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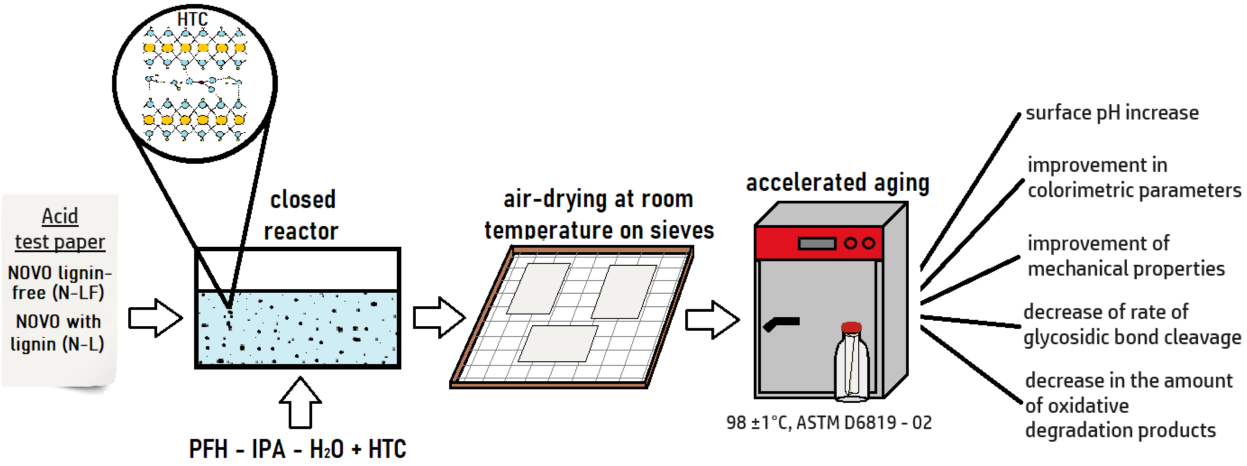
GRAPHICAL ABSTRACT



Development of New Systems Based on Hydrotalcites for Stabilization and Deacidification of Paper Information Carriers

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This study focuses on the effectiveness of a new substance in stabilizing paper information carriers - hydrotalcite applied to the paper in a partially polar environment. The effect of modification on the stabilization of paper during accelerated aging was investigated by measuring chemical (surface pH, rate of glycosidic bond cleavage), mechanical (coefficient of the relative increase of the lifetime for folding endurance), optical (colorimetry - CIE L*a*b*), and spectral (FTIR) properties. Three types of hydrotalcites differing in composition, particle size, and preparation conditions, were tested and compared. After the modification, all the properties of acidic test papers improved. The most promising type of hydrotalcite was prepared under the nucleation action of citric acid. The atomic ratio of Mg^{2+} to Al^{3+} of this hydrotalcite was equal to 5. Modification by this hydrotalcite led to an increase in surface pH by 1.3 to 2.7 units.

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INTRODUCTION

Paper information carriers represent a significant part of the world's cultural heritage. The main component of the paper is cellulose, which macromolecule can be relatively easily split into shorter fragments due to degradation (under certain conditions). Consequently, both the mechanical strength and quality of the paper information carrier are decreased (Zou *et al.* 1994; Erhardt and Tumosa 2005; Area and Cheradame 2011; Hubbe *et al.* 2023). Aging and degradation are a natural irreversible process. The basic degradation mechanisms are acid hydrolysis, oxidation, photochemical degradation, alkaline hydrolysis, and biological degradation (Area and Cheradame 2011; Vizárová and Reháková 2014; Vajová 2017). By acid hydrolysis, cellulose polymer chains are statistically split into shorter chains of glucose molecules (glucose oligomers) or glucose monomers. Consequently, or parallelly, the hydrolytic products are oxidized to various alcohols, ketons, aldehydes, and acids, which can enter further reactions; in addition, acid moieties catalytically enhance cellulose hydrolysis. Thus, a wide spectrum of degradation products (Area and Cheradame 2011; Małachowska *et al.* 2021; Potthast *et al.* 2022) is generated. Acid species, present in paper and causing the acid hydrolysis, are represented by acids added during paper production; acids produced during the aging process; acids formed from acid moieties present in the environment (*e.g.*, NOx, SO_2) absorbed from the air; Lewis's acids produced by inks and other components of documents added in their production (Vizárová and Reháková 2014; Hroboňová *et al.* 2023).

The problem with cellulose degradation in acid paper is solved by stabilization processes. One of the main shortages with the stabilization of acidic information carriers, books, and archival documents is currently insufficient conservation capacity, which is 2 to 3 times lower than the total of objects being held within the world library collections (Katuščák *et al.* 2009; Jablonský *et al.* 2013). The task of stabilization is to maintain the current state or extend the lifespan of the material. Mass deacidification technologies have solved the need for faster deacidification of a large number of paper information carriers (Schierholtz 1936; Smith 1972; Kundrot 1985; May and Jones 2006; Banik and Brückle 2018; Guzikiewiczová 2021).

In principle, several systems for the deacidification of paper are currently available, which differ in deacidification species (alkali compounds, mainly compounds of alkali metals), carriers (polar – *e.g.*, water, or non-polar – hydrocarbons, alcohols, ketones, fluorinated compounds, *etc*.), and the way of applying them (sprays, immersion to the bath of solution/dispersion). A necessary part of the conservation/deacidification process is drying and conditioning at a certain temperature and humidity. Just during conditioning the treated cellulosic subject partially swells, and the interior structure is more open, in the case of organic precursors of deacidification components they are hydrolyzed by condensed water from air humidity and can penetrate to the interior body of the subject (information carrier) more easily (Hubbe *et al.* 2017; Králik *et al.* 2021).

However, none of the deacidification methods is problem-free, which is why new deacidification agents and application procedures are still being sought. Experience shows (Katuščák *et al.* 2009, 2012) that in the development of deacidification processes, in addition to the effectiveness of acid neutralization and the creation of an alkaline reserve, it is also necessary to consider the universality (documents, books, writing/printing substances), environmental and safety risks, affordability and, user-friendly solutions. Perhaps, for these reasons, one of the widespread deacidification methods is based on the application of solid micrometric MgO particles in the form of a suspension in a non-polar environment, such as perfluorinated hydrocarbons, *e.g.* perfluoroheptane, the so-called Bookkeeper process (Kundrot 1985; Stauderman et al. 1996; Hubbe *et al.* 2017). The main disadvantage of the Bookkeeper process is non-reactivity of MgO in the absence of water. Under the completely non-aqueous conditions of treatment, the MgO particles fail to undergo the intended deacidification reaction to neutralize acidic species present in the dry paper (Hubbe *et al.* 2017). Fortunately, there are other liquid media that can be considered for distribution and treatment of acidic paper. In addition, in conservation research and praxis of deacidification and stabilization of paper, there are used other types of virtually non-soluble or low soluble materials besides MgO, such as $Ca(OH)_2$, $Mg(HCO_3)_2$, $CaCO_3$, $Ba(OH)_2$, *etc.* There are solid alternatives to Bookkeeper, *i.e.*, $Ca(OH)_2$ nanoparticles dispersed in short chain alcohols or hydrocarbons, which are advantageous mostly in that the particles are smaller and these systems do not need surfactants (Poggi *et al.* 2016, 2017). As for $Ca(OH)_2$, the resulting pH value of treated paper can be significantly higher than 7 even in the case of diluted solutions (*e.g.*, pH of 0.001 M solution of $Ca(OH)_2$ is 11.3). At these values of pH, alkaline hydrolysis of polymer cellulose chains can take place (Jablonský and Šima 2020).

Despite the intensive exploitation of hydrotalcites (HTC) (Thürmer 1998; Fink 2010) for stabilization of synthetic polymers, particularly, polyvinylchloride composites (Bocchini et al. 2008), they have not been reported as deacidifying agents for cellulose-based artifacts, so far. HTC belongs to the anionic clays, and the name "hydrotalcites," which is used as a reference name for several isomorphous compounds. In our research, they were chosen due to their specific properties. As illustrated in Fig. 1, HTC can be described as alkaline compounds containing magnesium and aluminum in their structure. They are capable of exchanging anions, and they typically have a large specific surface area. They typically are quasi-homogeneous mixtures in which small crystals are possible to be formed, and after calcination, they can reconstruct the original structure *(*Cavani *et al.* 1991; Conterosito *et al.* 2018).

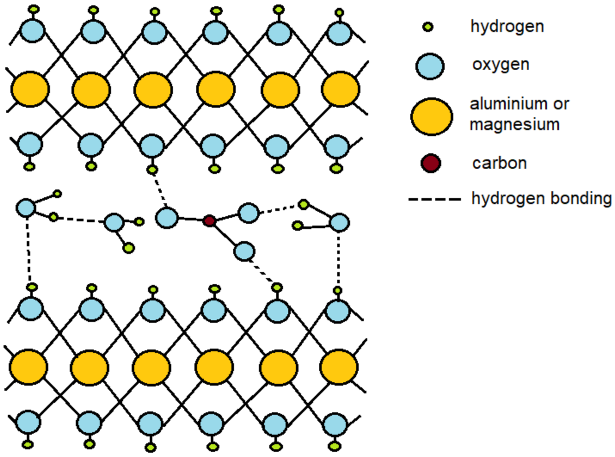

Fig. 1. Structure of hydrotalcite

Currently, HTCs are used in practice as stabilizers in the production of polyolefin goods (HTCs act as acid scavengers). In medicine, they are used as an antacid to neutralize stomach acid (Thürmer 1998; Fink 2010). In both cases, HTCs proved to be effective.

The preparation reaction for the most common form of an HTC is as follows:

$$6Mg(NO_3)_2 + 2Al(NO_3)_3 + Na_2CO_3 + 16NaOH + 4H_2O \rightarrow$$

$$Al_2Mg_6(OH)_{16}CO_3 \, . \, 4H_2O + 18NaNO_3 \qquad (1)$$

While the ratio of Mg^{2+} to Al^{3+} can be either lower or higher than 3, commonly it is in the range of 2 to 5. Basicity increases with the increase of this ratio (Calvini 2012; Conterosito *et al.* 2018). Alternatively, chlorides or organometallic compounds instead of nitrates can be used.

This work considered a series of acidic paper samples modified by various types of HTC and evaluated their suitability for use in the stabilization and deacidification of acidic paper information carriers. The main differences in the preparation of various types of HTCs include the addition of surfactants such as citric acid and/or magnesium stearate, preparation of HTCs from nitrates or chlorides, and different compositions of Mg and Al. Prepared HTCs were tested, and the influence of the different preparation processes on the resulting properties of the product was published by Jurišová (2023).

EXPERIMENTAL

Materials

The materials used for preparation of HTCs included $Mg(NO_3)_2.6H_2O$ p.a. Lachema; $Al(NO_3)_3.9H_2O$ p.a. Lachema; Na_2CO_3 p.a. Lachema; NaOH p.a. Centralchem; $MgCl_2.6H_2O$ p.a. Lachema; $AlCl_3.6H_2O$ p.a. Lachema; Citric acid, anhydrous, p.a. Centralchem; Magnesium stearate, puriss, Sigma Aldrich; Power Powder, Calgon®.

Solvents used for mixed solvent included isopropanol (IPA), (99%, CentralChem), perfluoroheptane (PFH) obtained by distillation of Bookkeepers Deacidification Spray (Preservation Technologies B.V.), and deionized water.

The experiments were preceded by a screening evaluation of various samples of HTC, which varied in preparation, composition, and particle size. The three most promising samples (Table 1) were chosen for more detailed experimentation.

Table 1. Samples of Hydrotalcite, Their Preparation, Composition, and Particle Size

Sample	Form	Preparation	Composition	Particle size (µm)
12B	Powder	Prepared from nitrates	Mg:Al = 5:1	1.94 ± 0.31
14B	Powder	Prepared from nitrates, the addition of 10% citric acid	Mg:Al = 5:1	1.61 ± 0.10
19B	Powder	Prepared from chlorides, the addition of 50% citric acid, 10% magnesium stearate (per product weight)	Mg:Al = 3:1	1.51 ± 0.21

Hydrotalcites were added to the mixed solvent (non-polar solvent – intermediate – water) and formed dispersions.

Synthesis of hydrotalcites

The HTCs were prepared by precipitation at high supersaturation. The HTCs synthesis was performed according to Eq. (1). The Mg:Al ratio was varied from 3:1 to 5:1. In some experiments, chlorides were used instead of nitrate reactants.

Precipitation at high supersaturation

1 M NaOH was poured into the Na_2CO_3 solution immediately in such an amount that after synthesis the $pH = 10$ was reached. At the same time, the solution containing magnesium and aluminum ions was poured into the prepared mixture. The mixture was stirred intensively for 10 min at a speed of 2500 RPM. The result of this rapid synthesis was a colloidal solution. After the end of the synthesis, the suspension was centrifuged and washed with deionized water until the nitrate ions were washed out. Then the product was dried in an oven at 60 °C and ground.

To influence the resulting structure and particle size of hydrotalcites several different surfactants were added to the reaction mixture. More details about the preparation of HTCs and their properties are reported by Jurišová *et al.* (2023).

Test Papers

NOVO-lignin (N-L) is an acidic lignin-containing paper from Klug-Conservation. The N-L sample contains more than 50% mechanical wood pulp (CTMP) with 17% lignin content, the rest consists of bleached cellulose pulp. Test paper N-L contains 12 to 15% kaolin filler. Stock sizing with rosin, and alum was carried out such as to achieve a $Cobb_{60}$

value of 21 g/m^2. The surface pH was 4.0 to 5.0. Grammage was 90 g/m^2. Test paper N-L does not contain any surface sizing, calendaring, or optical brighteners. According to chemical analysis, the treated acidic paper contained 0.87 mg sulfates/1 g of dry paper, 0.164 mg formic acid/1 g of paper, and 0.321 mg acetic acid/1 g of paper. Due to the presence of lignin, this paper undergoes oxidation similar to real lignin-containing papers. This type of degradation was monitored by FTIR spectroscopy to detect the oxidation products.

NOVO - lignin-free (N-LF) is an acidic paper that does not contain lignin, from Klug-Conservation. The N-LF sample contains more than 65% bleached sulfite pulp (hardwood or softwood) with hemicelluloses and can contain up to 35% of different bleached fiber material, and 10 to 15% kaolin filler. Stock sizing with rosin and alum gave a Cobb$_{60}$ value of 20 ± 2 g/m^2. Test paper N-LF does not contain any surface sizing and optical brighteners. This type of model paper allows an indirect determination of the rate of glycosidic bond cleavage, which will be described further in this part.

Modification of Acidic Test Papers by Dispersions with HTC Introduced in Table 1, Denoted as 12B, 14B, and 19B

The dispersion with concentration c = 4.3 g/l was prepared by combining the mixed solvent (PFH – 89.32 vol.%; H_2O – 0.69 vol.%; IPA – 9.99 vol.%) and powder hydrotalcite (Table 1). The test papers were modified by immersing the test papers in the dispersions in a closed reactor placed on a laboratory shaker for 10 min at 99 rpm. Subsequently, the samples were air-dried in a horizontal position at room temperature on sieves made of polyamide threads. All dried samples were stored in an air-conditioned room for 24 hours according to the ISO 187 standard practice (23 ±1 °C, 50 ±1% RH) (ISO 187:1990). Modified and unmodified (control) samples were subjected to accelerated aging for 0, 3, 5, 10, 15, and 30 days in a circulation oven in closed glass bottles at 98 ±1 °C according to the ASTM D6819 - 02 standard (2002).

The gravimetrically determined amounts of captured hydrotalcite on the paper were as follows: N-LF: (0.0097 ± 0.0036) g; and N-L: (0.0084 ± 0.0011) g

Surface pH

The surface pH was determined on the unmodified and modified acidic paper samples according to the standard practice (TAPPI T 529, 2021). The surface pH of the samples was measured by applying 1 drop of distilled water on the paper surface and placing a flat surface pH electrode on the moistened surface, the measurement lasted 2 minutes. The pH was measured on 2 sheets of paper from the top and bottom of the modified paper (min. 3x from both sides), and as the representative value their average value was considered.

Colorimetry

The changes in optical properties of paper samples after modification and accelerated aging were monitored (the change in lightness and color) using the coordinates of the CIE Lab color space (coordinates L^*, a^*, b^*) measured by the SpectroDens A 504009 device. Measurement conditions were D50, 2° observer, without a polarizing filter. The values for 1 sample were obtained as the average value of 10 measurements from the top and bottom of several sheets of paper. These changes were evaluated through the total color difference:

$$\Delta E_{ab}^{*} = \sqrt{(L_1^{*} - L_0^{*})^2 + (a_1^{*} - a_0^{*})^2 + (b_1^{*} - b_0^{*})^2} \tag{2}$$

where $L_0^{*}, a_0^{*}, b_0^{*}$ are values for the unmodified sample at 0 days of aging, and L^{*} lightness, a^{*}, and b^{*} are chromaticity coordinates.

The color change was referenced to the unmodified control sample at 0 days of aging. The ΔE_{ab}^{*} values refer to the change in color due to aging and at the same time to the change in color due to modification. Calculation of errors for total color difference were evaluated using Eq. 3.

$$s\Delta E_{\mathrm{ab}}^{*} = \sqrt{\frac{(L_2-L_1)^2{*}sL_2^2+(L_1-L_2)^2{*}sL_1^2+(a_2-a_1)^2{*}sa_2^2+(a_1-a_2)^2{*}sa_1^2+(b_2-b_1)^2{*}sb_2^2+(b_1-b_2)^2{*}sb_1^2}{(L_2-L_1)^2+(a_2-a_1)^2+(b_2-b_1)^2}} \tag{3}$$

where s is standard deviation.

Folding Endurance

The folding endurance (expressed by the number of double folds) was determined according to standard practice (ISO 5626 1978). The measurement was performed on a Tinius Olsen, MIT Folding Endurance Tester. The paper was subjected to tension and repeated 180 ° bending until it broke (Takeuchi *et al.* 2020). The samples were cut into strips in the machine direction of the fibers with a width of 15 mm and a length of at least 10 cm. The load was set to 0.3 kg. The stabilization effect was evaluated through the coefficient of relative increase of the lifetime for folding endurance (Katuščák *et al.* 2012):

$$S_{\tau,\omega} = \frac{t_{\log\omega=0,\mathrm{m}}}{t_{\log\omega=0,\mathrm{n}}} \tag{4}$$

where $t_{\log\omega=0,\mathrm{n}}$ is an unmodified (reference) sample, and $t_{\log\omega=0,\mathrm{m}}$ modified sample.

$$y = a + b{*}t \tag{5}$$

$$\log\omega = a + b{*}t_{\log\omega} \tag{6}$$

The lifespan of the sample ends when $\log\omega = 0$.

$$0 = a + b{*}\, t_{\log\omega} \tag{7}$$

$$t_{\log\omega} = -\frac{a}{b} \tag{8}$$

where a and b are regression coefficients.

According to the criteria of the Library of Congress and the Kniha$^{\mathrm{SK}}$ consortium, modification systems that ensure a life extension coefficient of at least three times: $S_{\tau,\omega} \leq 3$ are considered effective. In other words, the durability of treated paper should be increased by at least 300% (Katuščák *et al.* 2012).

Limiting Viscosity Number of Cellulose

The degree of polymerization (*DP*) of cellulose was determined by viscometry using a capillary viscometer. The limiting viscosity number was measured according to the standard practice ISO 5351-1 (1981), which specifies the method for the determination of the limiting viscosity number of cellulose in dilute cupriethylene diamine (CED) solution and applies to CED-soluble samples of cellulose.

The average degree of polymerization was expressed based on the limiting viscosity number using the Mark-Houwink equation (Evans and Wallis 1989; ISO/TS 18344 2015),

$$DP^{0.9} = 1.65 * [\eta] \tag{9}$$

where DP is the degree of polymerization, and $[\eta]$ is the limiting viscosity number (mL/g).

The rate of glycosidic bond cleavage was calculated following the procedure (Calvini 2012) using the relationship,

$$\frac{1}{DP_{\mathrm{t}}} - \frac{1}{DP_0} = k * t \tag{10}$$

where DP_0 is the degree of polymerization at 0 days of accelerated aging for a given sample, DP_{t} degree of polymerization at time t (time of accelerated aging, (days)), and k empirical constant (day^{-1}).

FTIR Spectroscopy

FTIR spectroscopy was used to monitor the changes in the absorption peaks belonging to the oxidative degradation products of the paper. The measurement was performed on a Thermo Scientific™ Nicolet IS20 benchtop FTIR spectrometer. The degree of oxidation was assessed by calculating the oxidation index (Łojewska *et al.* 2005),

$$oxidation\ index = \frac{I_{1730}}{I_{1620}} \tag{11}$$

where I is the standardized integral at a certain wavelength (the most intense maximum), I_{1730} is 1664 to 1837 cm^{-1}, and I_{1620} is 1500 to 1664 cm^{-1}.

These absorbance bands represent functional groups of cellulose oxidation products: carboxyl or aldehyde groups (1730 cm^{-1}) and carbonyl groups (1620 cm^{-1}).

Gravimetry

Papers N-L and N-LF were modified by dispersion with HTC 14B. Papers were cut to A6 format. 10 samples of each type of paper were used.

Paper samples were weighed before modification, then modified, air-conditioned for 24h (23 ±1 °C, 50 ±1% RH), and weighed again.

SEM – EDS

The measurement of Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was performed on a JOEL JMS – 7600F device with the detector WDS and EDS (Oxford instruments X-Max (50 mm^2). Before the measurement, all the samples were placed into the holder and coated with Au - Sputtercoater SCD 040, BalzersUnionPro. The elementary distribution was processed by picture analysis in Matlab.

Measurement parameters were WD 15.0 mm and acceleration voltage: 5 kV. Software evaluation was done using by INCA, with measurement mode: mapping - SmartMapSetup (Frames 500).

RESULTS AND DISCUSSION

In terms of evaluating the effectiveness of stabilization processes, one of the most important criteria is the ability to achieve complete and permanent neutralization of acids. The effectiveness of deacidification is determined by the measurement of the (surface) pH value of the deacidified paper (Buchanan *et al.* 1994; Directorate 2004).

According to the current research (Jurišová *et al.* 2023) on new deacidification systems, hydrotalcites in combination with mixed solvent (isopropanol – perfluoroheptane – water) represent a neutralizing agent that could provide deacidification of paper carriers. The presence of water ensures the swelling of cellulose fibers which promotes the penetration of hydrotalcite particles into the paper structure. In addition, water is expected to enable reaction between the acidic groups in the paper and the HTC. Isopropanol is an intermediate that ensures the miscibility of PFH with water, since PFH and water are immiscible under normal conditions. The ratio of these three substances is also important (Jurišová *et al.* 2023). An excessive amount of water and, in the present work, an intermediate has a negative effect on paper carriers of information. Therefore, they should be added in the smallest amount possible, but at the same time in such a way that they fulfill their function – ensuring miscibility.

The HTCs considered in this article differed in particle size, preparation, and composition. Citric acid was added to hydrotalcite 14B and 19B (Table 1) due to its ability to affect the resulting particle size. Magnesium stearate acts as an anticoagulant and was added to hydrotalcite 19B. Hydrotalcite 19B is also different in composition, in that the ratio of Mg:Al is lower than in the other two samples.

Surface pH

After modification of both test papers with all three HTCs dispersions, there was an improvement in the properties of the paper in terms of increased surface pH (compared to the control sample) (Fig. 2 and 3). The dispersion with the active substance 14B appeared to be the most suitable. The surface pH of the sample modified by using this substance increased the most when compared to the control samples. An increase of 1.3 to 1.9 units for N-LF and 1.6 to 2.7 units for N-L was recorded. The dispersion with the active substance 19B appeared to be the least successful; the pH of modified samples did not exceed the value of 5. Paper with lignin content (N-L) (Fig. 2) showed higher pH values after modification with all three modification systems than paper without lignin content (N-LF) (Fig. 3). With all the dispersions and both test papers, the acidic pH range was monitored, which means that no alkaline reserve had been formed. The error bars show the evenness of the distribution of hydrotalcite on the surface of the paper.

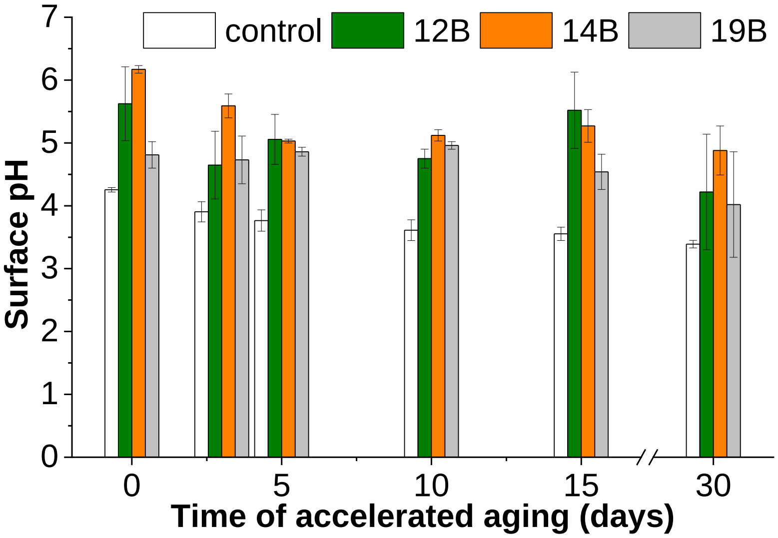

Fig. 2. Comparison of the pH of the control (unmodified) sample with the modified samples (12B, 14B, and 19B) on the testing paper N-LF

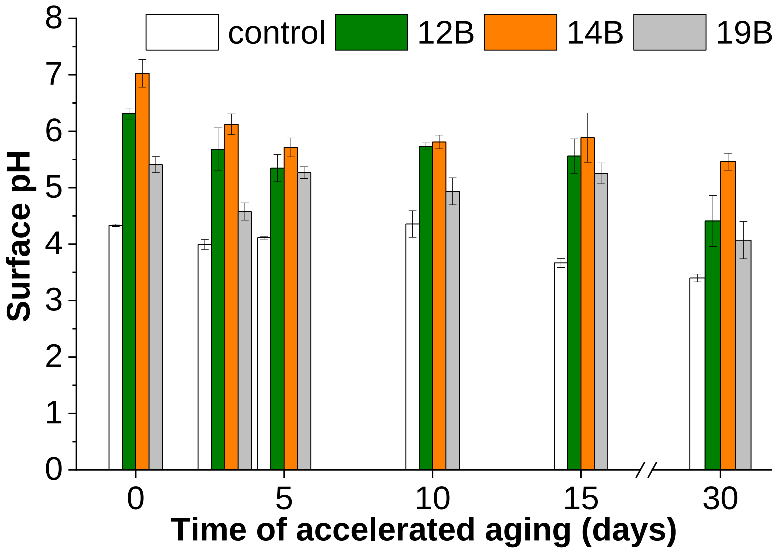

Fig. 3. Comparison of the pH of the control (unmodified) sample with the modified samples (12B, 14B, and 19B) on the testing paper N-L

Measurement deviations for N-L paper were small, which means an even distribution of hydrotalcites. For N-LF paper, the error bars increased after 30 days of accelerated aging, which can be caused by changes in paper structure during aging. In both cases (N-L and N-LF), dispersion with hydrotalcite 12B exhibited the largest measurement deviations compared to 14B and 19B. Due to the error bars, it can be said that hydrotalcite particles 14B and 19B were equally distributed for both types of paper, and 12B particles were equally distributed for N-L paper but not for N-LF.

Colorimetry

Aged acid papers darken and turn yellow due to degradation. Color changes due to aging can be objectively evaluated through trichromatic colorimetry. In this work, the CIE $L^*a^*b^*$ color model was used. The coordinate L^* stands for lightness, the a^* value indicates the red-green component of color, and the yellow and blue components are represented by the b^* value. The color change is evaluated using the total color difference ΔE^*_{ab}, which considers both the lightness difference and the difference in the chromatic plane (Singh *et al.* 2009).

As a result of aging, the L^* coordinate decreased. At the same time, the a^* and b^* coordinates also changed. The coordinate b^* changed more significantly than a^*. Samples mainly turned yellow and darkened due to aging.

The modification itself did not affect the color of the paper before aging (Fig. 4). The ΔE^*_{ab} values (relative to the unmodified unaged sample) increased with aging time for both the unmodified control sample and the modified samples (Fig. 5 and 6). However, after the modification of the N-LF paper, the changes of ΔE^*_{ab} values were much slower (Fig. 5), which signifies a prominent improvement of the optical properties after the modification (for all three dispersions). There was no such improvement regarding the N-L paper (Fig. 6). In the case of dispersions with the active substance 12B and 19B, the optical properties worsened compared to the control sample.

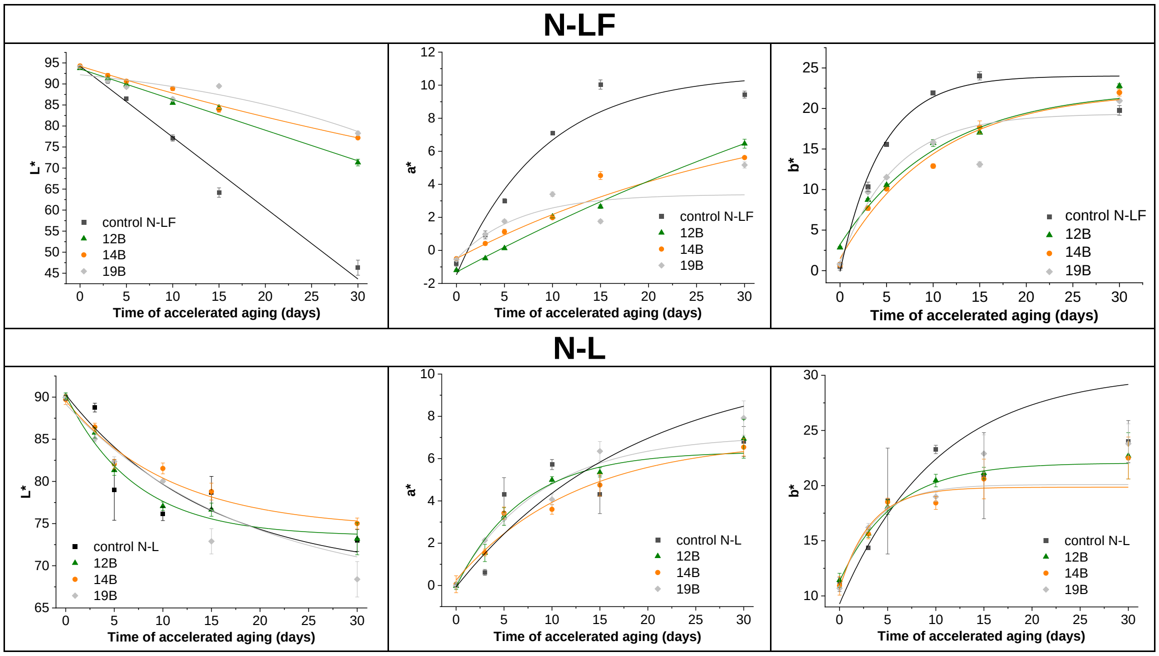

Fig. 4. Colorimetry results of *L*a*b** coordinates

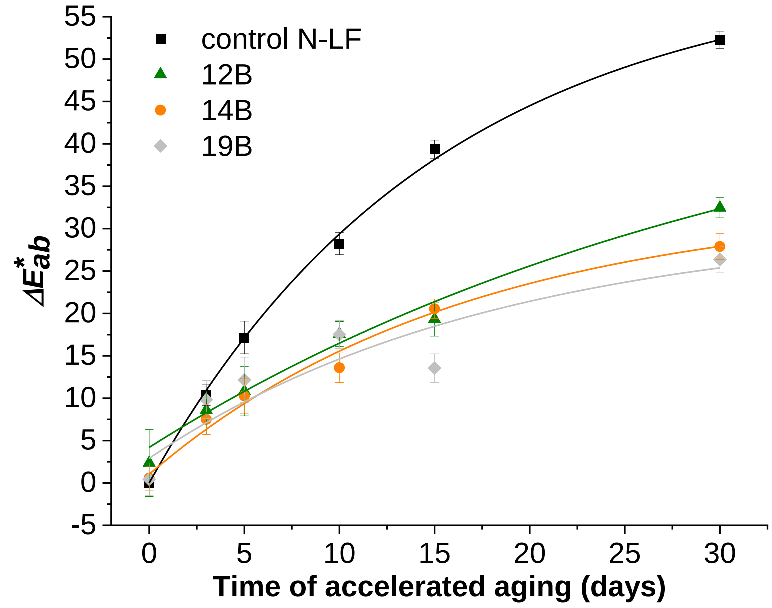

Fig. 5. Color changes of aged paper samples expressed by total color difference (ΔE^*_{ab}) of control and modified papers for test paper: N-LF. *ΔE^*_{ab} - values refer to an unmodified, unaged sample.

Consistent with the results of the surface pH measurement, the dispersion with the active substance 14B seems to be the most suitable one while the dispersion with the active substance 12B provides the worst results.

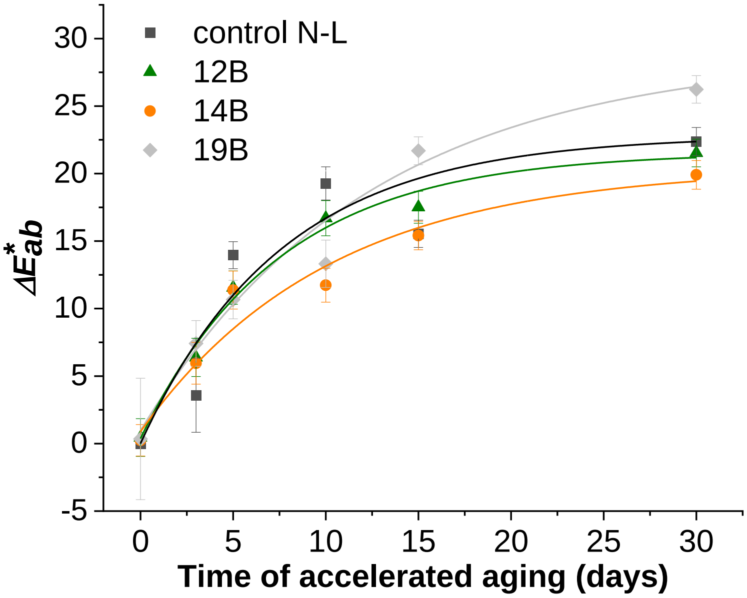

Fig. 6. Color changes of aged paper samples expressed by total color difference (ΔE^*_{ab}) of control and modified papers for test paper: N-L. *ΔE^*_{ab} - values refer to an unmodified, unaged sample

Folding Endurance

Folding endurance is a mechanical property that serves to express the life and durability of paper in terms of mechanical stress (fragility). Results from tests are in Table 2 and Fig. 7.

The change in mechanical properties after modification is expressed by the coefficient of relative increase of the lifetime $S_{\tau,\omega}$ and testifies to the effectiveness of the selected stabilization procedure.

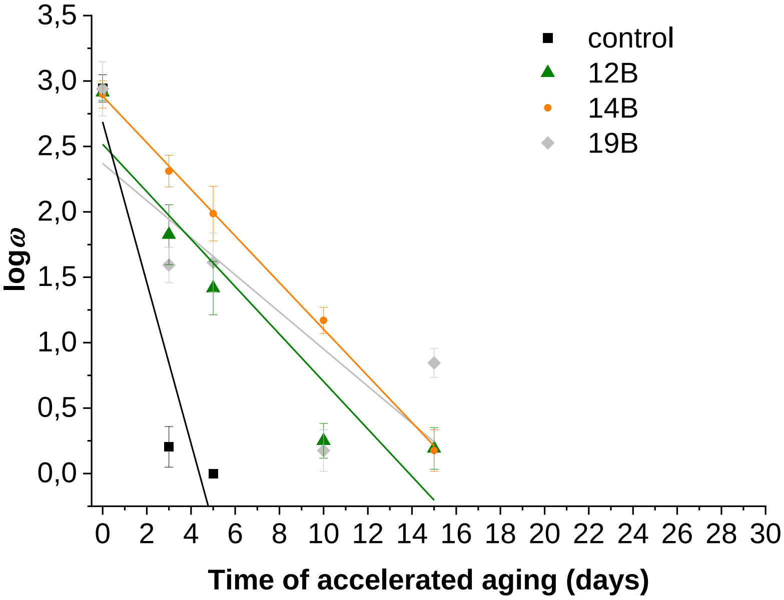

Fig. 7. Dependence of logω on time of accelerated aging for the control sample and samples modified with dispersion with active substance 12B, 14B, and 19B for test paper N-LF fitted by a linear function.

Table 2. Measurement of the Folding Endurance

	Time of accelerated aging (days)	**N-LF**		**N-L**	
		ω (double folds)	$S_{\tau,\omega}$	ω (double folds)	$S_{\tau,\omega}$
control	0	872 ± 195	-	420 ± 163	-
	3	2 ± 1		258 ± 113	
	5	1 ± 0		6 ± 1	
	10	0 ± 0		2 ± 0	
	15	0 ± 0		2 ± 0	
	30	0 ± 0		1 ± 0	
12B	0	819 ± 113	3.17	468 ± 108	1.11
	3	67 ± 32		189 ± 61	
	5	26 ± 12		33 ± 13	
	10	2 ± 0		2 ± 0	
	15	2 ± 1		2 ± 1	
	30	0 ± 0		2 ± 1	
14B	0	789 ± 186	3.70	493 ± 191	1.20
	3	205 ± 60		253 ± 117	
	5	97 ± 37		18 ± 5	
	10	15 ± 4		13 ± 6	
	15	2 ± 1		3 ± 1	
	30	0 ± 0		2 ± 1	
19B	0	871 ± 411	3.82	497 ± 137	1.01
	3	39 ± 12		103 ± 59	
	5	41 ± 21		27 ± 9	
	10	2 ± 1		3 ± 0	
	15	7 ± 2		2 ± 1	
	30	0 ± 0		1 ± 1	

Note: Folding endurance is expressed by the number of double folds "ω" and the value of the life extension coefficient of the modified and control samples for the N-LF and N-L test papers

The $S_{\tau,\omega}$ is calculated based on the linear relationship between log ω and time, which is shown in Fig. 7. The value of “time” at logω = 0 represents the point when it is no longer possible to measure the given property, *i.e.* the paper is completely fragile and falls apart.

In the case of lignin-free paper (N-LF), it was problematic to measure the unmodified control sample after only 5 days of accelerated aging (Table 2, Fig. 7). The values of the life extension coefficients of N-LF paper were higher than 3 in all three cases (Table 2), which illustrates a good stabilization effect. The values of the life extension coefficient of the N-L paper (Table 2) were lower than 3, which means insufficient stabilization in terms of mechanical properties. The highest value was recorded for the 14B dispersion ($S_{\tau,\omega}$ = 1.21).

Limiting Viscosity Number of Cellulose

The degree of polymerization (*DP*) decreases rapidly during the process of cellulose degradation in an acidic environment, especially due to acid hydrolysis (Ahn *et al.* 2019). The results are summarized in Table 4 and Fig. 8. The measurement was carried out according to (ISO 5351-1 1981), which states that at least 2 determinations shall be made and the difference between their results shall not be greater than 2.5%. In this case, the difference was 0.8%.

Table 3. Determination of Average Degree of Polymerization (*DP*) of Cellulose using Limiting Viscosity Number and Determination of Glycosidic Bond Cleavage *k*t* for N-LF

sample	Time of accelerated aging (days)	[*η*] ($ml \cdot g^{-1}$)	*DP*	*k*t*
control	0	465	1606	$1.03*10^{-3}$
	3	156	478	
	5	124	369	
	10	96	277	
	15	77	219	
	30	68	190	
12B	0	439	1505	$2.46*10^{-4}$
	3	258	834	
	5	219	694	
	10	168	517	
	15	146	442	
	30	96	278	
14B	0	474	1640	$1.04*10^{-4}$
	3	308	1016	
	5	250	805	
	10	201	633	
	15	161	495	
	30	105	307	
19B	0	447	1537	$4.05*10^{-4}$
	3	219	697	
	5	214	679	
	10	149	454	
	15	184	573	
	30	113	333	

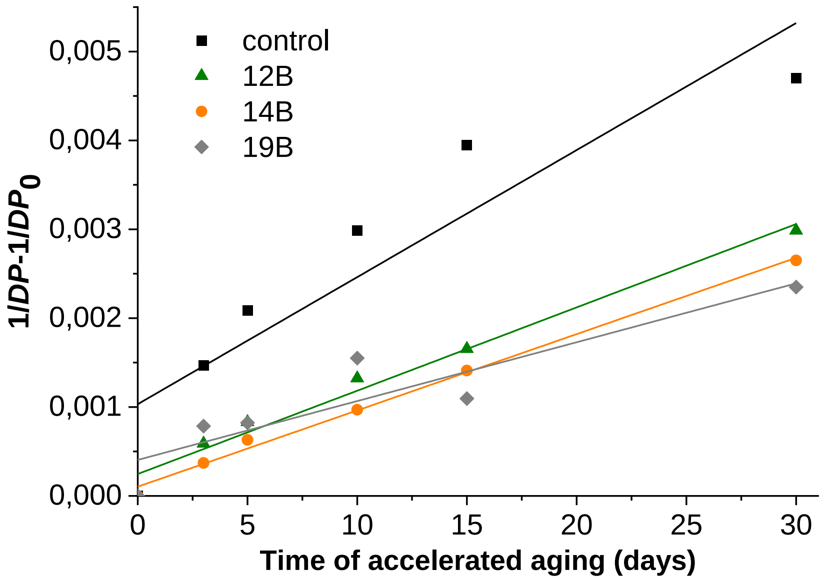

Fig. 8. Rate of glycosidic bond cleavage for control and modified sample with dispersion with active substance 12B, 14B, and 19B for test paper N-LF

The *DP* of the unaged samples did not change after the modification, which indicates that the modification itself did not cause changes in the chemical structure of the polymer. The *DP* values of the modified samples subjected to accelerated aging decreased more slowly significantly compared to the aged unmodified control sample (Table 3). Deacidification using dispersion of hydrotalcite 14B again achieved the best results.

The graph in Fig. 8 expresses the rate of glycosidic bond cleavage. The lower the value of the regression coefficient ($k*t$), the lower the rate of cleavage. As shown in the graph, the intercept values decreased by an order of decimal magnitude for all three dispersions. The dispersion with the active substance 14B achieved the slowest rate of glycosidic bond cleavage (Table 3).

FTIR

Values of absorbance belonging to the maxima at 1730 cm^{-1} representing carboxyl or aldehyde groups and at 1620 cm^{-1} representing carbonyl groups were obtained from the FTIR spectra. Figure 9 shows the values of the ratio of two integrals (I_{1730}, I_{1620}) - an index defining the oxidation state of cellulose (oxidation index). The oxidation index was read from the spectra shown in Fig. 10 (the spectra for the other modifications - 14B, and 19B have a very similar course). N-LF paper was not subject to oxidation and therefore FTIR was measured only on N-L paper. After modification with all three dispersions, there was a slight decrease in the formation of oxidation degradation products, which is indicated by the lower values of the oxidation index (Fig. 9).

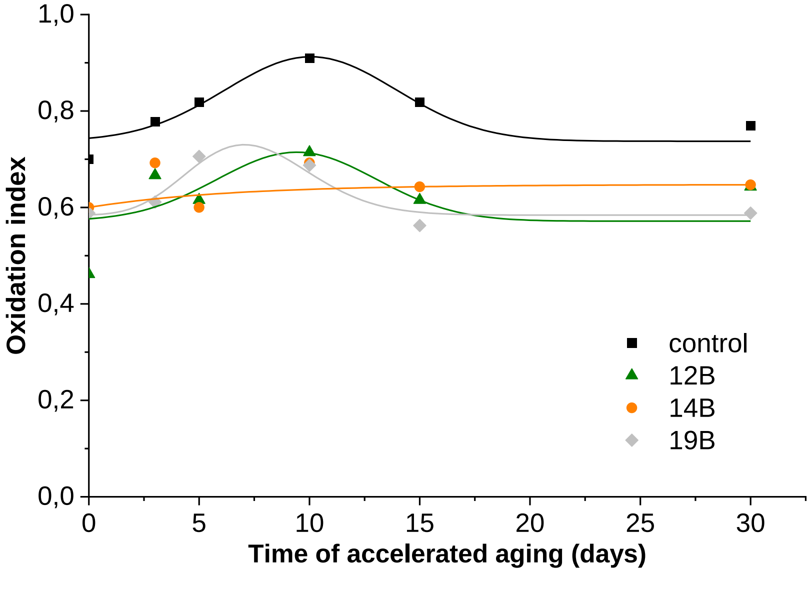

Fig. 9. Comparison of the oxidation index of control and modified samples for test paper N-L

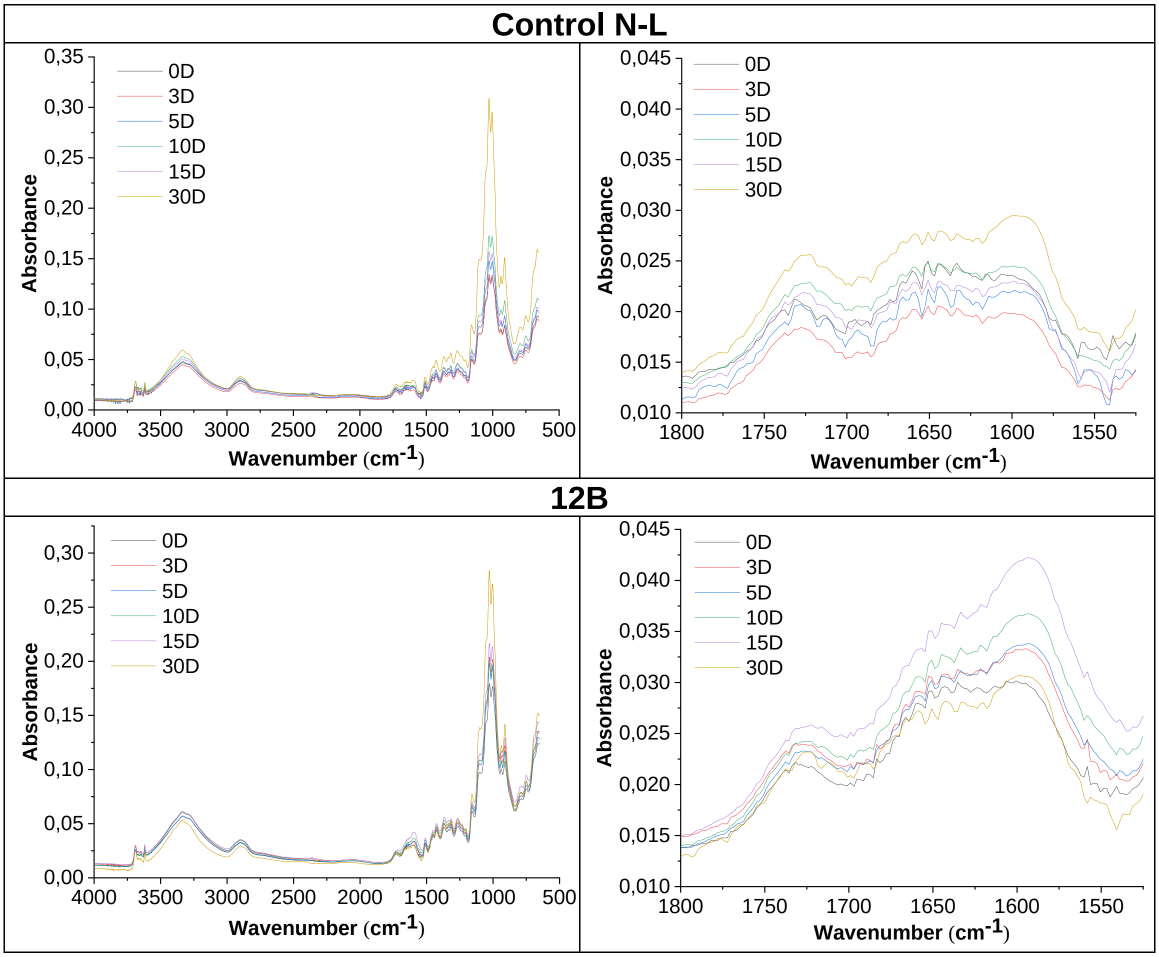

Fig. 10. FTIR spectra of Control N-L and modified N-L paper by HTC 12B

Analysis of Mechanism

In the sizing process of paper with rosin and alum, a hexadental complex of aluminum and acids in rosin (particularly abietic acid) is expected (Marton 1989; Hubbe 2004; Hubbe 2006; Bergvall 2013; Xu *et al.* 2016). This complex bound to oxygen groups on the cellulose polymer backbone has a positive charge, which is compensated by HSO^{4-} anions and polyanions (Sarpola *et al.* 2007). While the complex remains stable, the hydrolyzing effect of Al^{3+} cations and polycations, as well as hydrogensulfate anion and polynions are rather low (Sarpola *et al.* 2007). However, the oxidation stability of rosin acids is weak. For example, abietic acid can be oxidized at room temperature (Ren *et al.* 2015). Due to the action of aluminum atoms, this oxidation can be even increased (metal-oxygen catalysis). Degradation of rosin acid skeletons releases aluminum and sulfate moieties, hydrophobicity is lost, water can penetrate the body of paper more easily, and the degradation process of polymeric cellulose chains is accelerated. It is worth noting about Al$_2$(SO$_4$)$_3$ (AS) concentration and pH; a typical addition of alum to the pulp is less than 1 wt. % and the content of water in the paper under normal room/operation conditions is in the range of 5 to 10 %. If one considers the upper level (10 %), then the neighborhood of cellulose chains is 10 wt. % of Al$_2$(SO$_4$)$_3$, *i.e.* about 0.3 mol/kg of the dispersion. In the framework of the authors' research project (Ambrova *et al.* 2022), an investigation of pH in various dispersions and titration of HTC dispersion was carried out. It was found that pHs of AS solutions even of lower concentrations were very low: 1 wt.%: 3.22; 9.1 wt.%: 2.52; 16.7 wt.%: 2,20. So, hydrolytic conditions in the mutual vicinity of hydrophilic cellulose polymer chains are expected to be much more severe than indicated by pH measured at the surface. Titration experiments with HTCs ($Mg_6Al_2(OH)_{16}CO_3.4H_2O$), 1 wt. % water suspension, using H_2SO_4 and CH_3COOH (representant of organic acid degradation products) showed:

- Up to reaching about 30% extent of the reaction (12), the pH decreased from 8.3 to 4.

$$Mg_6Al_2(OH)_{16}CO_3.4H_2O + 9\ H_2SO_4 \rightarrow 6\ MgSO_4 + Al_2(SO_4)_3 + 21\ H_2O + CO_2 \quad (12)$$

- Up to 90 % of the extent of the reaction (12) the pH remained constant equal to about 4.
- From 90 % to 100 % extent of reaction (12) the pH dropped to about 2, i.e. close to the above-mentioned values of pH for concentrated AS.

This physical-chemical analysis showed that HTCs and their dissolved species can act as a buffer in the environment of cellulosic polymer chains. Since HTC exhibits mild alkaline properties only at the start of action, hydrolysis in alkaline conditions (Jablonský and Šima 2020), e.g. as in using magnesium, or even more severe: calcium, deacidifying agents, virtually does not exist. The positive effect of HTC was also shown by measurements of surface pH (Table 4) and SEM (Fig. 11) on samples 3 years after the treatment.

Figure 11 shows that the HTC particles dissolve over time.

Table 4. Surface pH of Modified Unaged Samples on N-L Paper after 3 Years of Natural Aging

	Right after modification	**After 3 years**
Control	4,33 ± 0,02	4,54 ± 0,02
12B	6,31 ± 0,10	5,78 ± 0,16
14B	7,03 ± 0,25	6,55 ± 0,12
19B	5,41 ± 0,14	5,93 ± 0,09

After 3 years of natural aging, the surface pH was almost unchanged, if the errors are considered.

Scanning Electron Microscopy SEM

Graphical illustrations of modified samples were added to better illustrate the changes after modification (Fig. 11). Figure 11 also shows the changes after 3 years of natural aging of modified paper.

Neutralization of acids in paper by hydrotalcite can take place in two ways. One way is that hydrotalcite acts as an acid scavenger when it traps acids in its structure. The HTC has ion exchange capabilities. The mechanism is shown in Fig. 12. The SO_4^{2-} ions were chosen for the neutralization demonstration because aluminum sulfate is considered to be the main source of acidity in paper according to Brønsted and Lewis's theory (Baty *et al.* 2010b). The second method of neutralization is the reaction of acids with Mg^{2+} ions, which enter the paper by dissolving HTC.

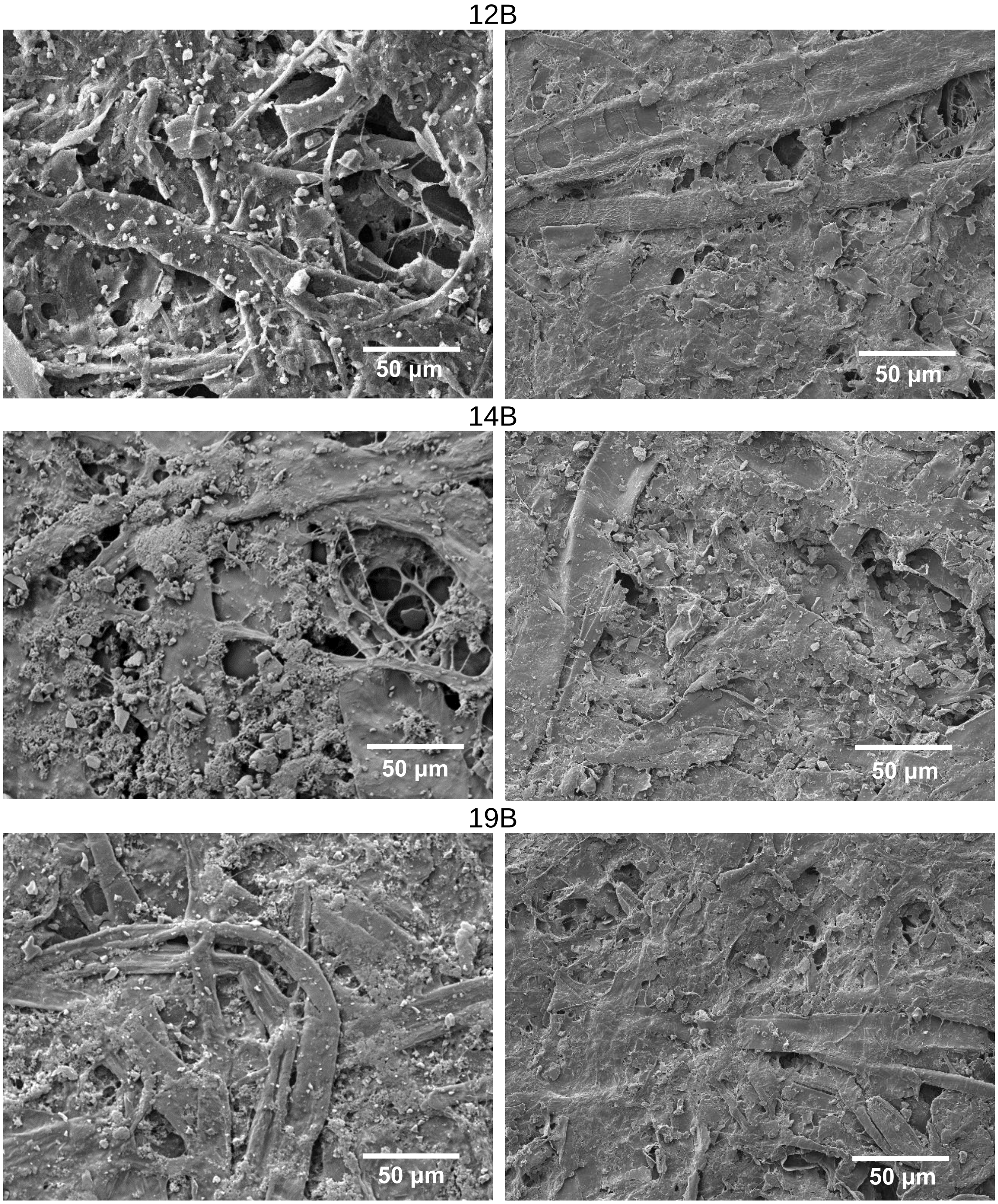

Fig. 11. SEM images of paper surface at 500x magnification of control and modified samples immediately after treatment (on the left) and after 3 years (on the right)

HTC is unstable in water and, depending on the pH, magnesium cations and possibly aluminum cations are released. In Jobbágy and Regazzoni (2011), it was reported that in the range $5.0 \leq pH \leq 9.0$, the dissolution of Al^{3+} from HTC was zero and only leaching of Mg^{2+} was observed. The amount of leached Mg^{2+} increased rapidly with decreasing pH, but it soon leveled off, despite the solution being undersaturated concerning $Mg(OH)_2$. Thermodynamically, in this pH range, the aqueous phase is supersaturated relative to amorphous $Al(OH)_3$, so the dissolution of HTC is incongruent and should be accounted for:

$$[Mg_xAl_y(OH)_{(3y+2x-2)}]CO_3 + 2x\ H_3O^+ \rightarrow$$
$$x\ Mg^{2+} + \ y\ Al(OH)_3\ (am) + (4*x-1)\ H_2O + CO_2 \qquad (13)$$

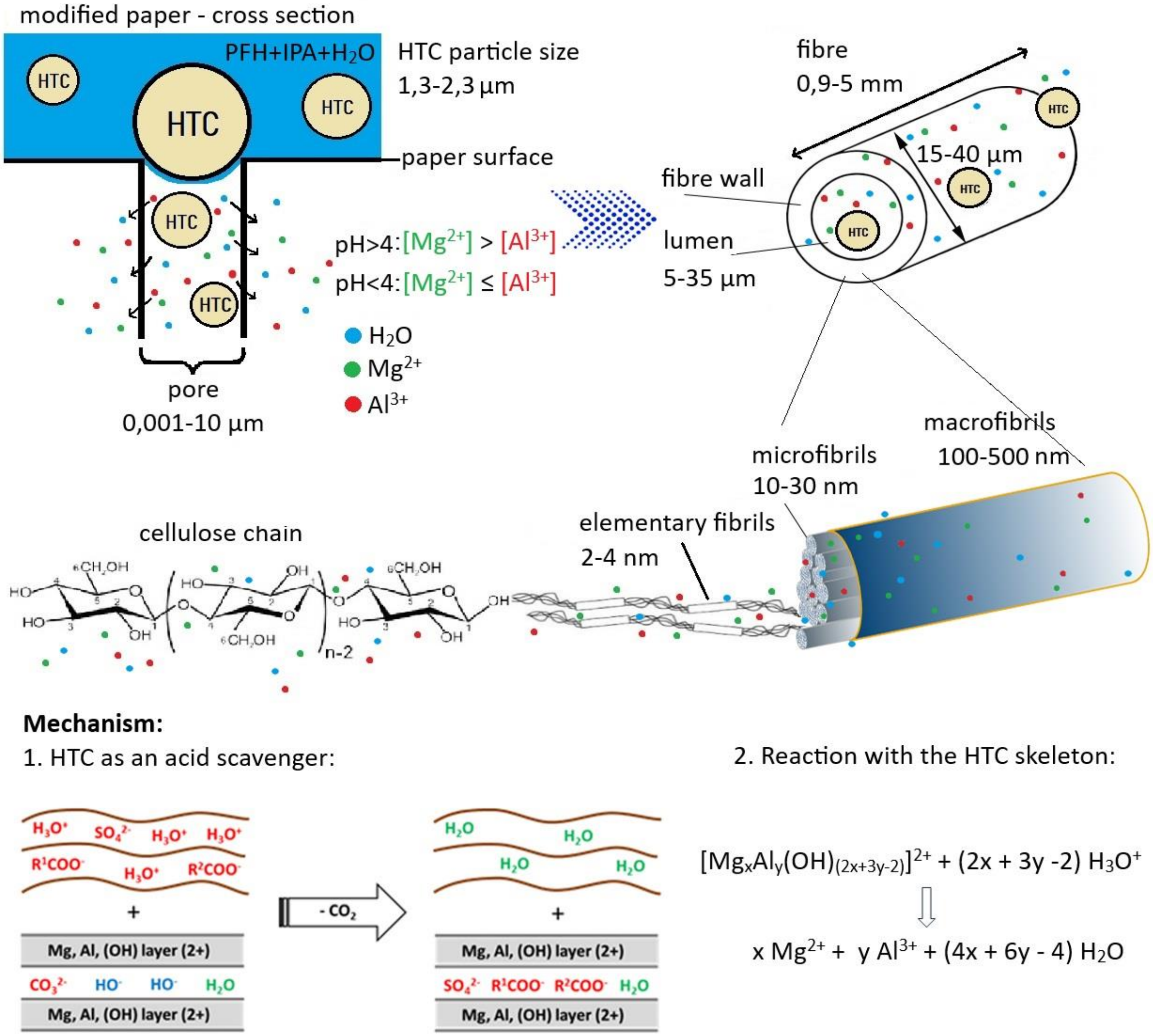

Fig. 12. Graphical illustration of mechanism analysis

The amorphous $Al(OH)_3$ formed a passive layer that prevented further leaching of Mg^{2+}. At pH ≤ 4.0, the HTC dissolved congruently. Al^{3+} dissolved and so did the passive layer that prevented further Mg^{2+} release.

$$[Mg_xAl_y(OH)_{(3y+2x-2)}]CO_3 + (2x+3y)\ H_3O^+ \rightarrow$$
$$x\ Mg^{2+} + \ y\ Al^{3+} + (4*x+6*y-1)\ H_2O + CO_2 \qquad (14)$$

Figure 12 also shows the penetration of HTCs into the paper structure as a function of particle size. The undissolved HTCs entered maximally into the lumen of the paper fiber.

Once the HTCs were dissolved, both Mg and Al ions reached the level of the cellulose chain where acid hydrolysis occurs.

The assumption of hydrotalcite penetration depth of the paper structure is supported by SEM-EDS (Scanning Electron Microscopy - Energy Dispersive Spectroscopy) measurements (Fig. 13). It was measured for papers modified by HTC 14B, as the HTC 14B showed the best results among all HTCs tested.

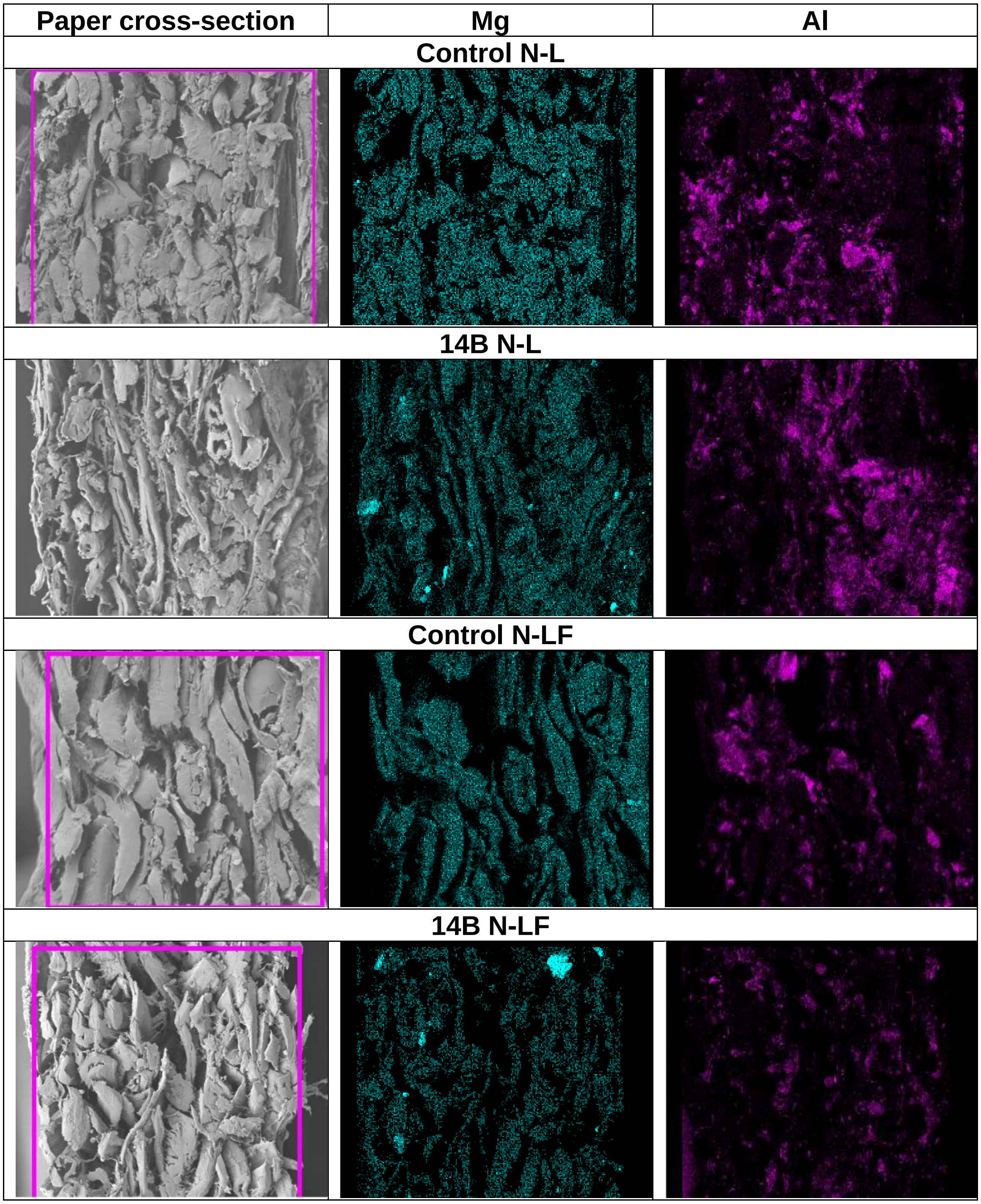

Fig. 13. SEM-EDS images of the cross-section of control paper and modified samples by HTC 14B

Table 5. Quantity of Analyzed Elements Before and After Modification

	Mg wt. %	Al wt. %
Control N-L	0.06	5.05
N-L 14B	0.43	7.66
Control N-LF	0.15	6.56
N-LF 14B	0.47	7.17

Figure 13 shows the elemental maps of Al and Mg as the main components of hydrotalcite and the distribution of these elements in the cross-section of the paper. The content of both elements increased after modification (Table 5). After modification, the larger particle clusters of Mg, representing HTC particles, were mainly visible on/near the paper surface area.

In the unmodified sample, Mg is found as a process element. It enters the paper from the water during pulping. It is used as a stabilizer in peroxide bleaching and is already present in the wood itself. Aluminum is added to the unmodified paper in the form of a filler – kaolin (Sixta 2006).

CONCLUSIONS

1. The experiments tested three differently prepared samples of hydrotalcites differing in Mg^{2+} to Al^{3+} ratio (12B, 14B, 19B) to determine the suitability of their use for stabilization and deacidification of acidic paper information carriers. All three hydrotalcite samples were in a powder form with an average particle size of 1.5 to 2 μm, and Mg:Al ratio 5:1 (12B, 14B), or 3:1 (19B). Two types of acidic test paper samples were chosen for treatment: with lignin (N-L), on which the effect of oxidation can be monitored, and lignin-free N-LF which enables monitoring of the glycosidic bond cleavage – the effect of hydrolysis. Using accelerated aging, the effectiveness of three different hydrotalcites as a deacidifying agent on modified samples was evaluated.
2. The surface pH after modification increased for all samples (aged and unaged). The major improvement occurred in the paper modified with dispersion with the active substance 14B. The surface pH increased by 1.3 to 1.9 units for N-LF paper and by 1.6 to 2.7 units for N-L paper. Probably these best results were obtained due to the high ratio of Mg:Al (equal to 5), low size of the particle (1.61 μm), and utilization of citric acid as a modifier during synthesis of HTC. However, no alkaline reserve was created, which is indicated by the fact that the surface pH values remained in the acidic range even after the modification.
3. Based on the evaluation of the optical parameters, the modification process itself does not affect the color of the paper and does not leave deposits of white hydrotalcite powder on the surface. In all three cases, an improvement in colorimetric parameters was detected in comparison to the unmodified control sample during accelerated aging.
4. The mechanical properties defined by the folding endurance measurement did not change immediately after the modification. After accelerated aging, the mechanical properties of all modified samples improved compared to unmodified samples. The coefficient of relative increase of the lifetime $S_{\tau,\omega}$ in the case of N-LF paper exceeded

the value of 3 for all three modifications. For the N-L paper the $S_{\tau,\omega}$ increased, but not enough (it did not exceed the value of 1.5).

5. Based on the measurement of the limiting viscosity number, the modification itself does not have a negative effect on the change in DP. The rate of glycosidic bond cleavage decreased by the order of decimal magnitude for all three modifications. After the modification, there was a decrease in the amount of oxidative degradation products.
6. From the point of view of the stabilization of acidic paper information carriers, based on the evaluation of all measurements, hydrotalcite 14B appeared to be the most promising type of hydrotalcite. The composition of hydrotalcite 14B differed from hydrotalcite 19B in the ratio of Mg to Al - the higher Mg content led to better results. Unlike hydrotalcite 12B, citric acid was added during the preparation of hydrotalcite 14B, which acted as a growth inhibitor. The particles of 14B were smaller. Smaller particles penetrate deeper into the paper structure, which ensures more effective deacidification of the paper, due to the penetration of the effective deacidification component deeper into the lower levels of the fibrous structure of the paper.
7. Although no experiment achieved an increase of pH to a value of 7, or higher, it is possible to consider HTCs as promising candidates for deacidification. Organic acids formed by hydrolysis and oxidation of cellulose are neutralized by hydrotalcite even at a pH lower than 7, hence, free acids do not accumulate in paper preserved in this way - similarly, to the action of HTCs as antacids. However, in the present case, the rate of transport of acidic and alkaline compounds in the paper should also be taken into consideration.

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REFERENCES CITED

Ahn, K., Zaccaron, S., Rosenau, T., Potthast, A., and Gadolin, J. (2019). “How alkaline solvents in viscosity measurements affect data for oxidatively damaged celluloses: Cupri-ethylenediamine,” *Biomacromolecules* 20(11), 4117-4125. DOI: 10.1021/acs.biomac.9b00956

Ambrová, M., Danielik, V., and Králik M. (2022). “Evaluation of applicability of hydrotalcites (Hodnotenie vhodnosti hydrotalkitov, in Slovak),” Report. Slovak University of Technology, Bratislava, project: MUFUSCEM, APVV-18-0155.

Anonymous (2004). “Library of Congress Technical specifications for mass deacidifications,” *Preservation Directorate Library of Congress*. (https://www.loc.gov/preservation/resources/rt/MassDeacidification.pdf)

Area, M. C., and Cheradame, H. (2011). “Paper aging and degradation: Recent findings and research methods,” *BioResources* 6(4), 5307-5337. DOI: 10.15376/biores.6.4.5307-5337

ASTM D6819 - 02. (2002). “Standard test method for accelerated temperature aging of printing and writing paper by dry oven exposure apparatus," ASTM International, West Conshohocken, PA, USA.

Banik, G., and Brückle, I. (2018). *Paper and Water : A Guide for Conservators* (Vol. 634), Siegl, München, Germany.

Baty, J. W., Maitland, C. L., Minter, W., Hubbe, M. A., and Jordan-Mowery, S. K. (2010b). "Deacidification for the conservation and preservation of paper-based works: A review," *BioResources* 5(3), 1955-2023.

Bergvall, N. (2013). "Optimizing the cost efficiency for internal sizing of kraft liner paper grades," Thesis. Umea University.

Buchanan, S., Bennett, W., Domach, M. M., Melnik, S. M., Tancin, C., Whitmore, P. M., Harris, K. E., and Shahani, C. (1994). "An evaluation of the bookkeeper mass deacidification process," Technical evaluation team report for the preservation directorate. www.loc.gov/preservation/

Calvini, P. (2012). "The role of the Ekenstam equation on the kinetics of cellulose hydrolytic degradation," *Cellulose* 19(2), 313-318. DOI: 10.1007/s10570-011-9645-5

Cavani, F., Trifirb, F., and Vaccari, A. (1991). "Hydrotalcite-type anionic clays: Preparation, properties, and applications," *Catalysis Today* 11, 173-301. DOI: 10.1016/0920-5861(91)80068-K

Conterosito, E., Gianotti, V., Palin, L., Boccaleri, E., Viterbo, D., and Milanesio, M. (2018). "Facile preparation methods of hydrotalcite layered materials and their structural characterization by combined techniques," *Inorganica Chimica Acta* 470, 36-50. DOI: 10.1016/J.ICA.2017.08.007

Directorate, P. (2004). "Library of Congress technical specifications for mass deacidification," (www.loc.gov/preservation/)

Ďurovič, M. (2002). "Mass deacidification of paper archives" ("Hromadné odkyslování papírových archiválií," in Czech), *Praha: Státní ústřední archiv*.

Erhardt, D., and Tumosa, C. S. (2005). "Chemical degradation of cellulose in paper over 500 years," *Restaurator* 26(3), 151-158. DOI: 10.1515/rest.2005.26.3.151

Evans, R., and Wallis, A. F. A. (1989). "Cellulose molecular weights determined by viscometry," *Journal of Applied Polymer Science* 37(8), 2331-2340. DOI: 10.1002/APP.1989.070370822

Fink, J. K. (2010). *A Concise Introduction to Additives for ThermopIastic PoIymers*. Scrivener Publishing, LLC, Beverly, MA, USA.

Grossenbacher, G. (2006). "Paper deacidification as a measure for preserving originals," Bern: Swiss National Library.

Guzikiewiczová, E. (2021). "Testovanie nových hydrotalkitov pre vývoj stabilizačných sústav," thesis, FCHPT STU.

Hroboňová, K., Jablonský, M., Králik, M., and Vizárová, K. (2023). "Advanced sampling, sample preparation and combination of methods applicable in the analysis of compounds in aged and deacidified papers. A minireview," *Journal of Cultural Heritage* 60, 95-107. DOI: 10.1016/J.CULHER.2022.05.002

Hubbe, M. A. "Additives and Ingredients". (https://hubbepaperchem.cnr.ncsu.edu/additives-and-ingredients/)

Hubbe, M. A. (2004). "Acidic and alkaline sizings for printing, writing, and drawing papers," *The Book and Paper Group Annual* 23, 139.

Hubbe, M. A. (2006). "Paper's resistance to wetting – A review of internal sizing chemicals and their effects," *BioResources* 2(1), 106-145.

Hubbe, M. A., Smith, R. D., Zou, X., Katuščák, S., Potthast, A., and Ahn, K. (2017).

"Deacidification of acidic books and paper by means of non-aqueous dispersions of alkaline particles: A review focusing on the completeness of the reaction," *BioResources* 12(2), 4410-4477. DOI: 10.15376/biores.12.2.4410-4477

Hubbe, M.A., Maitland, C., Nanjiba, M., Horst, T., Ahn, K. and Potthast, A. (2023). "Archival performance of paper as affected by chemical components: A Review," *BioResources* 18(3), 6430-6498. DOI: 10.15376/biores.18.3.6430-6498

ISO - ISO 5351:2010. (2010). "Pulps — Determination of limiting viscosity number in cupriethylene diamine (CED) solution," International Organization for Standardization, Geneva, Switzerland.

ISO 187:1990. (1990). "Paper, board and pulps — Standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples," International Organization for Standardization, Geneva, Switzerland.

ISO 5351-1 (1981). "Cellulose in dilute solutions — Determination of limiting viscosity number — Part 1: Method in cupriethylene diamine (CED) solution," International Organization for Standardization, Geneva, Switzerland.

ISO 5626 (1993). "Paper — Determination of folding endurance," International Organization for Standardization, Geneva, Switzerland.

ISO/TS 18344 (2015). "Effectiveness of paper deacidification processes," International Organization for Standardization, Geneva, Switzerland.

Jablonský, M., and Šima, J. (2020). "Stability of alum-containing paper under alkaline conditions," *Molecules* 25(24), 1-15. DOI: 10.3390/MOLECULES25245815

Jablonský, M., Vizárová, K., and Tiňo, R. (2013). "Možnosti využitia masových technológií pri ochrane a konzervovaní objektov kultúrneho dedičstva," *Slovac National Museum.*

Jobbágy, M., and Regazzoni, A. E. (2011). "Dissolution of nano-size Mg–Al–Cl hydrotalcite in aqueous media," *Applied Clay Science*, 51(3), 366-369.

Jurišová, J., Danielik, V., Malečková, S., Guzikiewiczová, E., Králik, M., Vizárová, K., Ambrová, M., and Fellner, P. (2023). "Preparation and characterization of hydrotalcites colloid dispersions suitable for deacidification of paper information carriers," *Chemical Papers* 78, 7819-1730. DOI: 10.1007/s11696-023-03200-9

Katuščák, S., *et al.* (2009). "Preservation, stabilization, and conservation of traditional carriers of information in Slovak Republic," *Kniha*^{SK}, State program of R&D, Ministry of Education, Slovak Republic, no.2003SP200280301 (2003-2008), final report.

Katusščák, S., Jablonský, M., and Holubková, S. (2012). "Comparative evaluation of deacidification processes," *Zeitschrift Für Bibliothekswesen Und Bibliographie Sonderbände*, 106(1), 149-176. www.knihask.eu

Králik, M., Horváth, B., Vizárová, K., Vajová, I., Gašparovičová, D., Danielik, V., and Jurišová, J. (2021). "Deacidification and preservation of cellulosic objects of cultural heritage," in: *8th Int. Conf. Chem. Technology*, pp. 121-127.

Kundrot, R. A. (1985). "Deacidification of library materials," U.S. Patent 4,522,843.

Łojewska, J., Miśkowiec, P., Łojewski, T., and Proniewicz, L. M. (2005). "Cellulose oxidative and hydrolytic degradation: In situ FTIR approach," *Polymer Degradation and Stability* 88(3), 512-520. DOI: 10.1016/J.POLYMDEGRADSTAB.2004.12.012

Małachowska, E., Pawcenis, D., Dańczak, J., Paczkowska, J., and Przybysz, K. (2021). "Paper aging: The effect of paper chemical composition on hydrolysis and oxidation," *Polymers* 13(7). DOI: 10.3390/polym13071029

Marton, J. (1989). “Fundamental aspects of the rosin sizing process Mechanistic differences between acid and soap sizing,” *Nordic Pulp & Paper Research Journal* 4(2), 77-80. DOI: 10.3183/npprj-1989-04-02-p077-080

May, E., and Jones, M. (2006). *Conservation Science: Heritage Materials* (Vol. 390). Royal Society for Chemistry.

Poggi, G., Giorgi, R., Mirabile, A., Xing, H., and Baglioni, P. (2017). “A stabilizer-free non-polar dispersion for the deacidification of contemporary art on paper,” *Journal of Cultural Heritage* 26, 44-52. DOI: 10.1016/j.culher.2017.02.006

Poggi, G., Sistach, M. C., Marin, E., Garcia, J. F., Giorgi, R., and Baglioni, P. (2016). “Calcium hydroxide nanoparticles in hydroalcoholic gelatin solutions (GeolNan) for the deacidification and strengthening of papers containing iron gall ink,” *Journal of Cultural Heritage* 18(November 2017), 250-257. DOI: 10.1016/j.culher.2015.10.005

Potthast, A., Ahn, K., Becker, M., Eichinger, T., Kostic, M., Böhmdorfer, S., Jeong, M. J., and Rosenau, T. (2022). “Acetylation of cellulose - Another pathway of natural cellulose aging during library storage of books and papers,” *Carbohydrate Polymers* 287(January). DOI: 10.1016/j.carbpol.2022.119323

Potthast, A., and Henniges, U. (2016). “Vertrauen ist gut, Kontrolle ist besser - Kriterien für Testpapiere zur Qualitätskontrolle in der Mengenentsäuerung nach der neuen ISO / TS 18344,” *ABI Technik* 36(2), 68-77. DOI: 10.1515/ABITECH-2016-0015

Ren, F., Zheng, Y. F., Liu, X. M., Yang, Q. Q., Zhang, Q., and Shen, F. (2015). “Thermal oxidation reaction process and oxidation kinetics of abietic acid,” *RSC Advances* 5(22), 17123-17130. DOI: 10.1039/C4RA16791K

Sarpola, A., Hellman, H., Hietapelto, V., Jalonen, J., Jokela, J., Rämö, J., and Saukkoriipi, J. (2007). “Hydrolysis products of water treatment chemical aluminum sulfate octadecahydrate by electrospray ionization mass spectrometry,“ *Polyhedron* 26, 2851-2858. DOI: 10.1016/j.poly.2007.01.035

Schierholtz, O. J. (1936). “Process for the chemical stabilization of paper and product,” U.S. Patent 2,033,452.

Singh, B., Parwate, D. V., and Shukla, S. K. (2009). “Radiosterilization of fluoroquinolones and cephalosporins: Assessment of radiation damage on antibiotics by changes in optical property and colorimetric parameters,” *AAPS PharmSciTech* 10(1), 34-43. DOI: 10.1208/s12249-008-9177-y

Sixta, H. (2006). *Handbook of Pulp*, Vol. 2, *Wiley-VCH Verlag*. DOI: 10.1002/9783527619887

Smith, R. D. (1972). “Treatment of cellulosic materials,” U.S. Patent 3,676,182.

Stauderman, S. D., Bruckle, I., and Bischoff, J. J. (1996). *Observations on the Use of Bookkeeper® Deacidification Spray for the Treatment of Individual Objects*.

TAPPI T 529 (2021). “Surface pH measurement of paper,” Technical Association of the Pulp and Paper Industry.

Takeuchi, Y., Ikeda, N., Tahara, K., and Takeuchi, H. (2020). “Mechanical characteristics of orally disintegrating films: Comparison of folding endurance and tensile properties,” *International Journal of Pharmaceutics* 589. DOI: 10.1016/J.IJPHARM.2020.119876

Thürmer, A. (1998). “Acid scavengers for polyolefins,” in: *Plastics Additives. Polymer Science and Technology Series* (Vol. 1), G. Pritchard (ed.), Springer, Dordrecht, pp. 43-48. DOI: 10.1007/978-94-011-5862-6_6

Vajová, I. (2017). *Účinnosť konzervačných technológií na predĺženie životnosti kníh a dokumentov*, Master’s Thesis, Slovac University of Technology, Bratislava, Slavakia.

Vizárová, K., and Reháková, M. (2014). “Position and importance of analytical methods in the process of protection of paper-based heritage objects,” in: *Proceedings of the* 5th *Interdisciplinary Conference of ALMA, Acta Artis Academica 2014*, pp. 119-137.
Zou, X., Gurnagul, N., Uesaka, T., and Bouchard, J. (1994). “Accelerated aging of papers of pure cellulose: Mechanism of cellulose degradation and paper embrittlement,” *Polymer Degradation and Stability* 43(3), 393-402. DOI: 10.1016/0141-3910(94)90011-6

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