Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology № 85, 2014: 241-245
(Ann. WULS - SGGW, For. and Wood Technol. 85, 2014)

The effect of deacidification with the use of magnesium hydroxide nanoparticles on optical properties of printed paper

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Abstract: *The effect of deacidification with the use of magnesium hydroxide nanoparticles on optical properties of printed paper.* The aim of this study was to assess the effect of deacidification of printed paper using magnesium hydroxide nanoparticles on its optical properties. Printed paper and newsprint showed a slightly greater ISO whiteness and a shift toward the blue colour (CIE L*a*b*). Print and pencil writing showed good resistance to deacidification conditions. Aniline ink stamp faded slightly.

Keywords: paper conservation, printed paper, deacidification, magnesium hydroxide, nanoparticles

INTRODUCTION

New raw materials (groundwood and chemical pulp) and sizing of paper with aluminium sulphate in an acid medium, introduced in the mid-19th century, resulted in a reduction of print paper prices, thus contributing to the development of readership and promoting a leap forward in the development of civilisation for societies in industrialised countries. However, acidification of paper during the production process causes progressing ageing degradation as a result of hydrolysis and oxidation of cellulose. Various techniques and chemical reagents are applied in paper deacidification processes (Baty et al. 2010). An important aspect in conservation processes is connected with the maintenance of possibly unchanged optical properties of papers. When applying naturally white magnesium compounds - MgO, $Mg(OH)_2$ - paper whiteness may be enhanced as a result of deposition of these reagents on paper surface (Kozielec 2009). Reduction of particle dimensions in the case of deacidification reagents may enhance their capacity to penetrate into the paper structure and limit the formation of depositions on its surface (Stefanis and Panayiotou 2007, 2008, 2010). This paper presents results of measured optical properties of printed papers subjected to deacidification with $Mg(OH)_2$ nanoparticles.

MATERIAL

The applied deacidifying reagent consisted of $Mg(OH)_2$ nanoparticles (p.f.a., 99.8% trace metal basis, Aldrich, No. 632309), with particles <100 nm (laser PSA, TEM, XRD). Analyses were conducted on two types of paper (samples of 4 × 4 cm, cut in the machine direction):

1. Printing paper from 1946, grammage 51.90 g/m^2, pH 4.65,
a/ unprinted samples, b/ printed samples, c/ samples with aniline ink stamp.
2. Newsprint from 1978, grammage 59.84 g/m^2, pH 4.45,
a/ printed samples, b/ samples with pencil writing, c/ samples with ballpoint pen writing.

Samples, after their moisture content had been determined, were deacidified applying a dispersion of $Mg(OH)_2$ nanoparticles in 2-propanol at a concentration of 0.0125%, introduced a room temperature by washing (2×0.5 h) in Petri dishes. Following deacidification the samples were dried for 10 days at room temperature, lightly pressed with a sheet of neutral blotting paper in order to provide smooth surface and their recorded pH was 6.44 (sample no. 1) and pH 7.28 (sample no. 2).

In order to determine the effect of solvent on optical properties, paper samples nos. 1 and 2 were washed separately in deionised water and in 2-propanol (2×0.5 h), next they were dried under identical conditions as deacidified samples.

METHODS

The reaction (pH) of paper samples was controlled by cold water extract analyses (Tappi T 509 om-02). Optical properties were measured at the same points using a L&W Elrepho apparatus, measuring colour according to the CIE L*a*b* system, while brightness was measured according to the ISO 2470 standard. Eight samples were analysed for each type of paper (1 and 2).

RESULTS AND DISCUSSION

Preliminary visual observations showed that unprinted papers deacidified in the medium of 2-propanol exhibited greater stability than similar samples following a water bath. These samples were smooth and unwrinkled, in contrast to papers soaked in water. Visual observation of the deacidifying suspension and cold water extracts (for determinations of pH) also showed that 2-propanol does not have a significant effect on extraction of paper components. In contrast, the water extract after water bath was distinctly coloured, which indicates the penetration of paper components to aqueous solutions.

Table 1. Optical properties of paper samples after soaking in water and 2-propanol.

Sample No	Printed paper (1946)								
	Before soaking in water				After soaking in water				
	L*	a*	b*	R 457	L*	a*	b*	R 457	ΔE
1	78.69	4.34	21.13	36.86	79.15	3.0	17.82	40.05	3.60
2	70.08	4.18	21.11	37.40	79.25	2.93	17.77	40.23	3.57
3	78.94	4.24	21.35	37.04	79.15	2.95	17.87	40.01	3.72
4	78.55	4.56	22.08	35.98	78.77	3.17	18.30	39.14	4.03
5	78.40	4.68	22.29	35.63	78.68	3.26	18.52	38.84	3.70
	Before soaking in 2-propanol				After soaking in 2-propanol				
1	79.96	3.43	19.62	39.78	79.86	3.46	19.35	39.85	0.29
2	79.99	3.09	19.22	40.13	79.91	3.10	18.85	40.31	0.38
3	79.71	3.16	19.57	39.47	79.72	3.16	19.15	39.80	0.42
4	79.30	3.50	20.45	38.22	79.18	3.53	20.13	38.29	0.34
5	79.32	4.16	21.17	37.69	79.15	4.18	21.01	37.57	0.23
	Newsprint (1978)								
	Before soaking in water				After soaking in water				
1	75.71	4.66	24.16	31.02	76.18	4.01	23.02	32.39	1.40
2	76.47	4.25	23.96	32.10	76.62	3.68	22.71	33.17	1.38
3	76.77	3.89	23.38	32.87	76.85	3.41	22.19	33.82	1.29
4	75.32	4.90	25.04	30.02	75.63	4.19	23.62	31.35	1.62
5	75.28	5.18	25.07	29.91	74.88	4.50	23.53	30.47	1.73
	Before soaking in 2-propanol				After soaking in 2-propanol				
1	68.10	3.94	22.73	23.63	69.07	3.80	22.23	24.90	1.1
2	66.96	3.37	20.76	23.58	66.86	3.31	20.38	23.70	0.4
3	65.35	3.59	20.98	21.89	65.96	4.20	20.24	22.90	1.14
4	62.75	4.16	21.04	19.48	62.77	4.86	20.36	19.87	0.98
5	67.83	4.50	22.95	23.21	66.32	5.43	21.66	22.47	2.19
6	70.30	4.55	23.80	25.24	69.88	4.50	23.50	24.99	0.52

Table 1 presents results of measurements of optical properties for samples washed in 2-propanol and in water. As it may be concluded, bath in 2-propanol caused no significant changes in optical properties of tested papers. However, both types of paper behaved slightly differently. In the case of newsprint lightness parameters (L*) changed slightly, while changes in parameter a* were more varied and as such they were more difficult to interpret, whereas a certain shift was recorded towards the blue colour based on changes in the b* values. A different trend is found for the results of the ISO brightness measurements, in which a general slight increase by approx. 1% was observed in the brightness parameter. In the case of older paper, made in 1946, the latter parameter (b*) also showed a shift towards the blue colour, but the other parameters (L* and a*) practically did not change in any significant manner. The ISO brightness parameter also changed within the range of 0.5%, which may be assumed to be a non-significant change. Paper produced with a considerable share of chemical pulp, although older, proved to be more stable optically in comparison to newsprint younger by almost 30 years and produced from mechanical pulp (ΔE results indicate that a standard observer does not perceive a difference in colours).

For comparative purposes optical properties were measured also on the same types of paper, this time subjected to a water bath (washing). Measurement results confirmed preliminary visual observations of colour in water extracts. Generally, water washing caused an increase in lightness in the CIE system and ISO brightness for both types of paper (from 1946 and 1978), while values of parameters a* and b* decreased, which indicates changes in colour towards green (a*) and blue (b*). The greatest changes were recorded for the sample of paper produced in 1946 (ΔE>3). Based on the conducted analyses these changes may not be definitely ascribed to ageing degradation of paper and its components, since we may not exclude the effect of its production technology (e.g. the share of water-soluble components).

Table 2. Optical properties of paper samples after deacidification with $Mg(OH)_2$ nanoparticles.

Sample No	Printed paper (1946)								
	Before deacidification				After deacidification				
	L*	a*	b*	R 457	L*	a*	b*	R 457	ΔE
1	75.23	2.68	17.32	35.13	75.17	2.73	16.09	35.92	1.23
2	75.93	2.86	17.79	35.70	75.67	2.95	16.61	36.20	1.21
3	77.00	3.31	18.74	36.41	76.68	3.32	17.41	36.96	1.37
4	77.77	5.03	22.77	34.45	77.49	4.91	21.30	35.14	1.50
5	78.38	4.57	21.91	35.88	78.12	4.53	20.56	36.51	1.38
6	78.50	4.27	21.66	36.23	78.08	4.23	20.47	36.54	1.26
7	76.57	2.30	19.11	35.63	75.56	0.11	16.65	36.17	3.45
Sample No	Newsprint paper (1978)								
	Before deacidification				After deacidification				
	L*	a*	b*	R 457	L*	a*	b*	R 457	ΔE
1	70.28	4.32	22.44	26.08	70.13	4.52	21.91	26.23	0.59
2	72.79	4.97	24.49	27.48	72.64	4.96	23.10	28.20	1.40
3	73.46	3.83	22.61	29.41	73.60	3.84	21.28	30.46	1.34
4	68.92	3.06	19.08	26.52	68.87	3.05	17.90	27.19	1.18
5	69.04	3.24	19.37	26.48	69.22	3.31	18.36	27.30	1.03
6	73.95	3.57	22.28	30.20	74.24	3.86	21.23	31.26	1.13

Printed paper (1946): samples 1,2,3 - with print; 4,5,6 - no print, 7 - with aniline stamp
Newsprint (1976): samples 1-3, 6 - with print; 4,5 - with pencil inscription

A comparison of optical properties of tested papers before and after deacidification with $Mg(OH)_2$ nanoparticles is given in Table 2. Both types of paper showed a slight increase in the ISO brightness. Since the change in brightness and ΔE is greater than that found during a bath in 2-propanol alone it may be assumed that in the case of the first paper (1946) it was the white colour of $Mg(OH)_2$ nanoparticles deposited on paper surface that resulted in this increase in brightness. Also in the case of the other paper sample (1978) the recorded differences in the ISO brightness are slightly greater than in the case of samples washed in 2-propanol alone, although in this case they are not as pronounced as in the former type of paper (1946). A different trend was observed for the results of measurements taken for the CIE colour (1978). Lightness (L*) decreased slightly (results of ΔE measurements indicate that differences in colours may be detected only by an experienced observer), values of parameter a* remained at a similar level, while results of b* measurements indicate a change in colour towards blue, which is correlated with the results of brightness measurements according to the ISO system (measurement of reflectance at the blue filter for the wavelength of 457 nm). Following deacidification no considerable changes were observed in optical properties in printed samples. A slight fading was observed for pencil writing and for the aniline ink stamp. Deacidification may not be applied in alcohol solutions in the case of ballpoint pen writing (this type of ink dissolves in alcohol). However, in old ballpoint pen writing, although the ink faded, it was not washed away in contrast to samples covered with new writing.

CONCLUSION

Deacidification with a dispersion of $Mg(OH)_2$ nanoparticles in 2-propanol applied to papers covered with print and writing does not result in changes in optical properties visible to inexperienced observers. Printing paper and newsprint showed slightly higher ISO brightness and a shift towards the blue colour according to the CIE system measurements. Print and pencil writing showed good resistance to deacidification conditions. The aniline ink stamp faded slightly.

ACKNOWLEDGEMENT

This study has been realized with the financial support of the National Science Center (Poland) grant No. DEC-2012/05/B/HS2/03999.

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Streszczenie: *Wpływ odkwaszania nanocząsteczkami wodorotlenku magnezu na właściwości optyczne papierów drukowych.* Celem badań była ocena wpływu odkwaszania papierów drukowych nanocząsteczkami wodorotlenku magnezu w 2-propanolu na ich właściwości optyczne. Testowano papiery zadrukowane, zawierające zapis ołówkowy, długopisowy i stemple anilinowe. Odkwaszanie nie spowodowało znaczących zmian właściwości optycznych papierów. Papier drukowy i gazetowy wykazywały nieznacznie wyższa białość ISO oraz przesuniecie w kierunku barwy niebieskiej wg oznaczeń w systemie CIE. Druk, zapis ołówkowy wykazały dobrą odporność na warunki odkwaszania. Stempel anilinowy wyblakł w nieznacznym stopniu. Zapis długopisowy jest nieodporny na obróbkę 2-propanolu.

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