Chapter 3

Application of Ionic Liquids in Paper Properties and Preservation

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/65860

Abstract

For centuries, paper has been an important medium of information. Currently, the basic risk to the paper collection is "acidic paper" and the action of enzymes secreted by microorganisms on them. In order to 'prolong life' of these materials, in recent years, various chemical compounds have been used. In this chapter, ionic liquids (IL) are explored as substances for deacidification of paper and its conservation, including antifungal activity. The use of these substances in the manufacturing of paper is possible, but the ingredients play an important role. Imidazolium IL cause an increase in the pH (deacidification) of historical papers and do not cause worsening of their strength properties, but these compound can cause a colour change. Benzalkonium DL-lactate and didecyldimethylammonium DL-lactate and derivatives of 1,2,4-triazole are used as effective inhibitors of growth of moulds on paper. The best antifungal activity in these ionic liquids is observed in the paper pine at a concentration of 5% and weakest in the samples from the pulp after chemical-thermomechanical treatment. New paper impregnated with ionic liquids is characterised by an increase in tear resistance, reduction of breaking length and a favourable influence on the paper colour.

Keywords: ionic liquids, paper deacidification, antifungal activity, paper properties

1. Introduction

Since the time of its invention, paper has been an essential carrier of historical, cultural, economic and scientific information. However, for the past several decades, paper has been facing competition with electronic media. Nevertheless, the majority of human knowledge and artworks of an inestimable historical value are recorded on paper.

Until the nineteenth century, paper was manufactured by craftwork in an alkaline environment, using pulped rags with highly polymerised cellulose. The increasing demand for paper was the reason for its production on an industrial scale, using wood fibres, commenced in the nineteenth century. Paper obtained in this manner is characterised by a lower degree of polymerisation and acidic pH (pH = 4.5–5.5), which additionally increases the rate of cellulose depolymerisation. This process is also assisted by microorganisms, in particular, moulds producing cellulolytic enzymes. All these factors adversely affect the durability and quality of the paper, resulting in reduced ageing resistance [1, 2].

In recent years, paper manufacturers have replaced the applied technologies with acid-free methods. However, the problem of accumulated vast collections of acidic paper in archives and libraries remains. Due to the extent of this problem, many million tonnes of paper collections are to be protected. Intensive measures are being taken on a global scale to preserve our heritage. A range of methods has been developed for deacidification on a large scale and for the partial preservation of the archive collections, but none of the methods devised thus far meet the expectations.

The factors causing paper degradation can generally be divided into endogenous—acidity, metal ions and lignin; and exogenous—UV radiation, humidity, pollutants and microorganisms. As previously mentioned, moulds dominate among the latter. Additionally, the quality of paper materials can be deteriorated by bacteria; however, bacteria, as compared with moulds, require more humidity for growth. Environmental conditions typically present in libraries, archives and museums are more suitable for the growth of moulds than bacteria.

Various chemical compounds are used in order to prevent the above-described factors from creating favourable conditions for paper degradation. They are paper disinfection, deacidification and coating. The substances used during the processes should provide a good chemical stability and ensure cost efficiency. They cannot be toxic to humans and the environment. Also, the effect on the material is important as it cannot undergo any negative changes. As antimicrobial agents, they should be characterised by a wide spectrum of action at low concentrations and in a short period of time [3, 4].

While selecting an agent for paper protection in the broad sense, one must bear in mind that the agent must possess marketing authorisation. Regulation (EU) No. 528/2012 of the European Parliament and of the Council of 22 May 2012, concerning the making available in the market and use of biocidal products has been in force since 1 September, 2013 [5].

In recent years, attention has been paid to chemical compounds generally known as ionic liquids (ILs), many of which show promising properties with the potential for use in the paper industry [6]. These are chemically, electrochemically and thermally stable compounds, which do not decompose at high temperatures. Due to low volatility, they are also recognised as environmentally sound. Moreover, they are characterised by incombustibility, antimicrobial activity or pH buffering capability [6–10].

http://dx.doi.org/10.5772/65860

2. Ionic liquids as neutralisers of acid paper

The reason for paper instability can be sought in two improvements that were introduced in the nineteenth century: a new method of paper sizing and a change in raw material. Paper sizing, necessary to obtain a writable surface, was improved by means of an adhesive added to the pulp before forming a paper sheet or band. Sizing with a resin adhesive added to the pulp required an additive such as aluminium sulphate as a coagulating agent. In an aqueous environment, the compound undergoes hydrolysis; as a result, sulphuric acid is produced, leading to an acidic reaction of the paper-pulp-water suspension. In addition, this causes continuous cellulose depolymerisation in the finished product. With the development of wood-based method of manufacturing, the quality of the manufactured paper product began to worsen compared to that of the paper that was until then manufactured using long, fibrous rag pulp. One of the problems faced today is disintegration of pages in books and documents that were printed in the nineteenth and twentieth century; however, the incoming flow of such materials to libraries and archives was fortunately stopped by new, less expensive and acid-free methods of paper manufacturing, which developed towards the end of the twentieth century [11–14].

The internal factor causing deterioration of paper properties with time is its chemical composition, and the factors are:

- type of the fibrous pulp used to produce paper (wood or wood-less pulp, fibre length, degree of polymerisation, cellulose content, lignin content)
- ancillary agents used during paper production (the amount of aluminium sulphate as an additive for paper sizing in pulp with resin adhesives should not exceed 5% in terms of the input mass of fibrous raw materials)

Symptoms of paper ageing mostly include yellowing and structure weakening (brittleness), resulting in some extreme cases in a complete lack of mechanical resistance. Paper ageing is a very complex process, because of the non-homogeneous composition of this fine material. According to the recent research, paper degradation and ageing are believed to mostly attribute to autocatalytic reactions of acid hydrolysis and oxidisation, i.e. processes accelerated by protons and active oxides, respectively [12, 15–21].

During acid hydrolysis, cellulose chains are torn apart into smaller pieces, which results in the following two phenomena:

- shorter average chain length, and as such—reduced paper tearing resistance;
- on both ends of the torn polymer chain, there are active groups which easily attach to the adjacent cellulose chains resulting in improved structural cross-linking, which enhances structural stiffness and the paper becomes brittle.

Cut cellulose fragments may also undergo oxidation to form carboxylic acids, such as formic acid and acetic acid. These organic acids reduce paper pH and accelerate acidic hydrolysis reactions, providing fuel to other reactions and causing autocatalytic degradation in paper.

Acidic hydrolysis is one of the most dangerous degradation reactions, which happens in libraries and archives worldwide [20–24].

There are millions of materials printed on unstable paper lying in libraries, archives and museums. In order to save and protect them from damage and disintegration into pieces, some methods have been developed which slow down cellulose degradation, namely deacidification, which involves introduction of excess alkali into the paper structure to prevent decomposition—the so-called alkaline reserve. In addition, to extend paper lifetime, objects undergoing deacidification are protected from acid-forming air components, and deacidification is combined with reinforcement of partially degraded paper (filling up material losses, patching, lamination) [12].

Features of a perfect deacidification method [11, 25] are as follows:

- it should be effective, ensuring that the deacidification substance can penetrate into the book or document;
- paper deacidification should take place within the entire thickness;
- it should leave permanent alkaline reserve in the paper to provide pH close to 8.5;
- it should not adversely affect any material in the book (paper, adhesives, printing inks, writing inks, illustration paints, leather and leather-like elements);
- it should not cause any formation of deposits on the surface left after deacidification;
- it should not cause any permanently unpleasant odour;
- it should be suitable for deacidification of any object regardless of the type of paper, its format and the degree of degradation;
- it should not leave any visible or sensible sign after the treatment;
- applied deacidification agents cannot sensitise paper to light or be allergic for humans;
- it should not adversely affect the environment;
- it should be efficient in use, inexpensive and available at the site where the collections at risk are stored;
- the deacidification agent should not promote flammability, hygroscopicity or paper susceptibility to microorganisms; and
- it should result in paper purification and strengthening.

There are many deacidification methods in the world; however, none of them can meet all of the mentioned requirements simultaneously. The application of ionic liquids in paper preservation increases great hopes. The discussed group of compounds appears to be promising in terms of their ability to change acidic pH of the paper as well as disinfection (removal of microorganisms) and disinsectisation (removal of insects and rodents).

The presented tests verified whether the selected ionic liquids had a deacidification effect on ‘acidic paper', whether they could change pH from acidic (pH < 7) to alkaline (pH > 7).

http://dx.doi.org/10.5772/65860

For test purposes, paper materials from old books were used (designated as A1 and A2 in the following text, **Table 1**). While selecting the materials for tests, the following criteria were applied: age of the book—publication year before 1970, i.e. age > 45 years; pH < 7 and the raw material composition—different content values of groundwood and cellulosic pulp.

Paper	Age	pH [-]	Fibrous composition
A1	48	2.83 ± 0.16	30% cellulose pulp and 70% groundwood
A2	56	4.75 ± 0.27	100% cellulose pulp

Table 1. Samples' fibrous composition and pH.

Solutions of the tested ionic liquids were prepared by dilution of 50% alcoholic solutions of ionic liquids using an appropriate amount of isopropyl alcohol (IPA).

The paper samples were impregnated using two methods. The first one was carried out on petri dishes for the liquids [C_4mim] [Bt] (1-butyl-3-methylimidazolium benzotriazol) and [C_4mim] [Tr] (1-butyl-3-methylimidazolium 1,2,4-triazolate). The ionic liquid was applied on the paper with a pipette (**Table 2**). Then, the paper was put aside for 24 h. As this method failed to be effective for the liquid [DDA][DL-lactate] and the impregnation was not complete, another impregnation method was employed using a closed container instead of a petri dish (**Table 3**). These samples were also put aside for 24 h (the container provided constant temperature and relative humidity during impregnation). After 24 h of impregnation, the samples were transferred onto petri dishes for another 24 h to remove the solvent (IPA) that evaporated naturally. This procedure enabled to obtain paper samples impregnated only with ionic liquids.

Ionic liquids	Paper			
	A1		A2	
	G [g/m^2]	Z [cm^3/g]	G [g/m^2]	Z [cm^3/g]
[C_4mim] [Bt] and [C_4mim] [Tr]	60	0.50	120	0.25
	60	1.50	120	0.75
	60	2.50	120	1.25
	60	3.50	120	1.75
	60	4.00	120	2.00

Note: G, paper grammage, g/m^2; *Z*, consumption of ionic liquid solutions per 1 g impregnated paper.

Table 2. The consumption of ionic liquid solutions per 1 g impregnated paper (petri dish).

Ionic liquids	Paper			
	A1		A2	
	G [g/m²]	Z [ml/g]	G [g/m²]	Z [ml/g]
[DDA] [DL-lactate]	60	5.00	120	2.50
	60	6.00	120	3.00
	60	7.00	120	3.50
	60	8.00	120	4.00
	60	9.00	120	4.50

Note: G, paper grammage, g/m²; *Z*, consumption of ionic liquid solutions per 1 g impregnated paper.

Table 3. The consumption of ionic liquid solutions per 1 g impregnated paper (closed container).

After impregnation of the A1 and A2 paper samples, the pH values were changed using the ionic liquids [C_4mim] [Bt] and [C_4mim] [Tr] at concentrations of 1–8%, and the solutions [DDA] [DL-lactate] (didecylodimethylammonium DL-lactate) at concentrations of 10–20%, as presented in **Table 4**.

Concentration of the solution %	Paper A1			Paper A2		
	pH 24 h after impregnation			pH 24 h after impregnation		
	[C_4mim] [Bt]	[C_4mim] [Tr]	[DDA] [DL-lactate]	[C_4mim] [Bt]	[C_4mim] [Tr]	[DDA] [DL-lactate]
1	4.96	4.39	–	5.99	5.66	–
3	7.55	5.76	–	7.24	7.59	–
5	**7.56**	7.93	–	**8.09**	7.83	–
7	9.01	8.02	–	8.45	7.92	–
8	9.60	**8.13**	–	9.22	**7.98**	–
10	–	–	4.05	–	–	4.61
12	–	–	4.11	–	–	4.60
14	–	–	4.14	–	–	4.62
16	–	–	4,16	–	–	4.65
18	–	–	4.24	–	–	4.68
20	–	–	4.34	–	–	4.59

Table 4. pH values of samples after impregnation of solutions of [C_4mim] [Bt]; [C_4mim] [Tr] and [DDA][DL-lactate].

Based on the results of A1 and A2 paper impregnation, it was found that the ionic liquid [C_4mim] [Bt] showed high capability of deacidification of acidic paper. In the case of both A1 and A2 paper samples, the 3% solution of the compound used for impregnation increased pH of the objects undergoing deacidification to more than 7, from 2.83 (A1 paper) and 4.85 (A2 paper), respectively. Moreover, it was observed that the increase in the concentration of the [C_4mim] [Bt] solution resulted in a noticeable rise in paper pH after impregnation. The

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liquid [C4mim] [Tr] proved to be a slightly less effective in deacidification. As a result of impregnation of the A1 and A2 paper samples with this liquid at 5% concentration, their pH values increased to more than 7. However, when [C_4mim] [Tr] at a concentration over 5% was used, pH of the A1 and A2 samples after implementation practically did not change and remained to be approximately 8.

Different results were obtained for [DDA] [DL- lactate], which was applied at a concentration of 10–20%, increasing pH of the A1 paper after impregnation from 2.83 to 4.05–4.34, respectively. For the A2 paper, its pH after impregnation practically did not change. For both the A1 and A2 papers, the pH value after impregnation remained at a practically constant level, independently of the applied concentration of the ionic liquid solution.

Due to the fact that neutralisation of acid paper should not leave any visible or detectable sign, once the treatment was completed, the effect of the ionic liquids on colouring substances as well as appearance and odour of the paper were checked.

Paper impregnated with solutions of the ionic liquids [C_4mim] [Bt] and [C_4mim] [Tr] was not affected in terms of print, odour and texture—no textural changes were noticed in the paper. Paper was not deformed either (no creasing or rolling occurred). Unfortunately, the liquids reduced non-transparency of the paper during impregnation; however, once the solvent evaporated, transparency was restored to the initial state. In addition, printing inks from illustrations spilled out and dyed the paper. While observing the paper after impregnation in a closed container, however, it was found that [DDA] [DL-lactate did not damage the print and the paper experienced no deformation during impregnation. As an effect of the solution of the liquid discussed above, the impregnated paper permanently lost its non-transparency.

Based on the results, it was concluded that, among the tested ionic liquids, [C_4mim] [Tr] and [C_4mim] [Bt] turned out to be effective in paper deacidification. The compounds changed paper pH to alkaline when solutions at a concentration exceeding 3% were used.

Paper deacidification is just preventive because paper degradation can be only stopped, not reversed. Unfortunately, basic deacidification methods fail to meet all the parameters which determine whether the method is effective or not. Nevertheless, ionic liquids create a new perspective in this area.

3. Effect of ionic liquids on paper properties

The application of chemical compounds to paper is only possible provided its original parameters can be maintained. Any change in properties of this organic material can contribute, for instance, to quality deterioration of particularly valuable antique works created on paper. Therefore, the effect of ionic liquids on selected optical and strength properties of the material was checked. For this purpose, hand sheets made of bleached pine pulp, recycled pulp and CTMP were used. The pine pulp beating was carried out in a valley beater according to ISO 5264-1:1979 [26]. Paper test sheets of approximately 70 g/m^2 were made under

laboratory conditions using the Rapid-Köthen apparatus in accordance with ISO 5269-2:2004 [27]. The test sheets were conditioned in accordance with ISO 187:1990(E) [28].

Then, the prepared paper was treated with ionic liquids: benzalkonium nitrate [BA][NO_3]; benzalkonium [BA][DL-lactate] and didecylodimethylammonium DL-lactate at a concentration of 3% and 8%. The paper samples underwent impregnation on petri dishes by analogy to the deacidification process.

3.1. Paper impregnation with ionic liquids versus paper brightness

Paper brightness is determined as a percentage ratio of the light reflected from the paper surface to the diffused light reflected from the surface of the masterpiece, the brightness of which is assumed to be 100%. Brightness was determined using SpectroEye supplied by GretagMacbeth, in accordance with ISO 11475:2004 [29].

Figure 1 shows a small increase in paper brightness as the effect of ionic liquids. In case of the pine pulp paper, lactates proved to be the most effective, although the effect depended on their concentration.

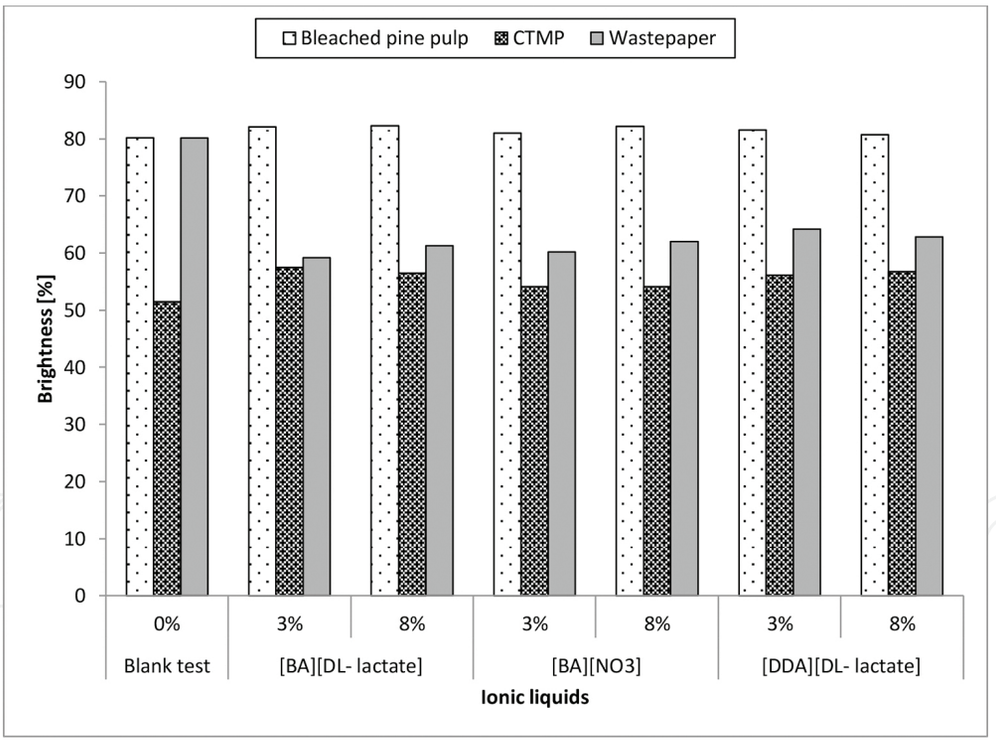

Figure 1. The brightness of paper impregnated with ionic liquids vs. blank test.

For [BA][DL-lactate], the highest brightness was obtained when the concentration was 8%, and for [DDA][DL-lactate]—a lower concentration was effective. The CTMP paper showed a regular increase in brightness as a result of each of the three applied compounds. In turn, the recycled paper obtained the highest increase in the parameter when [DDA][DL-lactate] was used.

3.2. Change in paper opacity after impregnation with ionic liquids

Paper opacity is an important performance parameter of publishing and packaging paper materials; it determines the resistance of paper against light penetration. This parameter is reciprocal to visible light penetration. It characterises non-transparent paper as completely impenetrable to visible light. The parameter was determined according to ISO 2471:2008 [30].

It is required that printing papers should feature the highest possible opacity because this enhances print legibility and aesthetics. Opacity of all tested papers—bleached pine pulp, CTMP and wastepaper—which were impregnated with ionic liquids, remains at a similar level (**Table 5**). A small 3–5% increase in opacity was observed for the pine pulp paper for all three tested compounds.

Ionic liquid	Concentration	Opacity [%]		
		Bleached pine pulp	CTMP	Wastepaper
Blank test	–	81.3	98.9	77.1
[BA][DL-lactate]	3%	84.8	99.1	100.0
	8%	84.3	99.4	99.2
[BA][NO_3]	3%	84.6	99.3	100.0
	8%	84.3	97.9	99.1
[DDA][DL-lactate]	3%	84.5	98.2	98.6
	8%	86.4	98.4	98.6

Table 5. The opacity tested papers.

3.3. Effect of paper impregnation with ionic liquids on breaking length

Another very important paper parameter is its breaking length. It should be emphasised that this parameter is not measured but it is calculated from tensile force at break, according to ISO1924-1:1992 [31]. Nevertheless, in papermaking field, the breaking length, not the tensile force, is used as one of the key parameters for characterising end-use properties of paper. Breaking length is generally used in the paper trade to characterise the inherent strength of paper. The breaking length is the paper strip length at which the sample would break by its own weight, if suspended vertically from one end. It affords an excellent basis for comparing the strength of papers made from different furnishes and having different basis weight.

All the three ionic liquids—benzalkonium nitrate [BA][NO_3]; benzalkonium lactate [BA][DL-lactate] and didecylodimethylammonium DL-lactate [DDA][DL-lactate]—reduced breaking length, compared to non-impregnated samples (**Figure 2**). Also, concentrations of the compounds play a significant role. As the concentration rises, breaking length of the paper sample decreases.

However, it must be emphasised that the average breaking length of publishing paper materials reaches approximately 2000 m, and hence impregnation with 3% compounds does

not disqualify any paper, except CTMP. While soaking with ionic liquids, the material structure was slackened, so that breaking length measurement could not be taken.

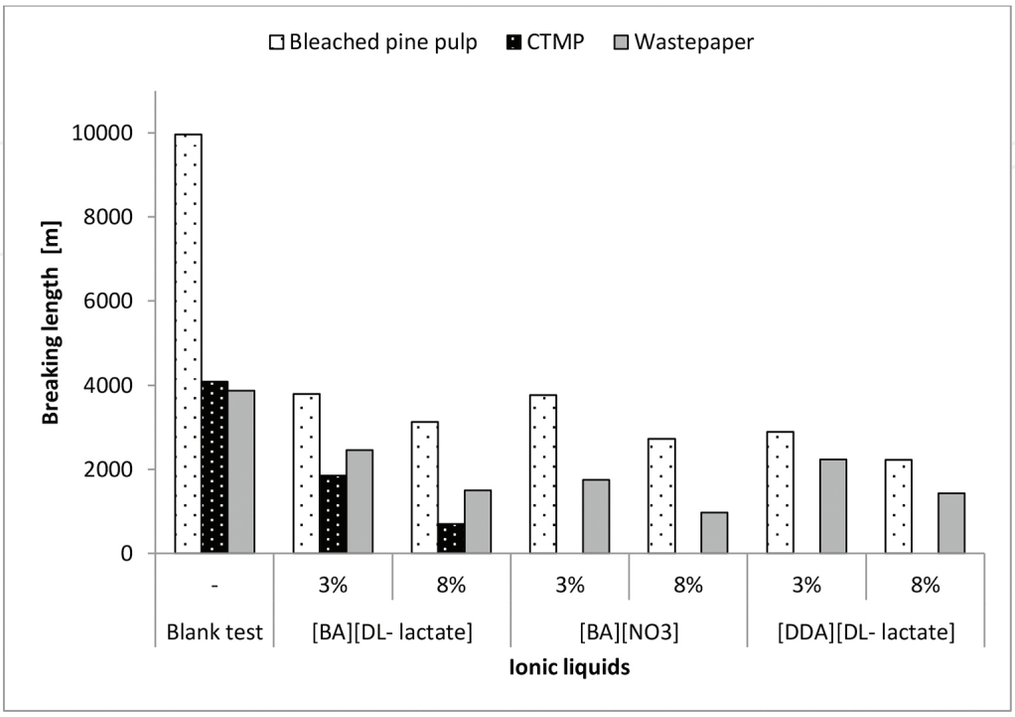

Figure 2. The breaking length of paper impregnated with ionic liquids vs. blank test.

3.4. Changes in tear resistance of the paper impregnated with ionic liquids

Tear resistance is the force required to tear a notched paper sample. This property depends on the length of fibres and their longitudinal or transversal arrangement. The result of tear resistance after application of ionic liquids on the paper samples was determined according to ISO 1974:1990 [32] as presented in **Figure 3**.

By the effect of [BA][NO_3], tear resistance of pine and wastepaper pulp (impregnation with a 3% solution) increases; for CTMP, compared with samples without ionic liquids, the value decreases. Tear resistance of the pine pulp paper, impregnated with [BA][DL-lactate] at a higher concentration, is also higher, compared to the non-impregnated paper. For the wastepaper pulp, it was found that tear resistance increased as concentrations of all three ionic liquids decreased.

3.5. Summary

Benzalkonium nitrate [BA][NO_3]; benzalkonium lactate [BA][DL-lactate] and didecylodimethylammonium DL-lactate [DDA][DL-lactate], as representatives of ionic liquids, showed a beneficial effect on paper optical properties. Depending on the ionic liquid concentration, paper brightness changes; higher concentration results in higher brightness. Also, raw material

http://dx.doi.org/10.5772/65860

composition of the tested papers plays a significant role. The highest brightness was encountered in the case of the pine pulp paper, whereas the highest opacity was observed for the CTMP paper. The paper samples impregnated with ionic liquids were characterised by worse static properties; however, dynamic strength properties were improved.

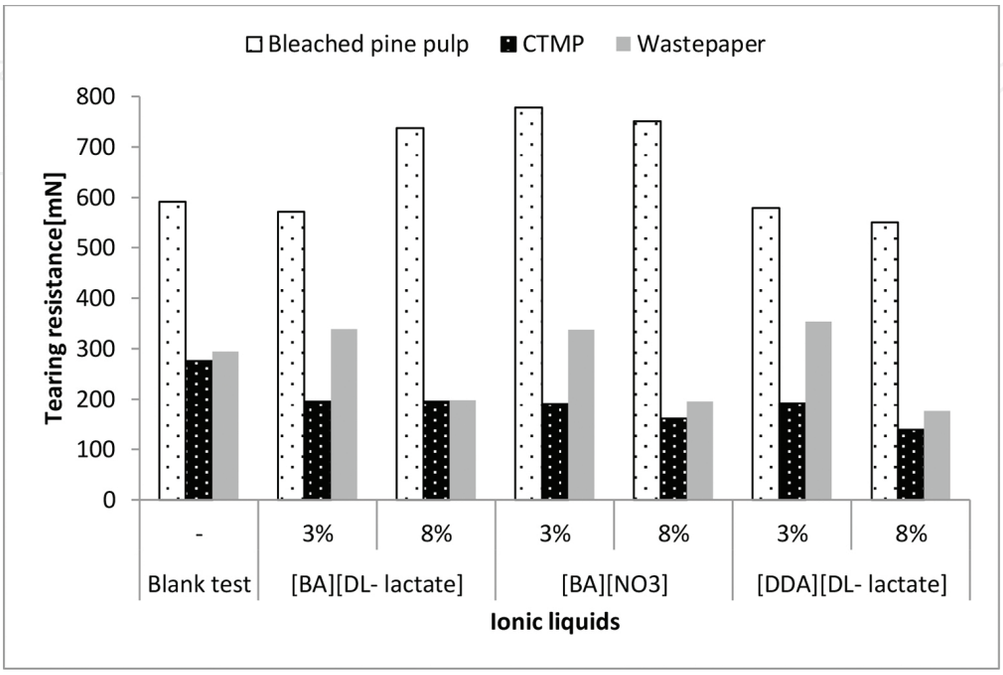

Figure 3. The tearing resistance of paper impregnated with ionic liquids vs. blank test.

The ionic liquids used in the research cause a high reduction in breaking length, which clearly depends on the concentration. Higher concentrations result in lower breaking length. It may be supposed that the change in this property by the effect of ionic liquids results from slackening of the structure and breaking bonds between fibres, which reduces paper strength.

In the case of paper impregnated with ionic liquids, an increase in tear resistance was observed. The best results were obtained for the pine pulp paper samples impregnated with [BA][NO_3].

4. Application of ionic liquids in protecting paper from the growth of microorganisms

Paper is an easily biodegradable material. It is particularly susceptible to microbiological decomposition as its main component—cellulose—is a polymer decomposed by many microorganisms, among which moulds are the most active group. They participate in oxygenic paper decomposition through the production of extracellular cellulases. Initially, moulds from the *Aspergillus*, *Penicillium*, *Trichoderma* and *Fusarium* genera, which require a less humid substrate, take part in the process. As the source of nutrients, they use components present in paper and, simultaneously, they prepare the substrate for other fungi—*Alternaria*, *Chaetomi-*

um and *Stachybotrys*—which, in turn, require higher humidity, but are capable of hydrolysis of resistant cellulose fibres. Cellulose decomposition can completely disqualify finished paper products since the degree of cellulose polymerisation is decreased by the activity of cellulolytic enzymes. An impairment of structure of the cellulosic fibre results in its reduced strength, and hence in the complete decomposition [33–35]. However, one must bear in mind that there are plenty of various types of paper in the world, and not every type is susceptible to microorganisms to the same extent. Paper biodegradation is affected by technological parameters of the material, the manufacturing process and environmental factors [36–38].

In recent years, biocides have been used more and more often and to a greater extent. They are used not only for disinfection, but also for finishing processes in cellulosic materials, and thus the latter may become less susceptible to the destructive action of microorganisms. Also, antimicrobial agents are used to protect different paper forms (books, photographs, paintings) stored in libraries, archives and museums [2, 15, 36, 39].

The aim of the presented study is to determine the antifungal activity of ionic liquids which, once added, protect paper from the growth of moulds.

4.1. Minimal concentrations of ionic liquids inhibiting the growth of moulds

Two of basic parameters determined during the control of the antimicrobial activity of various chemical compounds or mixtures are minimal inhibitory concentration (MIC) and minimal bactericidal/fungicidal concentration (MBC/MFC). The former describes the lowest compound concentration that inhibits the growth of microorganisms in the sample. Values of the latter parameter–MBC/MFC–refer to the lowest concentration of the antimicrobial agents required to reduce the viability of 99% microorganisms. In research on the antimicrobial activity of ionic liquids, these two parameters are determined most frequently, as reported in references [8, 10, 40–43]. Primary research methods used to determine MIC/MBC/MFC values include dilution tests and agar diffusion tests [10, 44].

To date, most of the research has focused on bacteria and yeast, while the biodegradation of paper is most frequently caused by moulds. For that reason, in course of authors' own research [45], the effect of the following ionic liquids on moulds was verified: benzalkonium DL-lactate [BA][DL-lactate], didecylodimethylammonium DL-lactate [DDA][DL-lactate], benzalkonium nitrate [BA][NO_3], 1-butyl-3-methylimidazolium benzotriazole [C_4mim][Bt], 1-dodecyl-3-methylimidazolium benzotriazole [C_{12}mim][Bt], and 1-butyl-3-methylimidazolium 1,2,4-triazolate [C_4mim][Tr].

Based on the results, it has been concluded that there are three compounds inhibiting the growth of moulds at concentration up to 100 ppm: lactates and nitrates (**Table 6**). Among them, the best antimicrobial properties were demonstrated by [DDA][DL-lactate], the MIC values of which were in the range of 19.5–78.2 ppm. Within the group of imidazole-based ionic liquids, the lowest MIC values were obtained for 1-dodecyl-3-methylimidazolium benzotriazole, which was effective at 30- to 60-fold lower concentrations compared to two other compounds —[C4mim][Bt] and [C4mim][Tr].

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Ionic liquids	Mould strains				
	A. niger ATCC 16404	*A. terreus* ATCC 10020	*A. versicolor* ATCC 9577	*P. aurantiogriseum* ATCC 18382	*P. chrysogenum* ATCC 60739
I GROUP					
[BA] [DC-lactate]	78.2	39.1	39.1	78.2	78.2
[DDA] [DC-lactate]	78.2	39.1	39.1	39.1	19.5
[BA][NO_3]	156.3	39.1	39.1	78.2	39.1
II GROUP					
[C_{12}mim][Bt]	107.9	107.9	107.9	215.8	107.9
[C_4mim][Bt]	3439.5	3439.5	3439.5	6879	6879
[C_4mim][Tr]	6145	6145	6145	>6145	6145

Table 6. Value of minimal inhibitory concentration [ppm] [45].

Taking the strains of the investigated moulds into account, it was *Aspergillus niger* that was found least susceptible to the action of ionic liquids in Group 1. For imidazoline ionic liquids in Group 2, the highest MIC values were recorded for two strains of the genus *Penicillium*.

The ionic liquids used in the research show good antifungal activity, but their effectiveness essentially depend on the molecular structure. The lowest MIC values were obtained for didecylodimethylammonium DL-lactate and 1-dodecyl-3-methylimidazolium benzotriazole. These are compounds, the structures of which contain long alkyl chains responsible for the antimicrobial activity of the compounds. The results are confirmed by the work conducted by Demberelnyamba et al., who managed to determine MIC values of quaternary 1-alkyl-3-methylimidazolium compounds against bacteria, yeasts and algae. The lowest values were obtained for compounds containing 12–14 carbon atoms in the alkyl chain. The relationship between MIC and the length of the alkyl chain in ionic liquids was also repeatedly as proven by Refs. [9, 41]. Overall, it was found that the highest antimicrobial activity across all the groups of ionic liquids is obtained for the compounds with an alkyl chain substituent of 12 carbon atoms on the cation.

4.2. Evaluation of the antifungal activity of paper modified with ionic liquids

A series of testing methods have been developed for the evaluation of antimicrobial properties of paper; the differences lie in the intended use of the tested paper materials, time of exposure to microorganisms, and their physical properties. Selecting adequate microorganisms, depending on the chosen testing method is also an important element of the tests.

The methods to evaluate the bioactive effect on paper products can be divided into quantitative and qualitative. They are described in various standards developed by, for instance, ASTM International (ASTM E723, ASTM E875, ASTM E1839, ASTM D2020) and the Technical Association of the Pulp and Paper Industry (TAPPI T449, TAPPI T487) [4]. For paper testing,

the standards developed by the Association of Textile, Apparel & Materials Professionals (AATCC 100, AATCC 147) are followed as well.

4.2.1. Antifungal activity of paper: qualitative method

The qualitative methods are used to determine the bioactivity of paper materials containing biocides and make it possible to evaluate the bacteriostatic and fungistatic properties. The methods essentially consist in placing a paper sample on an agar substrate with cultivated microorganisms with the appropriate density of inoculum. If the tested paper shows antimicrobial properties, a zone where the growth of microorganisms under the sample and around it has been inhibited, will be present. The usual good effect of the biostatic action of paper for this method is indicated by the lack of growth of microorganisms in the sample.

In course of authors' own research [35], paper samples were soaked with four of the most effective ionic liquids: benzalkonium DL-lactate [BA][DL-lactate], didecylodimethylammonium DL-lactate [DDA][DL-lactate], benzalkonium nitrate [BA][NO_3] and 1-dodecyl-3-methylimidazolium benzotriazole [C_{12}mim] [Bt]—at concentration of 3% and 5%. Next, the spore suspension (10^6 conidia/mL) was placed on petri dishes containing malt extract agar (Merck). Prepared paper stripes with ionic liquids were then placed there one by one. The dishes were incubated at 28°C for 24–72 h. Once the experiment was completed, the efficiency of ionic liquids action on the paper against the moulds was evaluated. The growth of microorganisms between the medium and the tested sample was checked for this purpose. In addition, the inhibition zones around the sample relative to the reference sample without ionic liquids were determined. The results are presented in **Table 7**.

It was found that the ionic liquids in the paper at concentration of 3% do not show potent antifungal properties against the tested species. A very good antifungal activity relative to the studied strains was not obtained until compounds at concentration of 5% were used. The best antifungal activity among the four biocides was demonstrated by 1-dodecyl-3-methylimidazolium benzotriazole. For the *Aspergillus terreus* strain—the most sensitive one among the studied strains—growth inhibition zones on pine paper are more than 4-fold higher compared with the *Aspergillus niger* strain The tested microorganisms can be ordered according to their decreasing sensitivity as follows: *Aspergillus niger* > *Penicillium aurantiogriseum* > *Penicillium chrysogenum* > *Aspergillus versicolor* > *Aspergillus terreus*.

Taking the type of paper into account, the largest inhibition zones were observed for pine paper, whereas the smallest for CTMP paper. CTMP paper, obtained using cellulosic mass after chemical-thermo-mechanical treatment with the tested compounds at concentration of 3%, showed limited antimicrobial activity against *A. niger* and *P.aurantiogriseum.* For pine paper, the growth inhibition zones of the mentioned strains were twice as large compared with the CTMP paper.

The interpretation of the results in qualitative methods is based on an analysis of the growth inhibition zone, which can indicate not only high antimicrobial activity of the tested paper materials, but also the weak binding of the biocide with the surface of the material in question. Also in the TAPPI T487 test, the evaluation of paper resistance to moulds involves

macroscopic observation. Despite the fact that they are less labour consuming, qualitative methods should not be the final tests aimed to obtain result at the antimicrobial evaluation of selected materials.

Mould strains	**Kind of paper**	**Kind of ionic liquid**							
		[BA] [DL-lactate]		**[DDA] [DL-lactate]**		**[BA][NO_3]**		**[C_{12}mim] [Bt]**	
		3	**5**	**3**	**5**	**3**	**5**	**3**	**5**
***A. niger* ATCC 16404**	Bleached pine pulp	1	2	3	5	3	4	1	2
	Wastepaper	1	2	2	3	2	3	1	2
	CTMP	0	2	0	2	0	2	0	1
***A. terreus* ATCC 10020**	Bleached pine pulp	6	9	4	6	8	10	13	16
	Wastepaper	6	8	5	6	7	9	12	14
	CTMP	4	6	3	4	5	7	10	10
***A. versicolor* ATCC 9577**	Bleached pine pulp	7	10	4	6	10	11	5	7
	Wastepaper	7	8	4	5	7	9	5	8
	CTMP	4	7	3	5	7	10	2	4
***P. aurantiogriseum* ATCC 18382**	Bleached pine pulp	3	4	4	4	3	5	5	6
	Wastepaper	1	3	3	3	4	4	3	4
	CTMP	0	3	0	2	2	3	2	3
***P.chrysogenum* ATCC 60739**	Bleached pine pulp	4	5	3	4	5	6	4	6
	Wastepaper	4	5	2	3	4	5	4	5
	CTMP	3	4	2	3	3	5	3	4

Table 7. Growth inhibition zones [mm] observed for moulds under the influence of ionic liquids contained in paper samples [35].

4.2.2. Antifungal activity of paper: quantitative method

In the next stage of the study, the changed amount of conidia on paper samples with ionic liquids within 24 h was determined. For the test purposes, *A. niger* was selected as a strain which is least susceptible to ionic liquids, and the CTMP paper and pine BKP paper containing benzalkonium DL-lactate [BA][DL-lactate], didecylodimethylammonium DL-lactate [DDA][DL-lactate], benzalkonium nitrate [BA][NO_3] at concentrations of 3 and 5% were used. Papers without biocide constituted reference samples. On each paper sample, 0.1 mL

of conidia suspension (10^7 conidia/mL) was placed in petri dishes. The dishes with the samples were incubated for 24 h at 28°C and the relative humidity RH of 80%. After 0, 3, 6, 12 and 24 h, the samples were shaken in a saline solution with a neutraliser in order to leach microorganisms from the test material. Next, the suspension was diluted and transferred onto petri dishes and the MEA (Merck) medium was poured them. The dishes were incubated at 28°C, RH 80%, for 72 h. Taking the dilutions into account, it was possible to calculate the conidia that survived on the paper surface. The results were presented as log conidia per paper cm^2 in **Figures 4** and **5**.

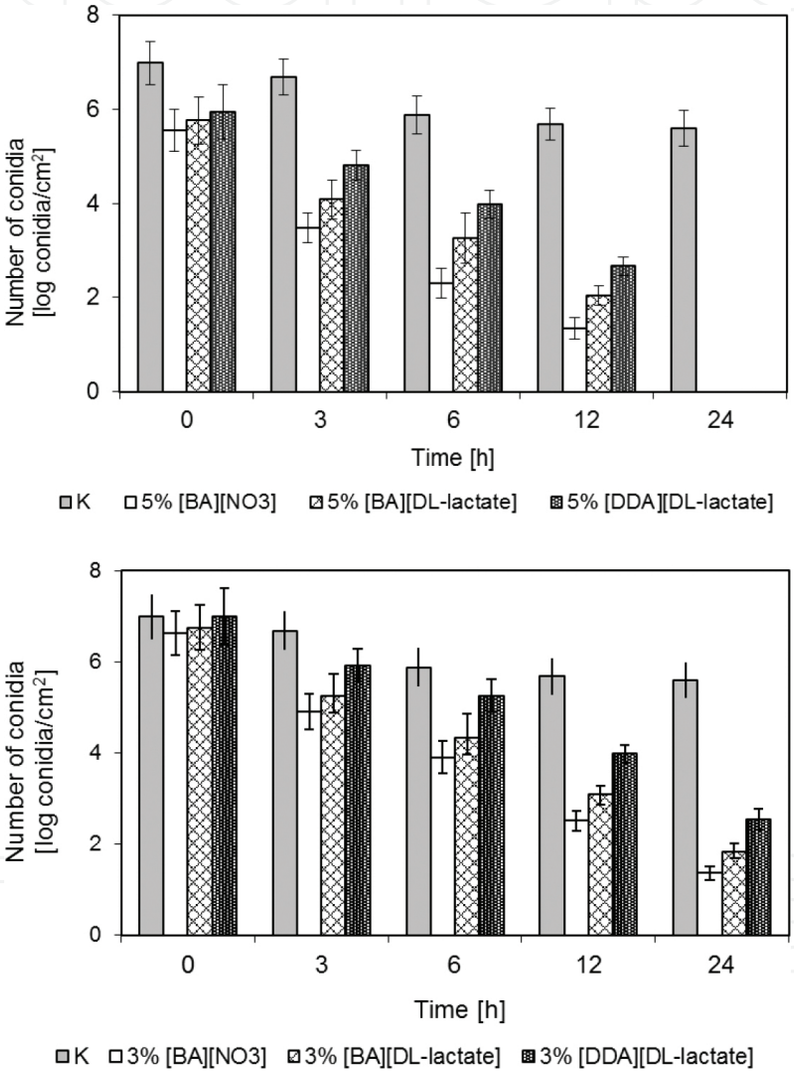

Figure 4. Changes the number of conidia on the surface of the tested paper stripes with CTMP modified with ionic liquids. Concentration of ionic liquids in the samples: (a) 5% and (b) 3% [35].

Active conidia (see **Figure 4**) were still observed after 24 h on the paper made of CTMP pulp with an addition of each of the three ionic liquids at concentration of 3%. This number decreased by more than 5 log in samples with benzalkonium nitrate and didecylodimethylammonium DL-lactate. On paper materials modified with didecylodimethylammonium, DL-

http://dx.doi.org/10.5772/65860

lactate amount of conidia was reduced by 4.5 log and equalled 2.5 log. The reduction of the number of conidia by 4–5 log as the disinfecting effect is high. However, even conidia at such a low concentration (10^2 conidia/sample) in paper with higher humidity can develop into mycelium and cause material destruction. For this reason, ionic liquids were added to other samples in an amount of 5%.

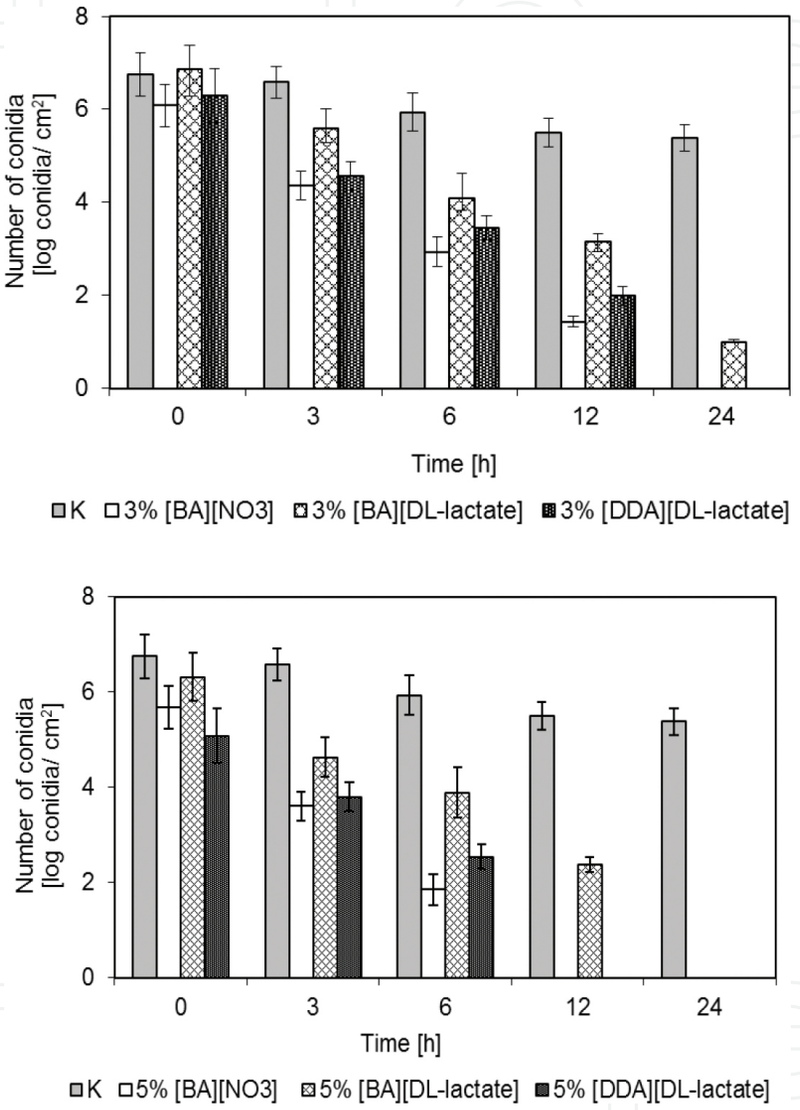

Figure 5. Changes the number of conidia on the surface of the tested paper stripes (pine bleached kraft pulp) modified with ionic liquids. Concentration of ionic liquids in the samples: (a) 3% and (b) 5% [35].

A higher concentration proved to be much more effective. After 24 h, no presence of conidia was found on any paper, except the reference sample (the one without biocide).

The ionic liquids in the pine BKP paper were more reactive compared to the CTMP paper; the same conclusion was drawn during the already presented qualitative tests. For paper materials with 3% [BA][NO_3] or [DDA][DL-lactate], no growth of conidia was observed after 24 h. An exception was presented by [BA][DL-lactate], for which the number of conidia decreased by 6

log compared with the initial concentration, but active forms were still present. The increase in concentration by 2% contributed to a quicker reduction of conidia. After 24 h, no growth of moulds was recorded on any tested paper. As soon as after 12 h, the reduction of active conidia amounted to 100% for the samples with [BA][NO_3] and [DDA][DL-lactate]. The number of spores within the period reached 2.4 log for paper materials with the additive of [BA][DL-lactate].

5. Conclusion

In recent years, ionic liquid have enjoyed more and more interest, both in research and in practical applications. Their various aspects are discussed, such as antimicrobial properties [8, 10, 42, 46] used in histopathologic diagnostics [47], in paper protection [6] and in wood preservation [48]. In the presented research, ionic liquids were used as an additive to paper to neutralise acid paper and as antifungal compounds. Ionic liquids create an alternative to currently used compounds; a great number of combinations (10^{18}) due to their ionic structure is the reason why this type of liquids seems to be an almost inexhaustible resource. Thus, newer and newer compounds with improved properties can be designed, and such compounds can be applied for purposes of paper protection, too.

Acknowledgements

The study was supported by KBN grant 'The research of paper conservation with the use of ionic liquids' N N209 199238.

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