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Development of new systems based on hydrotalcites for stabilization and deacidification of paper information carriers

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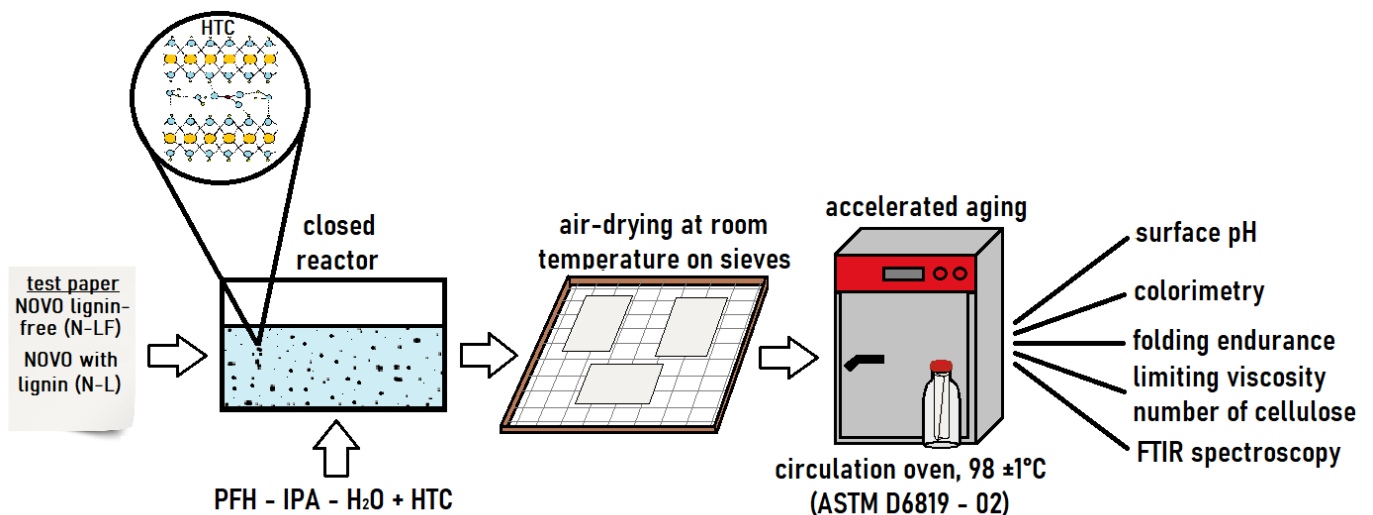
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Abstract

Stabilization and deacidification of paper information carriers is still a highly discussed topic. It is very important to continue in searching for new, more effective, and affordable methods of paper stabilization because none of the currently known processes is ideal. 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 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.

Graphical abstract



Keywords: paper, degradation, deacidification; hydrotalcites; dispersion

Introduction

Paper is a material closely connected to human history. Paper information carriers represent a significant part of the world's cultural heritage. Researchers face the challenge of preserving the degrading paper artefacts before they are lost forever together with the information they contain. Aging and degradation is a natural process, however, it is important to know what influences, how quickly and to what extent it happens. Material aging is an irreversible phenomenon, the consequences of which are changes in physico-chemical and mechanical properties. The basic degradation mechanisms are acid hydrolysis, oxidation, photochemical degradation, alkaline hydrolysis, and biological degradation (Area and Cheradame 2011). The most problematic paper materials are documents and books produced from the second half of the 19th century till the first half of the 20th century because acid resin sizing containing aluminum sulfate began to be used in the production processes. Acid resin sizing contributes significantly to the amount of acids present in the paper causing acid hydrolysis of cellulose, which contributes to the degradation of paper information carriers the most (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, acids, which can enter further reactions, thus generating a wide spectrum of degradation products (Area and Cheradame 2011). Acid species present in paper causing acid hydrolysis are represented by acids added during paper production (resin size with $\text{Al}_2(\text{SO}_4)_3$, bleaching chemicals, additives), acids produced during the aging process, acids formed from acid moieties (e.g. NO_x , SO_2) absorbed from the air, acids produced by inks and other components of documents added in their production (Vizárová and Reháková 2014; Hroboňová et al. 2023). A decrease in pH to the acidic region, increased temperature, and an increase in the concentration of the catalyst (hydrogen ion) significantly accelerates the acid hydrolysis (Solár 2001).

The problem with degradation is solved by stabilization processes. One of the main challenges with the stabilization of acidic information carriers, books, and archival documents is currently insufficient conservation capacity, which is 2 to 3 times lower than accounted by the world library funds.. 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 a faster deacidification of large number of paper information carries (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, ketons, fluorinated compounds, ...) 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, the interior structure is more open, in case of organic precursors of deacidification components they are hydrolyzed and can penetrate to interior body of the subject (information carrier) more easily. However, none of deacidification methods is problem-free, what is a reason why new deacidification agents and application procedures are still being sought. One of the widespread methods is based on the application of solid micrometric MgO particles in the form of a suspension in a non-polar environment, like perfluorinated hydrocarbons, e.g. perfluoroheptane, the so called Bookkeeper process (Stauderman et al. 1996). This process was used as a reference in this work.

In conservation research and praxis of deacidification and stabilization of paper, there are used beside MgO other types of virtually non-soluble or low soluble materials, such as $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{HCO}_3)_2$, $\text{Ba}(\text{OH})_2$, etc.. In spite of intensive exploitation of hydrotalcites (HTC) – Fig. 1 (Fink, 2010; Thürmer, 1998) for stabilization of synthetic polymers, particularly, polyvinylchloride composites (Bocchini et al. 2008), they have not been reported as deacidifying agents for cellulose-based artefacts, so far. HTC belong to the anionic clays, and the name "hydrotalcites" is used as a reference name for several isomorphous compounds. In our research, they were chosen for their specific properties. HTC are alkaline compounds containing magnesium and aluminium in their structure, capable to exchange anions, they are typical with a large specific surface area, quasi-homogeneous mixtures with small crystals are possible to be formed, and after calcination they have the ability to reconstruct the original structure (Cavani et al. 1991; Conterposito et al. 2018).

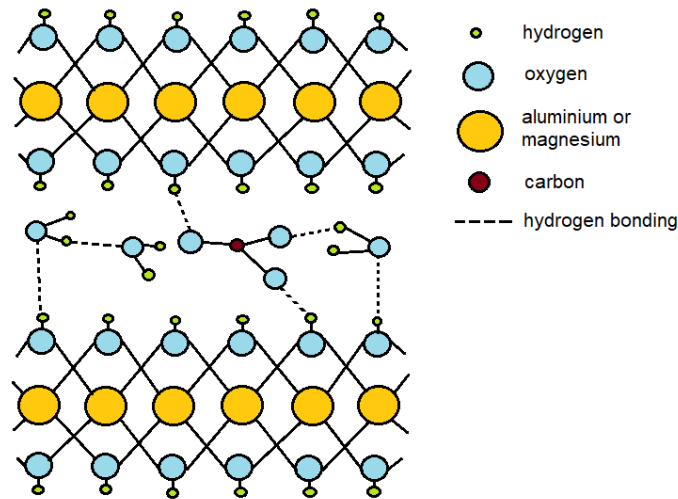
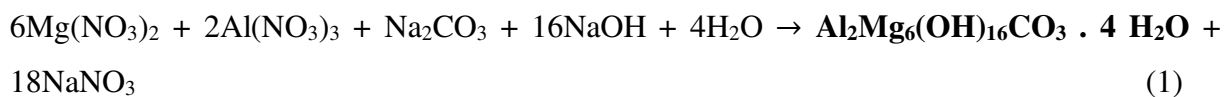


Fig. 1. Structure of hydrotalcite.

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

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



whereas the ratio of Mg^{2+} to Al^{3+} can be lower or higher than 3, commonly in the range 2-5. Basicity increases with the increasing of this ratio (Cavani et al. 1991; Conterposito et al. 2018).

Alternatively, chlorides instead of nitrates can be used.

The aim of this work has been to test a series of acidic paper samples modified by HTC and to verify their suitability for use in the stabilization and deacidification of acidic paper information carriers. Various prepared hydrotalcites were tested and the influence of the different preparation processes (addition of surfactant as citric acid and/or magnesium stearate, preparation of HTC's from nitrates or chlorides, different composition of Mg and Al) on the resulting properties of the product was studied. HTC's were added to a partially polar environment (non-polar solvent - intermediate - water) and colloidal dispersions were prepared. Subsequently, these deacidification systems were applied to the two types of test paper (with lignin and lignin-free). Both modified and unmodified control samples were subjected to accelerated aging.

Nowadays, the criteria for evaluating the effectiveness of deacidification are not fixed and unified, but one of the most common and widespread criteria is the measurement of the surface pH, which should be in the slightly alkaline region after modification, i.e. $\text{pH} > 7$, and evaluation of the degree of polymerization (ISO - ISO 5351:2010; Potthast and Henniges 2016). Our work has been focused on the comparison of mechanical, optical, and chemical (surface pH) properties of modified samples and the properties of unmodified control samples as an indicator of the efficiency of deacidification of the selected systems.

Materials and Methods

Materials

Main 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.

Solvents:

- isopropanol (IPA), (99 %, CentralChem)
- perfluoroheptane (PFH) obtained by distillation of Bookkeepers Deacidification Spray, Preservation Technologies B.V.
- deionized water

Test papers:

- **NOVO with lignin (N-L):** is an acidic lignin-containing paper from Klug-Conservation. The N-L sample contained more than 55 % mechanical wood pulp (CTMP) + bleached paper pulp; lignin 17 %, filler (12 - 15) % kaolin. Sizing Cobb₆₀ OS 19/SS 21 g/m², rosin, and alum. pH (4.0 – 5.0) (adjustment with alum), grammage 90 g/m². Paper does not contain any surface sizing, calendaring, and 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. This type of degradation can be monitored by FTIR spectroscopy able to detect the oxidation products.
- **NOVO lignin-free (N-LF):** resin-bonded test paper with alum, acid, wood paper (60 % CTMP pulp, 25 % sulfate bleached pulp, 12 – 15 % kaolin), lignin content 17 %, surface pH 4.5; manufacturer KLUG-CONSERVATION.
 - On this paper it is possible to indirectly monitor the rate of glycosidic bond cleavage through the measurement of the properties of cellulose solution, which cannot be performed on paper with lignin content.

Methods

Modification of acidic test papers by dispersions with HTC introduced in Table 1, denoted as 12B, 14B, and 19B

- 1.) The dispersion with concentration $c = 4.3$ g/l was prepared by combining the mixed solution (PFH – 89.32 vol. %; H₂O – 0.69 vol. %; IPA – 9.99 vol. %) and powder hydrotalcite (Table 1).

- 2.) 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.
- 3.) All dried samples were stored in an air-conditioned room for 24 hours according to the ISO 187 standard practice ($23 \pm 1^\circ\text{C}$, $50 \pm 1\%$ RV) (ISO 187:1990).
- 4.) 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 $98 \pm 1^\circ\text{C}$ according to the ASTM D6819 - 02 standard (ASTM D6819 - 02).

Surface pH

The surface pH was determined on the modified acidic paper samples according to the standard practice (STN 50 0374 (50 0374)). The surface pH of the samples was measured using the Jenway 5310 pH meter. The pH was measured on 2 sheets of paper from the top and bottom of the modified paper (min. 3x from both sides). The measurement lasted 2 minutes, and as the representative value their average value was considered.

Colorimetry

The change in optical properties was monitored (the change in color) using the coordinates of the CIE Lab color space (coordinates L^* , a^* , b^*) measured by the SpectroDens A 504009 device.

Measurement conditions: 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.

Calculation of the total color difference ΔE_{ab}^* :

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

where L_0^* , a_0^* , b_0^* are values for the unmodified sample at 0 days of aging, L^* brightness, a^* , 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.

Folding endurance

The folding endurance (expressed by the number of double folds) was determined according to the standard practice (ISO 5626:1978). The measurement was performed on a Tinius Olsen, MIT Folding Endurance Tester.

The paper is subjected to tension and repeated 180 ° bending until it breaks (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 (Katuscak et al. 2012):

$$S_{\tau,\omega} = \frac{t_{\log\omega=0,m}}{t_{\log\omega=0,n}} \quad (3)$$

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

$$y = a + b*t \quad (4)$$

$$\log\omega = a + b*t_{\log\omega} \quad (5)$$

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

$$0 = a + b* t_{\log\omega} \quad (6)$$

$$t_{\log\omega} = -\frac{a}{b} \quad (7)$$

Where a , b are regression coefficients.

According to the criteria of the Library of Congress and the Kniha^{SK} consortium, modification systems that ensure a life extension coefficient of at least three times: $S_{\tau,\omega} \leq 3$ are considered effective. The durability of treated paper should be increased by at least 300 % (Katuscak 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 (STN ISO 5351/1).

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

$$DP^{0.9} = 1.65 * [\eta] \quad (8)$$

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

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

$$\frac{1}{DP_t} - \frac{1}{DP_0} = k * t \quad (9)$$

where DP_0 is degree of polymerization at 0 days of accelerated aging for a given sample, DP_t degree of polymerization at time t , 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):

$$\text{oxidation index} = \frac{I_{1730}}{I_{1620}} \quad (10)$$

where I is the standardized integral at a certain wavelength (the most intense maximum),

I_{1730} : 1664 - 1837 cm^{-1} ,

I_{1620} : 1500 - 1664 cm^{-1} .

Results and Discussion

Surface pH

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 surface pH (Buchanan et al. 1994; Directorate 2004).

According to the current research on deacidification systems, hydrotalcites represent a neutralizing agent that provides deacidification. The presence of water ensures the swelling of cellulose fibers which promotes the penetration of hydrotalcite particles into the paper structure. 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. An excessive amount of water and, in our case, 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.

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

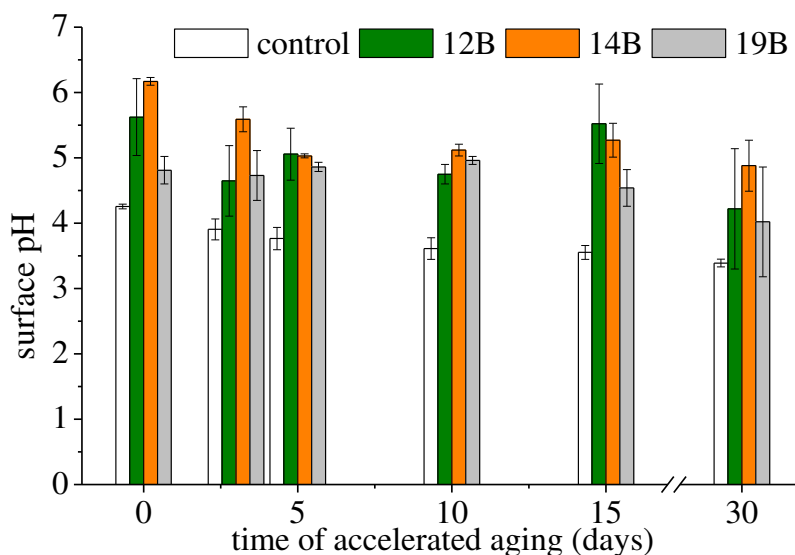


Fig. 2. Comparison of the pH of the control (unmodified) sample with the modified samples (12B, 14B, and 19B) on the testing paper N-LF.

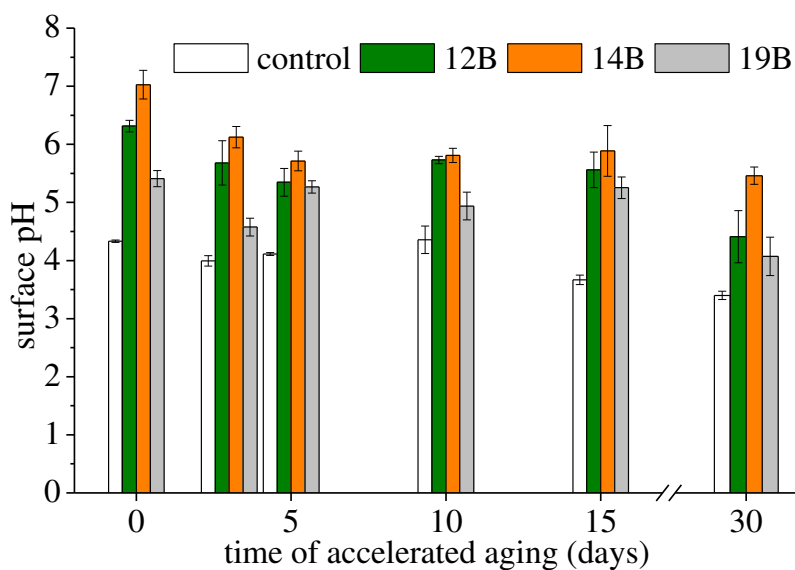


Fig. 3. Comparison of the pH of the control (unmodified) sample with the modified samples (12B, 14B, and 19B) on the testing paper N-L.

After modification of the both test papers with all the 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 appears to be

the most suitable one. 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 – 1.9 units for N-LF and 1.6 – 2.7 units for N-L was recorded. The dispersion with the active substance 19B appears 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) shows 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 has been formed.

Colorimetry

Aged papers darken and turn yellow due to degradation. Color changes due to aging can be objectively evaluated through trichromatic colorimetry, which is used by several color systems. In this work the CIE $L^*a^*b^*$ color model was used. The coordinate L^* stands for brightness, 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 takes into account both the lightness difference and the difference in the chromatic plane (Singh et al. 2009).

Table 2. Colorimetry results and calculated values of total color difference ΔE_{ab}^* for test paper N-LF

sample	accelerated aging (days)	L	a	b
control (N-LF)	0	93.84 ± 0.28	- 0.78 ± 0.18	0.53 ± 0.46
	3	90.83 ± 0.72	0.94 ± 0.24	10.34 ± 0.58
	5	86.48 ± 0.36	3.00 ± 0.13	15.56 ± 0.23
	10	77.15 ± 0.74	7.11 ± 0.11	21.90 ± 0.16
	15	64.17 ± 1.12	10.04 ± 0.28	24.04 ± 0.52
	30	46.30 ± 1.80	9.43 ± 0.21	19.76 ± 0.60
12B	0	93.75 ± 0.18	- 1.20 ± 0.06	2.85 ± 0.12
	3	91.31 ± 0.30	- 0.48 ± 0.05	8.73 ± 0.15

	5	89.84 ± 0.17	0.13 ± 0.04	10.54 ± 0.16
	10	85.49 ± 0.29	2.05 ± 0.08	15.73 ± 0.42
	15	84.37 ± 0.44	2.65 ± 0.11	17.02 ± 0.12
	30	71.31 ± 0.79	6.46 ± 0.27	22.76 ± 0.28
14B	0	94.29 ± 0.33	-0.50 ± 0.10	0.71 ± 0.27
	3	91.99 ± 0.54	0.42 ± 0.11	7.70 ± 0.28
	5	90.64 ± 0.47	1.13 ± 0.15	10.09 ± 0.20
	10	88.91 ± 0.51	1.98 ± 0.08	12.89 ± 0.26
	15	83.88 ± 0.61	4.53 ± 0.24	17.69 ± 0.78
	30	77.18 ± 0.13	5.62 ± 0.08	21.96 ± 0.43
19B	0	94.07 ± 0.37	-0.55 ± 0.05	0.81 ± 0.11
	3	90.75 ± 0.40	0.97 ± 0.08	9.70 ± 0.19
	5	89.29 ± 0.39	1.76 ± 0.10	11.51 ± 0.10
	10	86.39 ± 0.50	3.40 ± 0.14	15.82 ± 0.27
	15	89.50 ± 0.37	1.76 ± 0.11	13.10 ± 0.32
	30	78.27 ± 0.52	5.17 ± 0.19	20.95 ± 0.22

* ΔE_{ab}^* - values refer to an unmodified, unaged sample

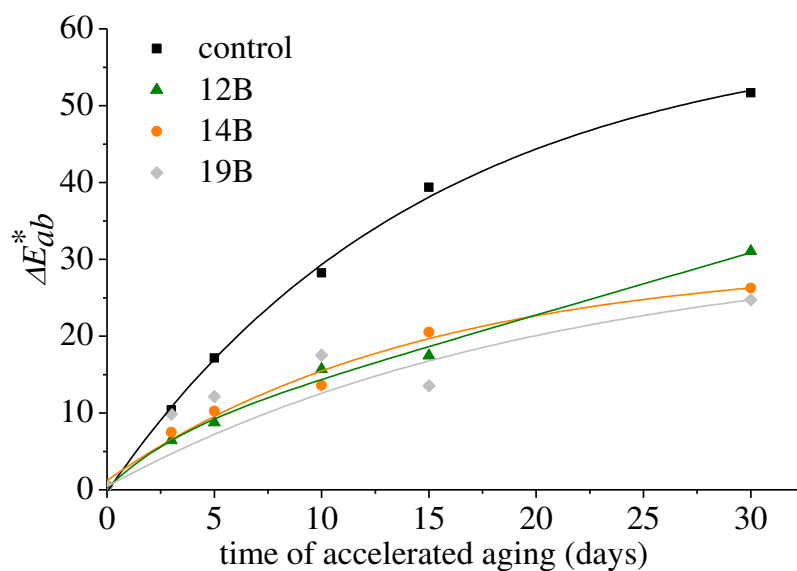


Fig. 4. Color change of modified paper samples expressed by total color difference (ΔE_{ab}^*) of control and modified papers for test paper: N-LF.

Table 3. Colorimetry results and calculated values of total color difference ΔE_{ab}^* for test paper N-L

sample	accelerated aging (days)	L	a	b
control (N-L)	0	89.91 ± 0.29	0.008 ± 0.058	11.03 ± 0.63
	3	88.75 ± 0.52	0.62 ± 0.14	14.36 ± 0.17
	5	79.00 ± 3.60	2.00 ± 4.30	18.60 ± 4.80
	10	76.17 ± 0.81	5.72 ± 0.24	23.28 ± 0.38
	15	78.70 ± 1.90	3.20 ± 3.30	20.90 ± 3.90
	30	73.00 ± 1.30	6.81 ± 0.71	24.00 ± 1.90
12B	0	90.13 ± 0.37	- 0.02 ± 0.17	11.42 ± 0.63
	3	85.78 ± 0.64	1.54 ± 0.41	15.65 ± 0.34
	5	81.33 ± 0.60	3.26 ± 0.42	18.05 ± 0.65
	10	77.06 ± 0.50	4.99 ± 0.16	20.46 ± 0.57
	15	76.65 ± 0.78	5.35 ± 0.22	21.13 ± 0.53
	30	73.20 ± 1.90	6.94 ± 0.92	22.70 ± 2.10
14B	0	89.70 ± 0.58	0.06 ± 0.40	10.92 ± 0.85
	3	86.45 ± 0.45	1.56 ± 0.16	15.62 ± 0.45
	5	82.05 ± 0.57	3.42 ± 0.29	18.51 ± 0.35
	10	81.54 ± 0.64	3.60 ± 0.23	18.43 ± 0.59
	15	78.80 ± 1.00	4.75 ± 0.52	20.60 ± 1.80
	30	75.01 ± 0.65	6.54 ± 0.42	22.50 ± 1.90
19B	0	89.96 ± 0.42	0.00 ± 0.14	10.69 ± 0.13
	3	85.04 ± 0.36	2.14 ± 0.07	16.20 ± 0.37
	5	82.35 ± 0.57	3.15 ± 0.25	17.87 ± 0.27
	10	80.03 ± 0.20	4.07 ± 0.26	18.99 ± 0.42
	15	72.90 ± 1.50	6.35 ± 0.46	22.90 ± 1.70
	30	68.40 ± 2.10	7.92 ± 0.81	23.80 ± 1.80

* ΔE_{ab}^* - values refer to an unmodified, unaged sample

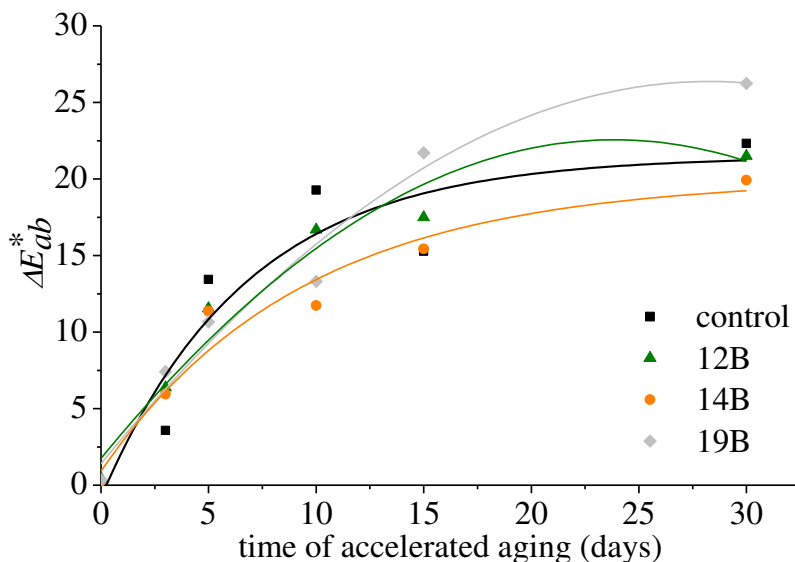


Fig. 5. Color change of modified paper samples expressed by total color difference (ΔE_{ab}^*) of control and modified papers for test paper: N-L.

As a result of aging, the L^* coordinate decreases, at the same time the a^* and b^* coordinates also change. The coordinate b^* changes more significantly than a^* . Samples turn yellow and darken due to aging.

The modification itself does not affect the change in the color of the paper (Table 2 and 3). The ΔE_{ab}^* values (relative to the unmodified unaged sample) increase with aging time for both the unmodified control sample and the modified samples (Fig. 4 and 5). However, after the modification of the N-LF paper, the changes of ΔE_{ab}^* values are much slower (Fig. 4), which signifies a prominent improvement of the optical properties after the modification (for all three dispersions). There is no such improvement regarding the N-L paper (Fig. 5). In the case of dispersions with the active substance 12B and 19B, the optical properties worsened compared to the control 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.

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 our tests are in Table 4 and Figs. 6 and 7.

Table 4. Measurement of the folding endurance 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 papers

	time of accelerated aging (days)	N-LF			N-L		
		ω (double folds)	$S_{\tau,\omega}$		ω (double folds)	$S_{\tau,\omega}$	
control	0	872 ± 250	-	412 ± 110	-		
	3	2 ± 1		254 ± 83			
	5	1 ± 0		6 ± 2			
	10	0 ± 0		2 ± 0			
	15	0 ± 0		2 ± 0			
	30	0 ± 0		1 ± 0			
12B	0	837 ± 267	3.24	468 ± 108	1.11		
	3	66 ± 31		189 ± 61			
	5	26 ± 11		33 ± 13			
	10	2 ± 1		3 ± 1			
	15	2 ± 1		2 ± 1			
	30	0 ± 0		2 ± 1			
14B	0	790 ± 190	3.78	493 ± 191	1.21		
	3	210 ± 60		251 ± 79			
	5	97 ± 37		18 ± 5			
	10	15 ± 4		14 ± 5			
	15	2 ± 1		3 ± 1			
	30	0 ± 0		2 ± 1			
19B	0	870 ± 410	3.86	497 ± 137	1.03		
	3	39 ± 12		113 ± 47			
	5	41 ± 21		27 ± 9			
	10	2 ± 1		3 ± 1			

	15	7 ± 2		2 ± 1
	30	0 ± 0		1 ± 1

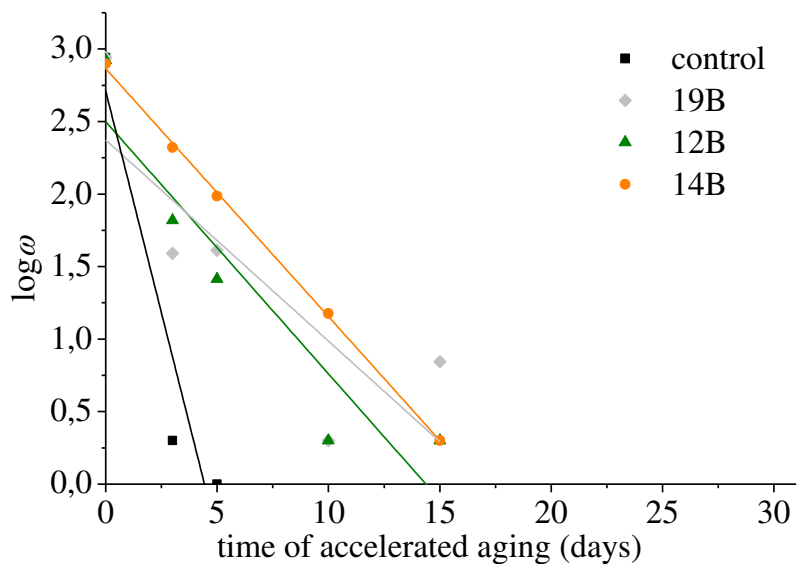


Fig. 6. Dependence of $\log \omega$ on time of accelerated aging for control sample and samples modified with dispersion with active substance 12B, 14B, and 19B for test paper N-LF.

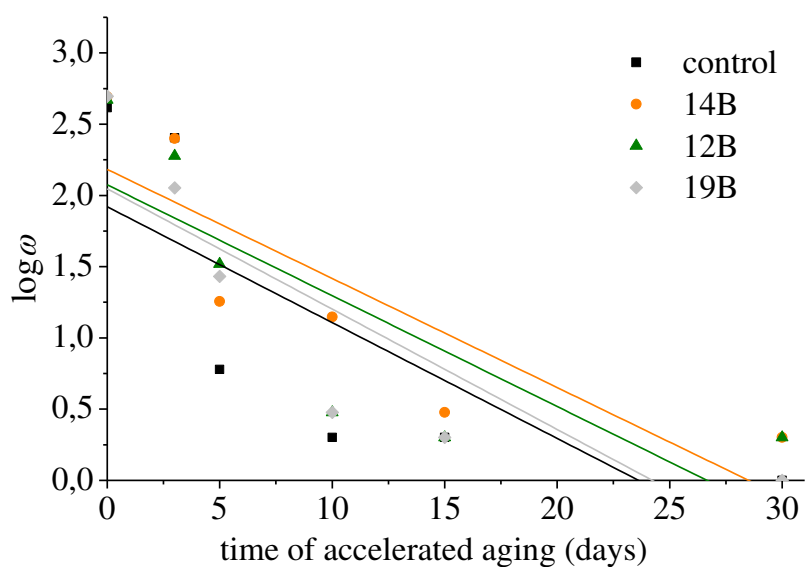


Fig. 7. Dependence of $\log \omega$ on time of accelerated aging for control sample and samples modified with dispersion with active substance 12B, 14B, and 19B for test paper N-L.

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.

The value $\log\omega = 0$ 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 4, Fig. 6). The values of the life extension coefficients of N-LF paper were higher than 3 in all three cases (Table 4), what illustrates a good stabilization effect.

The values of the life extension coefficient of N-L paper (Table 4, Fig. 7) 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). Results from our testing are summarized in Table 5 and Fig. 8.

Table 5. 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)	$[\eta]$ (ml·g ⁻¹)	DP	k^*t
control	0	445	380	1.03*10 ⁻³
	3	142	136	
	5	120	117	
	10	89	89	
	15	75	76	
	30	68	70	

12B	0	439	375	$2.46 \cdot 10^{-4}$
	3	258	232	
	5	219	200	
	10	168	158	
	15	146	139	
	30	96	95	
14B	0	474	402	$1.04 \cdot 10^{-4}$
	3	308	273	
	5	250	226	
	10	201	186	
	15	161	152	
	30	105	103	
19B	0	447	381	$4.05 \cdot 10^{-4}$
	3	219	201	
	5	214	196	
	10	149	142	
	15	184	171	
	30	113	111	

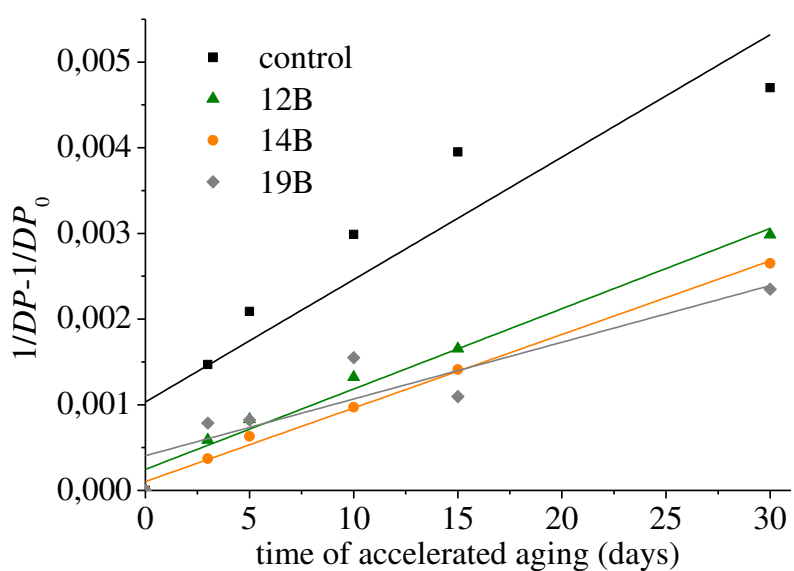


Fig. 8. Rate of glycosidic bond cleavage for control and modified sample with dispersion with active substance 12B, 14B, and 19B for test paper N-LF.

The *DP* of the unaged samples did not change after the modification, which tells us that the modification itself does not cause changes in the chemical structure of the polymer. The *DP* values of the modified samples subjected to accelerated aging increased significantly compared to the aged unmodified control sample (Table 5). 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 magnitude for all three dispersions. The dispersion with the active substance 14B achieved the slowest rate of glycosidic bond cleavage (Table 5).

FTIR

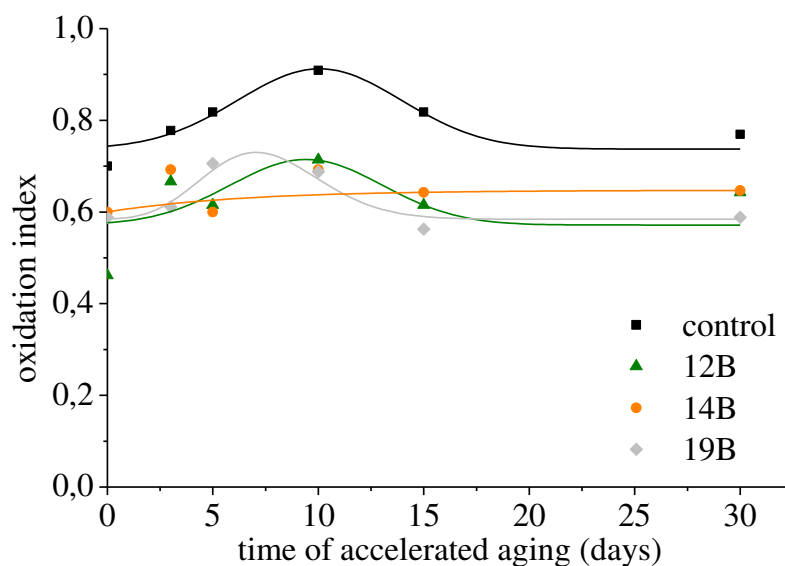


Fig. 9. Comparison of the oxidation index of control and modified samples for test paper N-L.

Values of absorbance belonging to the absorption band 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).

N-LF paper is 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).

Conclusions

The aim of the work was to test three differently prepared samples of hydrotalcites differing in Mg^{2+} to Al^{3+} ratio (12B, 14B, 19B, see Table 1) and to determine the suitability of their use for stabilization and deacidification of acidic paper information carriers. All the three hydrotalcite samples were in a powder form. 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.

All the monitored properties (mechanical, optical, and chemical) of aged acidic test papers were improved after modification.

The surface pH after modification increased for all samples (aged and unaged). The most significant improvement occurred in the paper modified with dispersion with the active substance 14B when the surface pH increased by 1.3 – 1.9 units for N-LF paper and by 1.6 – 2.7 units for N-L paper. Probably the best results were obtained due to the high ratio of Mg : Al (equal to 5) and low size of particle (1.61 μm). However, no alkaline reserve was created, which is indicated by the fact that the surface pH values remain in the acidic range even after the modification.

Based on the evaluation of the optical parameters, it is evident that 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 the three cases, an improvement in colorimetric parameters was detected in comparison to the unmodified control sample during accelerated aging.

The mechanical properties defined by the folding endurance measurement do not change immediately after the modification. After subjecting the samples to accelerated aging, the

mechanical properties of all modified samples improve compared to unmodified samples. The coefficient of relative increase of the lifetime $S_{\tau,\omega}$ in the case of N-LF paper exceeds 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).

Based on the measurement of the limiting viscosity number, it was proven that 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 magnitude for all three modifications.

After the modification, there was a decrease in the amount of oxidative degradation products.

From the point of view of the stabilization of acidic paper information carriers, based on the evaluation of all measurements, hydrotalcite 14B appears to be the most promising type of hydrotalcite. The composition of hydrotalcite 14B differs from hydrotalcite 19B in the ratio of Mg to Al - the higher Mg content leads to better results. Unlike hydrotalcite 12B, citric acid was added during the preparation of hydrotalcite 14B, which acts 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.

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Declaration

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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