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Degradation of paper products from waste pulp types A, B and C with an addition of color pigments under the influence of UV radiation and temperature

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Abstract: *Degradation of paper products from waste pulp types A, B and C with an addition of color pigments under the influence of UV radiation and temperature.* The aging process of paper products made from waste pulp types A, B and C with varying additions of color pigments under the influence of UV radiation and elevated temperature was investigated in this study. Sheets of paper were manufactured under laboratory conditions with an addition of ferric color pigments (a mixture of Fe_2O_3 and FeO(OH)) Bayferrox 140 at 2 and 5% in relation to d.w. Analyses showed that the change in color caused by aging with an increase in the contents of color pigments is markedly smaller than in the case of control samples or those filled with titanium white.

Keywords: waste pulp, pigment, aging, degradation, UV radiation, thermal aging, UV aging

INTRODUCTION

The problem of paper product degradation under the influence of abiotic factors such as light or temperature is relatively well-known. The situation is different in the case of papers manufactured from waste paper pulps. Different types of sizing additives and chemical auxiliaries are used in the process of paper production. These additives influence final properties of the end product, such as paper thickness, its apparent density, dimensional stability, water absorption, air permeability, whiteness, opacity and dimensional properties.

The aim of this fragment of the study was to investigate the degradation process caused by UV radiation and temperature in paper products from waste paper pulp types A, B and C with varying additions of ferric color pigments. It was also attempted to assess the degree of degradation on the basis of changes in the chemical composition of control samples.

MATERIALS AND METHODS

Materials. Sheets of paper with basis weight of 85 ± 5 g/m^2 manufactured under laboratory conditions in a Rapid – Köthen apparatus (PN-EN ISO 5269-2:2007) had the following properties:

- slowness 30° SR
- moisture content 7.5 ± 2% according to PN-P-50150:1985

Analyses were conducted using waste paper type A (weak types, egg trays), B (medium types, newspapers) and C (quality types, office paper) (Przybysz *et al.* 2001). Waste pulp was supplemented with inorganic, synthetic ferric pigment (a mixture of Fe_2O_3 and FeO(OH) - Bayferrox 140 by LANXESS: 2 and 5% sizing additives). Control samples were manufactured with no pigment additive.

Methods. The primary criteria in the assessment of degradation of paper products were color difference (ΔE) and breaking length. Color measurements were taken both before and after the completion of each aging cycle in a Datacolor 600® spectrophotometer in the D65 standard and a 10° field of view and the CIE L*a*b* space. In this space a mathematical description of three components is used: L – lightness (luminance), a – colors from green to red, and b – colors from blue to yellow. Color difference (ΔE) may be calculated from changes in these components according to the following formula:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

This index is always a positive value. It is assumed that a standard observer can see the difference in the following manner:

0 < ΔE< 1 - no difference may be seen; 1 < ΔE< 2 - only an experienced observer can see the difference; 2 < ΔE < 3.5 - an inexperienced observer can see the difference; 3.5 < ΔE< 5 - a marked difference in color may be seen; and 5 < ΔE - the observer perceives two different colors.

Breaking length was determined on the Schopper apparatus according to the PN-P-50133:1983 standard.

The test of aging caused by elevated temperature was run at a temperature of 105±3°C according to the PN-P-50174-01:1993 standard as modified by the team from the Institute of Chemical Wood Technology, PULS. The duration of sample thermal treatment was successively: 24, 48, 72 and 96 h. Aging by UV radiation was performed on the felt side of samples. One cycle was composed of 2, 4, 6, 8 and 10 h. Moreover, paper products manufactured from waste paper pulp types A, B and C were analyzed to determine selected chemical properties and the degree of polymerization, which consisted in the analyses of contents of substances soluble in hot water according to TAPPI T207 cm-08; contents of substances soluble in 1% NaOH according to TAPPI T212 cm-07; contents of substances soluble in 1% H_2SO_4 according to TAPPI T212 cm-07; the share of α-cellulose according to TAPPI T203/by the Seifert method according to PN-P-50092:1992 and contents of mineral substances according to PN-ISO 2144:1996.

In the tested products the degree of polymerization was determined by gel chromatography using a chromatographic system, composed of an Isocratic Pump HP 1050, a Manual Injector (Model 7125-Rheodyne Inc.), a Differential Refractometer Detector HP 1047A, a Column Set: 3x Plgel Mixed A, 20 µm + guard and PL Caliber GPC Software ver. 5.1. Chromatograhic analyses was performed under the following conditions: solvent DMAC/0.5% LiCl, flow rate of 1 ml/min, concentration of 0.05%, sample volume 100 ml, temperature 80 ± 1°C, number of replications 3.

The degree of polymerization was calculated according to the formula:

$$SP = \frac{M_W}{mer\ of\ cellulose},$$

where:

M_w – mass-average molecular weight, mer of cellulose – molecular weight of D-glucose, amounting to 162 g/mol.

RESEARCH RESULTS

Three waste paper pulps from among the four types according to the European nomenclature, i.e. A, B and C, were selected for analyses. The selection of waste paper pulps was connected with the fact that these are the three most frequently recovered and recycled types of waste paper pulps.

Pigments are water-insoluble substances and in comparison to dyes they show limited affinity to fibers. For this reason they exhibit low dyeing power, but they show high resistance to light and other factors (Przybysz 1997). It was the intention of the authors to conduct tests on paper subjected to artificial aging. Thus the pigment most resistant to UV radiation and elevated temperature was selected for testing purposes.

Table 1 presents results of analyses of chemical composition for samples made from three types of waste paper pulp (A, B and C) before and after artificial aging.

In each case a deterioration was observed in their properties. An increase was recorded in contents of substances soluble in hot water, 1% NaOH and 1% H_2SO_4. Contents of α-cellulose in each case decreased by approx. 20 percentage points, while the reduction of the degree of polymerization was close to 100.

A reduction in the basic strength parameter, i.e. breaking length (table 2), under the influence of UV radiation was non-significant and changes were not linearly dependent on the aging process.

What is of interest, considerable average changes were observed in breaking length under the influence of aging caused by elevated temperature (table 3), in contrast to changes presented in Table 2. The greatest change (upon the completion of the aging cycle) was recorded for samples made from waste pulp type C and a 2% addition of pigment (1077 m), while it was lowest for samples produced from waste paper pulp type A with no pigment added.

Averaged measurements of changes in color difference (ΔE) for papers aged by UV radiation showed the greatest changes for light-colored waste pulp papers (B and C) with no pigment added (Table 4). This was caused by marked yellowing, which was limited by pigments.

Tab. 1 Mean results of selected chemical properties of paper products

Type of waste pulp	**Before degradation**						**After thermal degradation**						**After degradation by UV radiation**					
	H_2O	**1% NaOH**	**1% H_2SO_4**	***α*-cellulose**	**mineral substances (ash)**	**Degree of polymerization**	**H_2O**	**1% NaOH**	**1% H_2SO_4**	***α*-cellulose**	**mineral substances (ash)**	**Degree of polymerization**	**H_2O**	**1% NaOH**	**1% H_2SO_4**	***α*-cellulose**	**mineral substances (ash)**	**Degree of polymerization**
A	2.4	15.1	10.2	91.2	14.0	1102	3.4	16.1	9.0	70.8	12.2	890	2.9	15.2	9.1	70.2	12.0	865
B	1.9	11.2	9.7	95.1	10.8	1169	2.5	14.3	7.8	72.4	8.3	1097	2.2	13.8	8.2	74.5	7.9	1080
C	1.5	8.1	6.9	94.0	17.8	1250	3.8	12.3	5.2	75.3	12.0	1108	3.1	12.0	4.9	73.9	11.8	1102

Tab. 2 Means of breaking length [m] of paper samples aged under the influence of UV radiation

Duration of aging by UV radiation [h]	**Type of waste pulp**								
	A			**B**			**C**		
	Concentration of pigment [%]								
	0	**2**	**5**	**0**	**2**	**5**	**0**	**2**	**5**
	Breaking length [m]								
0	2217	2638	2400	4064	3616	3468	2642	2942	2784
2	2490	2461	2485	4459	3911	3719	2662	2654	2365
4	2420	2426	2504	4525	3788	3264	2540	2389	2071
6	2540	2425	2637	4539	3772	3630	2665	2257	2223
8	2413	2289	2654	4147	3822	3627	2474	1951	2421
10	2569	2493	2332	4352	4027	3824	2678	2328	2486

Tab. 3 Means of breaking length [m] of paper samples aged under the influence of high temperature

Duration of aging by high temperature [h]	**Type of waste pulp**								
	A			**B**			**C**		
	Concentration of pigment [%]								
	0	**2**	**5**	**0**	**2**	**5**	**0**	**2**	**5**
	Breaking length [m]								
0	2510	2638	2521	4504	4412	4135	2642	2942	2784
24	2478	2713	2359	4429	4324	3772	2510	2119	2514
48	2349	2457	2272	4204	3771	3698	2546	2372	2630
72	2369	2438	2351	4097	3844	3870	2399	1725	2528
96	2319	2359	2189	4061	3824	3642	1951	1865	2231

Tab. 4 Means of color difference (ΔE) of paper samples aged under the influence of UV radiation

Duration of aging by UV radiation [h]	**Type of waste pulp**								
	A			**B**			**C**		
	Concentration of pigment [%]								
	0	**2**	**5**	**0**	**2**	**5**	**0**	**2**	**5**
	ΔE								
2	1.35	1.27	1.24	1.65	1.81	1.07	2.56	1.27	0.39
4	1.52	1.48	0.95	2.04	2.17	1.22	3.67	1.60	0.59
6	1.81	1.77	1.26	2.70	2.52	1.57	5.50	2.46	1.58
8	2.20	1.80	1.67	3.83	2.85	2.25	5.83	2.96	1.80
10	2.32	2.11	2.51	4.61	3.45	2.37	6.28	3.61	2.30

In turn, for papers aged by elevated temperature considerably greater changes were observed for color difference (ΔE) (Table 5). Yellowing was more marked and degradation was greater. The greatest change was recorded for waste pulp paper type C (office waste pulp paper) with no pigment added, while its addition at 2% by weight reduced this index over three-fold.

Tab. 5 Means of color difference (ΔE) of paper samples aged under the influence of high temperature

Duration of aging by high temperature [h]	**Type of waste pulp**								
	A			**B**			**C**		
	Concentration of pigment [%]								
	0	**2**	**5**	**0**	**2**	**5**	**0**	**2**	**5**
	ΔE								
24	1.55	1.52	1.91	2.25	1.15	2.47	5.67	1.59	1.43
48	2.36	2.49	2.26	2.93	2.49	1.91	10.54	1.76	2.99
72	6.34	4.91	3.39	6.60	5.96	5.55	14.79	4.19	4.91
96	6.82	5.42	3.35	7.65	6.27	5.19	16.87	4.74	5.52

CONCLUSIONS

Tests showed that the change in paper color decreases with an increase in the share of pigment and the reduction of breaking length is not rapid in the case of paper samples subjected to UV radiation. Paper yellowed markedly. This is the most evident result of tests as a result of the artificial aging process under the influence of temperature. Total color difference ΔE provides a complete and comprehensive picture of paper aging.

When analyzing testing results it was found that the addition of ferric pigments to paper products made from paper waste pulp is advantageous. Their presence delays the aging process and it has no considerable effect on mechanical strength. Despite the fact that complete color change does not fall within the limits for the printing industry, it needs to be remembered that these tests are to present changes in color after many years of use of the paper.

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Streszczenie: *Degradacja wytworów papierniczych wytworzonych z makulatury typu A, B i C z dodatkiem pigmentów barwnych starzonych promieniowaniem UV i podwyższoną temperaturą.* W niniejszej pracy zbadano proces starzenia się wytworów papierniczych wykonanych z makulatury rodzaju A, B i C z różnym dodatkiem pigmentów barwnych pod wpływem działania promieniowania UV oraz podwyższonej temperatury. Arkusiki papieru wytworzono w warunkach laboratoryjnych z dodatkiem żelazowych pigmentów barwnych (mieszanina Fe_2O_3 oraz $FeO(OH)$) Bayferrox 140 w ilości 2 i 5% w stosunku do s. m. Badania wykazały, iż wraz ze wzrostem zawartości pigmentów barwnych zmiana barwy na skutek starzenia jest zdecydowanie mniejsza niż w przypadku próbek kontrolnych lub wypełnionych bielą tytanową.

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