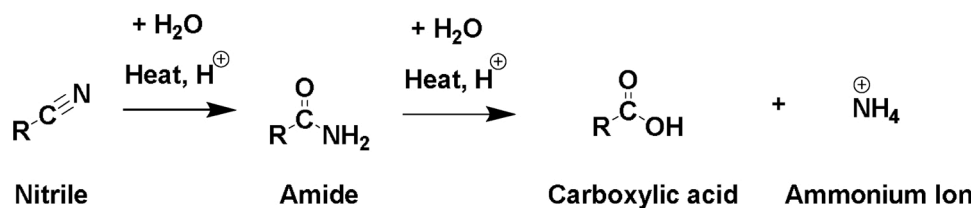
Generally, the aim of chemical modification of cellulosic insulation material is to replace parts of the hydroxyl groups with more stable functional groups that are less susceptible towards the respective degradation processes. Alternatively, the added functionalities might scavenge water and/or acids, this way stabilizing the pulp by neutralizing degradative components that have already been formed. The most prominent chemical modification of paper pressboard insulation is cyanoethylation which was patented in the early 1960ies by the General Electric Company (1963).

The classical way to obtain cyanoethylated paper is to treat it with acrylonitrile in aqueous alkaline media (General Electric Company patent, Unknown, 1963; Klemm et al., 1998b). The reaction uses standard conditions (alkalinity, heterogeneous system) for cellulose etherification and employs the cheap acrylonitrile which, however, is a toxic reagent. In the formation reaction, a (deprotonated) hydroxyl group of cellulose adds to the vinyl group of acrylonitrile in a Michael-type process (cf. Scheme 4), resulting in a stable cellulose ether. According to the patent by the General Electric Company (1963), the optimum nitrogen content is in the range of 1 to 3 % based on the paper weight. Nehls, Wagenknecht, Philipp, & Stscherbina (1994) established that cyanoethylated cellulose of very low degree of substitution (DS) is preferentially etherified at C6 position. Based on this, it can be assumed that this holds true as well for insulation pressboards featuring a nitrogen content of up to 3%, which corresponds to a DS of approximately 0.5 in case of pure cellulose substrate (Klemm et al., 1998b).

It is well-known that cellulose ethers compared to native cellulose generally feature higher resistance against acid catalyzed hydrolysis (Klemm et al., 1998a; Yoneda et al., 2016) and that cyanoethylation reduces the hydrophilicity of cellulosic substrate (Klemm et al., 1998b;



Scheme 4. Cyanoethylation of hydroxyl groups (e.g. in cellulose) with acrylonitrile (Klemm et al., 1998b). R = cellulose.



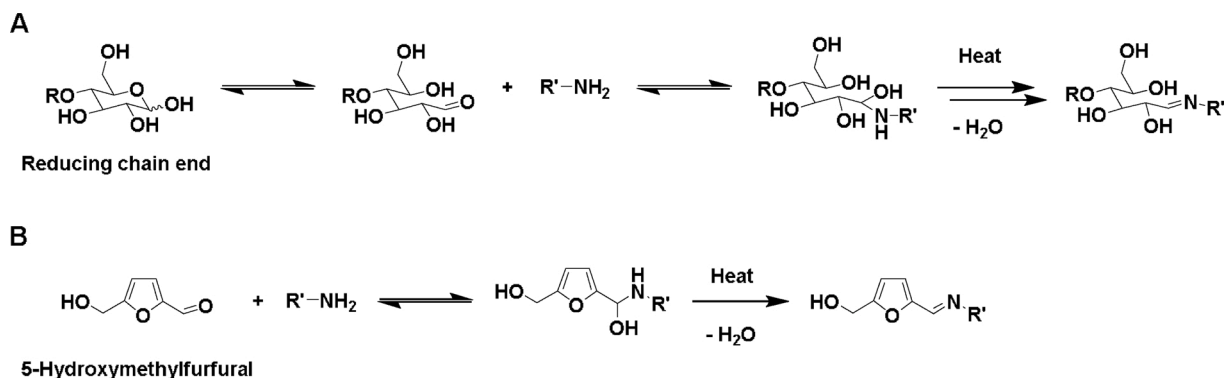
Scheme 5. Stepwise hydrolysis of nitrile group (Larock and Rozhkov, 2018).

Prevost and Oommen, 2006). Additionally, the nitrile group in the case of cyanoethylated cellulosic insulation materials counteracts the autocatalytic nature of thermal cellulose degradation by trapping water molecules. When heat is applied, a nitrile group is hydrolyzed in aqueous acidic media (cf. Scheme 5) (Larock and Rozhkov, 2018), first to an amide under consumption of one equivalent of water and then to an ammonium salt under consumption of another water equivalent. In the presence of reduced copper particles (Cu(0)) from the electrical coils, the transformation of a nitrile group to an amide can take place already at 90 °C in neutral environment (Ravindranathan et al., 1982). To the best of our knowledge, it has not yet been experimentally proven that cyanoethylated paper pressboard undergoes such hydrolysis, but given the conditions in an aged transformer it would be logical to assume that the protective effect is – at least partly – due to such water consumption reaction. This thought was as well articulated by Lundgaard and his co-workers (Lundgaard et al., 2004). Apart from demonstrating the increased thermal stability of cyanoethylated pulp, Nada and Adel also showed that cyanoethyl groups and especially the hydrolyzed intermediate, the amide, are suitable metal ion scavengers (Nada and Adel, 2007). This could lead to a decreased formation of hydroxyl radicals and ions delaying the initial autoxidative degradation, although the concentration of such transition metals in real-world insulation systems and its changes during aging over time have never been studied in detail. Still, the combination of these beneficial attributes, water scavenging and transition metal complexation ability, seem to be the origin of the frequently stated satisfying thermal properties of such modified cellulosic insulation material (Arroyo-Fernandez et al., 2017; Lundgaard et al., 2004; Liang et al., 2018; Prevost, 2005). Although never specifically addressed, the release of cyanide, acrylamide, and toxic nitriles, albeit a faint possibility, cannot be excluded, especially when taking into account the harsh conditions of high temperatures. From the viewpoint of recycling and also work safety, such systems might pose challenges and offer ample opportunities for research.

Apart from cyanoethylation of cellulose as the dominating approach, also cellulose acetylation is mentioned as a measure to improve the thermal stability of cellulosic insulation material (Arroyo-Fernandez et al., 2017; Prevost, 2005). In the 1960ies, Griggs and Brooks suggested

to use partially surface-acetylated paper as suitable electrical insulation and proved that the more hydrophobic paper had better electrical properties as well as higher dimensional stability (Griggs and Brooks, 1965). Furthermore, their ageing studies indicated that the acetylated paper was of superior thermal stability in comparison to the non-acetylated parent. However, the few reported thermogravimetric experiments performed with comparable specimens – acetylated and non-acetylated flax and wood fibers – gave rather ambiguous results regarding the thermal performance (Glasser et al., 1999; Zafeiropoulos et al., 2000). All samples investigated in these publications had a similar acetyl content of 15 % to about 20 % by weight. Ando, Nakatsubo, & Yano (2017) prepared acetylated ground wood pulp of higher thermal stability than the untreated reference. They attributed this result mainly to the acetyl substitution pattern of the lignin fraction. In a follow-up study they also pointed out the importance of the inherent bonding structure of lignin combined with the respective positions of the acetyl groups on the lignin molecule for the pulp's thermal stability (Ando et al., 2019). The aging experiments of Griggs and Brooks (1965) did not surpass 200 °C. Shen et al. analyzed the degradation products of beech wood xylan (*Fagus sylvatica*), which naturally carries a significant amount of acetyl groups, by means of thermogravimetric analysis combined with Fourier transformed infrared spectroscopy (Shen et al., 2010). The results obtained indicated that acetyl groups are cleaved off from the carbohydrate backbone above 200 °C, reaching a maximum of acetic acid release at 260 °C. These temperatures are indeed higher than normal working temperatures (60–90 °C) expected in a transformer. Yet again, in the course of a 40-year life span overloads or electrical faults are likely to occur, which would shift the temperature close to such critical values, at least locally restricted. Additionally, in thermally stressed acidic systems acetyl groups on cellulose become increasingly unstable (Yamashita and Endo, 2004).

In general, cleavage of acetyl groups from cellulose acetates, no matter according to which pathway or in response to which trigger, generates acetic acid which might contribute to further cellulose degradation upon long-term thermal stress. Therefore, cellulose acetylation does not seem to represent a suitable way to increase long-term stability in power transformer applications. At the same time, it seems plausible that increased hydrophobicity could be beneficial for the



Scheme 6. Reaction of reducing sugars with primary amines (A) (Collins and Ferrier, 1995). Reaction of 5-hydroxymethylfurfural with primary amines (B) (Painter, 1998). R = Cellulose residue or H, R' = residue of stabilizer or H (ammonia).

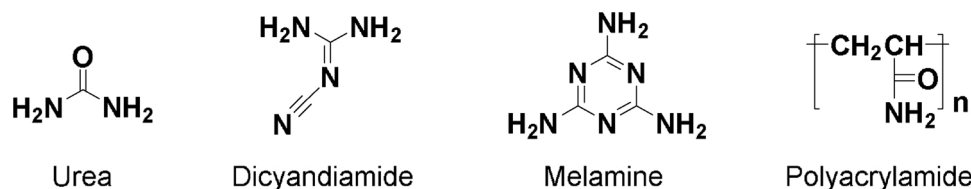


Fig. 2. Frequently used additives for thermally upgraded paper.

ageing performance of paper considering the accelerating effect of water on cellulose degradation. This was emphasized by a patent (Westinghouse Electric Corporation patent, Tierney, 1969), which demonstrated that acetylation alone does not improve the thermal stability of Kraft paper, because of the dominating negative effect of released acetic acid. In contrast, acetylation combined with slightly alkaline nitrogen-containing stabilizers that would act as long-term scavengers of released acetic acid (and other acids) was stated to result in superior permanence of the insulation paper. The synergy of the hydrophobic material and the acid-neutralizing alkaline compounds was proven, because the combination gave better results than the addition of the stabilizers alone.

### 3.2. Incorporation of stabilizing agents into the paper

One general drawback of replacing the hydroxyls of cellulose with less polar functional groups is a loss of mechanical properties of the paper sheets due to a disturbance of the hydrogen bond network (Prevost and Oommen, 2006). To circumvent this problem, the incorporation of additives, mostly nitrogen-containing ones, into the paper has been further developed and optimized. According to a Westinghouse Electric Corporation patent, this alternative additionally turned out to be very convenient for the manufacturing process as on the paper machine the partially dried cellulose fibers could be easily impregnated with an aqueous additive solution during sheet formation (Westinghouse Electric Corporation, Ford, 1963).

The most frequently applied thermal stabilizers for power transformer paperboards are urea, dicyandiamide, melamine, and polyacrylamide particles (Arroyo-Fernandez et al., 2017; Liang et al., 2018; Lundgaard et al., 2004; Prevost, 2005). All these compounds are weak nitrogenous bases, with a structural abundance of amino groups (cf. Fig. 2). In the course of a series of accelerated aging experiments with paper equipped with such amine additives Lundgaard et al. (2004) shed light on the basic principle of their action upon thermal degradation of cellulose. There are three major functions fulfilled by these slightly alkaline compounds. First, carboxylic acids – present ones and generated ones as soon as they are formed – are partially neutralized by forming a stable salt with the respective amines (cf. Scheme 1 and 2). This resembles the concept of the ‘alkaline reserve’ in cellulose conservation science, applied by librarians and archivists to better preserve historic acidified papers and books (Ahn et al., 2013). The second function of these stabilizing agents is withdrawal of water molecules which are released during the thermal degradation of cellulose (cf. Scheme 2 and 3) (Lundgaard et al., 2004). It was demonstrated that in comparison to conventional Kraft paper, paper with such additives incorporated was characterized by a reduced water release throughout the ageing experiment. Furthermore, when water was added it was actively consumed by the stabilized system. This behavior was not observed by the conventional Kraft paper tested. The lower moisture content of additive-stabilized paper was also observed by Liang et al. (Liang et al., 2018). Both Lundgaard et al. (2004) and Liang et al. (2018) suggested that this could be a consequence of amino group hydrolysis: an amino group would be transformed into a hydroxy group by consuming a water molecule and releasing an ammonia molecule. Such nucleophilic substitutions – even more under neutral conditions – are less likely from the viewpoint of general organic

chemistry. It seems more plausible that nitrile, amide and triazine functions in the stabilizers in Fig. 2 would consume water upon hydrolysis, which is enhanced at higher temperatures. Furthermore, if the mechanism of amino group hydrolysis was indeed operative, the release of gaseous ammonia, certainly an undesired outcome, should have been observed.

The third function fulfilled by these additives is stabilizing reducing end groups of carbohydrates and furfural-related intermediate degradation products, such as 5-hydroxymethylfurfural, against further degradation and conversion into carboxylic acids (cf. A and 6B). Determination of the cellulose’s DP and subsequent chemical analysis of the oil in which the samples were aged revealed that specimens containing nitrogen-based stabilizing agents released significantly less furfural per number of chain scissions than the series of conventional Kraft paper (Lundgaard et al., 2004). It had been demonstrated beforehand that the amount of furfural detected in insulating oil during accelerated ageing experiments can be closely correlated with the DP of aged conventional Kraft paper (Emsley et al., 2000) and this held true for the non-upgraded paper tested by Lundgaard et al. (2004). Consequently, the observed stabilization effect implied that production of furfural-related compounds was impeded by the thermal stabilizers by reacting with their precursor compounds, such as 5-hydroxymethylfurfural and levoglucosan formed at temperatures of 100–200 °C (Scheirs et al., 1998). As plausible explanation for this phenomenon the Maillard reaction was evoked. When heat is applied, a stable covalent bond could be established between the nitrogen of a primary amine and the carbon of a carbonyl group by a nucleophilic attack whilst a water molecule is released (cf. Scheme 6B) (Painter, 1998). Hence, the further decomposition would be hampered. The same mechanism stabilizes the reducing ends of carbohydrates eventually forming a glycosylamine (cf. Scheme 6A) (Collins and Ferrier, 1995).

Theoretically, also the by-product of nucleophilic amino group displacement, *i.e.* ammonia, should interact analogously with reducing end groups and should contribute to the neutralization of acids despite its gaseous state. Arroyo-Fernandez et al. (2017) subjected paper stabilized with dicyandiamide, melamine, and polyacrylamide immersed in transformer oil to accelerated ageing for 3500 h at 170 °C. For a paper sample with an initial nitrogen content of 4.4 % by weight a residual nitrogen content of around 3.5 % was determined after ageing. They argued that if ammonia had been just released as a gas without interacting with the decomposition products of cellulose, a much lower residual nitrogen content would have been determined. However, while it was evident from the lower N-content that some volatile nitrogen components had been released into the gas phase, the results of infrared spectroscopy seemed to prove that the additives reacted with water by hydrolysis rather than by nucleophilic substitution of amino groups. For instance, the characteristic nitrile band (2194 to 2154  $\text{cm}^{-1}$ ) of dicyandiamide disappeared already in the initial state of the experiment, proving nitrile hydrolysis rather than ammonia release or ammonia reactions. Tensile strength tests of aged paper strips revealed that a higher nitrogen content (4.4 %) compared to a lower content (1.2 %) was accompanied by a better preservation of tensile strength. A gradual decrease of the nitrile band of infrared spectra as ageing proceeded was also observed by other researchers working with similar paper samples (which however were exposed to lower temperatures (100–124 °C) (Mildemberger et al., 2016, Saldivar-Guerrero et al., 2016).



The Westinghouse Electric Corporation patent (Ford, 1963) mentions an ideal amine stabilizer amount and an optimized combination of amine stabilizers with regard to the retained burst strength after ageing. The nitrogen content should sum up to 3 % based on the paper weight, and the additives should be composed of 1 part melamine, 2 parts dicyandiamide, and 0.1 part of polyacrylamide. These proportions might vary depending on the pulp, but from the available information about commercial thermally upgraded papers it appears that this recipe did not change much throughout the last decades. Gilbert et al. (2010) determined the nitrogen content of four commercially available thermally upgraded papers. The nitrogen content varied between 0.91 wt% and 3.9 wt%, which is in accordance with the definition of thermally upgraded paper of the IEEE Standards Association (1 to 4 % of nitrogen by weight) (IEEE Std. C57.12.80-2010). Also other additives have been proposed in patent literature as suitable thermal stabilizing agents for cellulosic insulation in electrical power transformers, but no solid proof of their positive effects has been produced. Only the aforementioned amines (cf. Fig. 2) have been used continuously since the first corresponding patents had been issued in the 1960ies and their benefit demonstrated (Ford, 1963, Tierney, 1969). This might be due to a favorable combination of safety issues, efficiency, and price for these stabilizers that could not be met by later alternatives. Melamine even has been “re-discovered” recently for insulation paper purposes (Chen et al., 2020). Melamine was grafted onto cellulose nanocrystals to increase the thermal resilience of the cellulose crystallites. Subsequently, they were added to insulation paper samples. Thereby, it was possible to increase the tensile index and the alternating current breakdown strength of paper.

#### 4. Conclusions

In this literature review, we discussed possible measures to decelerate thermal cellulose degradation processes causing deterioration of oil-immersed paper insulation in electrical power transformers. These measures comprised both chemical modification of the cellulosic pulp as well as use of stabilizing additives. The action modes of both approaches as given in the literature were presented and critically discussed.

For more than a century cellulosic paper has been a well-established and reliable insulation material in electrical engineering, which has been studied in quite a number of accounts. Still, the complex mechanisms of paper degradation in general – and the special case of oil-immersed paper in power transformers in particular – are still not fully understood and offer ample opportunities for scientific research and industrial optimization and product innovation. It is not difficult to identify crucial issues that must be addressed by successful strategies to enhance the thermal stability of transformer papers. When the temperatures of the insulating system exceed the design values, acidity combined with moisture start the vicious circle of paper decomposition. Presumably, oxidative pre-damage of the pulps and autoxidative cellulose degradation triggered by transition metal ions are the initiators which introduces carboxylic acid functionalities into the paper. Their dissociation, and consequently acidic hydrolysis, is facilitated by water molecules deriving from thermal dehydration and degradation that generates new acids. Thereby the way is paved for autocatalytic acid hydrolysis of the paper. The autocatalytic nature of this process makes it so dangerous. Hence, any effective general method for increasing the thermal resilience of paper would consume water molecules, neutralize acids already present and prevent their de novo formation. The addition of stabilizers with amino functions, such as dicyandiamide, or partial cyanoethylation of cellulose are methods that cause satisfying thermal stability of paper insulations. Both with non-modified pulps and with modified pulps, the desired service life of 40 years for cellulosic insulation in electrical power transformers can be achieved, even though the conditions in these systems are highly challenging. All approaches employing cellulose modification or auxiliary addition suffer from certain drawbacks. Cyanoethylation of cellulose requires vast amounts

of the hazardous and toxic reactant acrylonitrile and carries the inherent risk of release of highly toxic degradation products upon thermal aging. Such a process poses a considerable threat from the viewpoints of environmental protection and work safety, and must therefore be run with highest security precautions. A general drawback of amino group-bearing stabilizers is the release of ammonia, not only from the viewpoint of generation of a gaseous phase and pressure built-up, but also because of toxicity and corrosiveness concerns. In general, release of toxic compounds restricts the potential applications, especially for systems with direct human interaction. In this context, it is hoped that the present account does not only summarize literature and presently used approaches to cellulosic power transformer papers, but also gives some incentive to look for less toxic, more environmentally compatible – and at the same time equally or even more effective – solutions. New, maybe bio based, approaches to improve the thermal stability of cellulosic pulp could give the old application mode in electrical power transformers a new face and provide it with renewed attractiveness.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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