# STUDY OF THE EFFECT OF OZONIZATION ON ARCHIVE MATERIALS

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#### **1 INTRODUCTION**

Documents that are inundated in floods frequently have a typical "post-flood" smell after drying. This smell makes further use unpleasant or even impossible. Consequently, the technology of ozonization has been proposed for eliminating this smell; its principle is based on briefly placing the archive materials in an environment with elevated ozone concentration.

Ozone is a gas with a characteristic smell and is heavier than air. It is highly reactive, acts as a strong oxidizing agent and is very unstable. It decomposes relatively rapidly to oxygen  $O_2$ . The decomposition half time is 45 minutes at a temperature of 20 °C and pressure of 101.3 kPa. The decomposition half time is only 20 minutes at a temperature of 30 °C at the same pressure.

Ozone is formed by the action of an electric discharge or short-wave UV radiation on an oxygen molecule. In practice, ozone is produced in generators from the air or from pure oxygen or from oxygen-rich gases using a silent electrical discharge. At a temperature of -112 °C, it condenses to form a dark blue liquid and a black-purple solid substance is formed at a temperature of -192.5 °C. Both substances are explosive and decompose to form oxygen.

The human sense of smell is especially sensitive to the smell of ozone and is thus able to register ozone at a concentration of only 2 ppm. Ozone is toxic and corrosive for all organisms. Prolonged presence on places with elevated ozone concentrations (above approx.  $350 \ \mu g/m^3$ ) leads to a burning sensation in the eyes, nose and throat and, in some cases, also in the chest, with a cough and headache. Ozone concentrations above approx.  $1100 \ \mu g/m^3$  cause serious irritation of the eyes and upper respiratory tract, accompanied by a headache. Concentrations above approx.  $2150 \ \mu g/m^3$  cause very serious irritation of the membranes of the respiratory tract, bronchospasmic states and a cough within a very few minutes. Concentrations above  $21000 \ \mu g/m^3$  lead to unconsciousness, bleeding and eventually death, depending on the exposure time

Regulation of the Government of the Czech Republic No. 178/2001 Coll. stipulates a permissible exposure limit (PEL) of  $100 \ \mu g/m^3$ , which must not be exceeded on a full-shift average. Short-term exceeding of this value is permissible up to a value of HPC-P, i.e. to  $200 \ \mu g/m^3$  (the HPC-P value is the highest permissible concentration, which must not be exceeded under any conditions). Decree of the Ministry of Health of the Czech Republic No. 6/2002 Coll., stipulates the hygiene limits for chemical, physical and biological indicators

for an indoor environment in the residential rooms of certain structures. The limiting hourly concentration of ozone has been set at  $100 \ \mu g/m^3$ .

Ozone is considered to be an important external degradation factor damaging archive materials. Consequently, on the basis of a request by Belfor Czechia, spol. s r. o., the National Archives prepared the following study, which was intended to verify the effect of the ozonization technology on the chemical, optical and mechanical properties of various kinds of paper and on typical recording media.

# **2 EXPERIMENTAL PART**

# 2.1 Materials employed

The following were employed to study the effect of ozonization on the chemical, optical and mechanical properties of various kinds of paper supports:

_	Whatman filter paper, $1.90 \text{ g/m}^2$	<i>(W)</i>
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- Paper for documents according to ISO 9706, 80  $g/m^2$  (ISO 9706)
- Groundwood paper, glazed on one side,  $60 \text{ g/m}^2$  (DP)
- Wood-free writing paper CSN 502251,  $60 \text{ g/m}^2$  (BPP)
- Bleached sulphite cellulose pulp,  $80 \text{ g/m}^2$  (*MgBi*)
- Chemothermomechanical cellulose pulp, 75 g/m<sup>2</sup> (*CTMP*)

The following were employed to study the effect of ozonization on some selected aryl methane dyes and real archive materials:

Samples of Whatman No. 1 filter paper coloured with the following aryl methane dyes:
 Acid Red 87 (AR), Acid Green 16 (AG), Basic Violet 1 (methyl violet – MV), Basic
 Blue 6 (methylene blue – MB), Basic Green 4 (malachite green – MG).

0.1 % (wt) solutions of the dyes in ethanol were prepared, into which samples of Whatman No. 1 filter paper (5x5 cm) were immersed and were then dried in the air. Only for Basic Blue 6 was 50% ethyl alcohol employed.

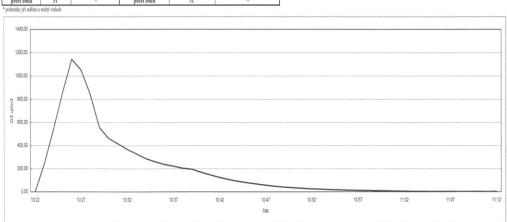
 Samples of archive documents from the 19th and 20th centuries with various types of recording media (ink, stamps, printing, typewriter writing,...)

# 2.2 Description of ozonization of samples

Sheets of paper were hung individually on lines in space, the coloured papers were placed on grids roughly at the height of the Thermo Environmental Model 49 ozone analyzer, which monitored the progress of the ozonization (concentration, time). The experiment progressed from 10:22 A.M. to 11:12 A.M. at an initial temperature of 26.6 °C and relative humidity of 58.6 %. After the Airozon Supercracker (model POCS-500, Trotec, Germany) was turned on, the ozone concentration in the chamber increased over 10-15 minutes to the maximum value of  $1144 \,\mu\text{g/m}^3$  and then decreased. The changes in the ozone concentration in dependence on time are depicted in *Fig. 1*. The temperature and relative concentration at the time of termination of the experiment were 18.3 °C and 55.3 %.

	1 min prům.	1 min prům.		1 min prům.	1 min prům.
ĊAS	O3* ul/m3	O3, ug/m3	ĆAS	O3* ul/m3	O3, ug/m3
10:22	1,39	2,77	10:53	22,3	44,5
10:23	244	487	10:54	19,0	37,9
10:24	541	1 079	10:55	16,4	32,7
10:25	860	1 716	10:56	14,1	28,1
10:26	1 144	2 282	10:57	11,9	23,7
10:27	1 052	2 099	10:58	10,4	20,7
10:28	845	1 686	10:59	9,00	18,0
10:29	557	1 111	11:00	7,51	15,0
10:30	463	924	11:01	6,53	13,0
10:31	418	834	11:02	5,10	10,2
10:32	370	738	11:03	4,55	9,08
10:33	331	660	11:04	3,78	7,54
10:34	290	579	11:05	3,13	6,24
10:35	262	523	11:06	2,77	5,53
10:36	240	479	11:07	2,27	4,53
10:37	223	445	11:08	1,55	3,09
10:38	206	411	11:09	1,83	3,65
10:39	196	391	11:10	2,02	4,03
10:40	169	337	11:11	1,96	3,91
10:41	147	293	11:12	2,37	4,73
10:42	125	249			
10:43	106	211			
10:44	91,1	182	3.50	*	
10:45	79,1	158		2	
10:46	67,9	135	(*)		
10:47	57,1	114			
10:48	48,9	97,6			
10:49	41,7	83,2	1.00		
10:50	35,8	71,4			
10:51	31,2	62,2			
10:52	25,9	51,7			
nax.hodnota/min	1 144	2 282	max.hodnota/min	1 144	2282
min.hodnota/min	1,39	2,77	min.hodnota/min	1,39	2,77
počet bodů	51		počet bodů	51	

Belfor Czechia, spol. s r.o., Měření ozonu při sanaci papírových dokumentů, 12.10.2007



#### *Fig. 1* **Progress of sample ozonization**

# 2.3 Artificial ageing of samples

The samples were artificially aged in damp and dry atmospheres:

- According to ISO 5630/3-1981: Moist heat treatment at 80 °C and 65% relative humidity in an air-conditioning chamber (Sanyo Gallenkamp PLC, Great Britain) for a period of 30 days.
- According to ISO 5630/1-1981: Dry heat treatment at 103 °C in a chamber (Sanyo Gallenkamp OMT OVEN, Great Britain) for a period of 30 days.

#### 2.4 Method of determination of mechanical, chemical and optical properties

### 2.4.1 Preparation of samples prior to determining the mechanical properties

Prior to measurement, samples with a width of  $15 \pm 0.1$  mm were conditioned according to ISO 187 at 23 °C and 50% relative humidity for 24 hours. The mechanical properties of the sample were measured in the longitudinal and transverse directions. The samples were treated as average samples.

The results of measurement of the mechanical properties were processed statistically. The arithmetic mean, standard deviation and reliability interval were calculated at a significance level of  $\alpha = 0.05$ .

#### 2.4.2 Determination of the folding endurance

The folding endurance was determined according to ISO 5626 of the test instrument according to Köhlera-Molina (AB Lorentzen & Wettre, Sweden) using a weight of 400 g (total weight of 600 g). 20 measurements were performed for each direction.

#### 2.4.3 Determination of the tensile strength

The breaking load, elongation at break and breaking length were determined on instrument Alvetron TH1 (Lorentzen & Wettre, Sweden) according to CSN EN ISO 1924-2, Paper and Cardboard Determination of the tensile properties. The distance between the clamps was  $100 \pm 0.1$  mm. 10 measurements were performed for each direction.

### 2.4.4 Determination of the total colour difference $\Delta E *$

The colour difference was determined using a CM-2600d portable spectrophotometer (Minolta, Japan). Monitoring was performed of the total colour difference  $\Delta E_*$ , brightness deviation  $\Delta L_*$ ,  $\Delta a_*$  and  $\Delta b_*$ , depicting the difference in the positions in the CIEL colorimetric diagram \*a\*b\*.

Measuring conditions: observer angle 2°, illumination source D65 (chromaticity temperature 6504 K), average measured area 8 mm.

#### 2.4.5 Reflection UV/VIS spectra

The reflection spectra in the ultraviolet and visible spectral regions (250–750 nm) of Whatman No. 1 filter paper samples, which were coloured with aryl methane dye, were measured on a UV 500 UV/VIS Spectrometer (Unicam, Great Britain).

#### 2.4.6 Determination of the decoloration number DC<sub>457</sub>

Decoloration number  $DC_{457}$  is defined according to CSN 50 0409 by the following relationship:

$$DC_{457} = {}^{o}(K/S)_{457} - {}^{a}(K/S)_{457}$$

where the ratio factor  ${}^{o}(K/S)_{457}$  calculated according to the Kubelka-Munk equation corresponds to the original sample and ratio factor  ${}^{a}(K/S)_{457}$  of the sample following the relevant decoloration change (ozonization, artificial ageing). The DC value is positive for lightening – i.e. *positive decoloration number*, the decoloration number is negative for darkening – i.e. *negative decoloration number*. A Leukometr instrument (Carl Zeiss, Jena, Germany) was used for the measurement.

### 2.4.7 Determination of the pH

The pH values were determined by the cold extraction method according to CSN ISO 6588 on a PerpHecT–meter, model 310 instrument using AquaPro pH combined extraction electrodes (ORION, USA).

#### 2.4.8 Visual evaluation of the colour changes of archive documents

Archives from the 19th and 20th century, cut into strips, were employed to study the effect of ozonization on real archive documents. Some of the strips were subject to ozonization and artificial ageing. Evaluation of the effect of ozonization on colour changes in the paper support and the actual recording media were evaluated visually and recorded photographically using a digital camera.

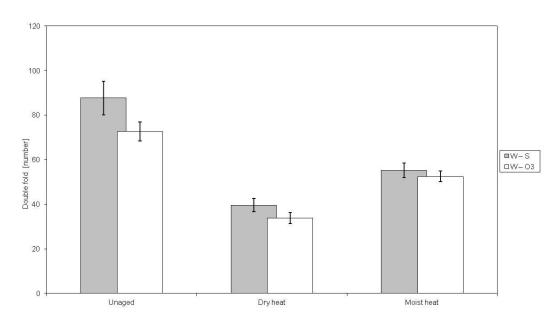
#### 2.4.9 Determining the effect of ozonization on selected micro-organisms

The effect of ozonization on micro-organisms was studied using selected commonly occurring species of fibrous fungi (moulds) derived from the depositary archives - Aspergillus niger, Penicillium aurantiogriseum and Trichoderma koningii. The mould spores were applied to the surface of paper squares with a size of  $2 \times 2$  cm and stored in paper envelopes (only one sample of each kind in each sample). Ten of these envelopes were distributed at various places in the chamber and subjected to the effect of ozone. Then the samples were aseptically removed from the envelopes and placed on the surface of malt wort nutrient agar. Cultivation proceeded at  $24 \pm 4$  °C for 7 days. The growth of mould was monitored and was compared with the untreated (control) samples.

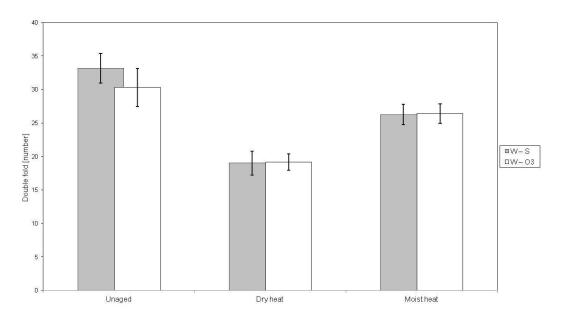
# **3 RESULTS AND DISCUSSION**

# 3.1 Folding endurance

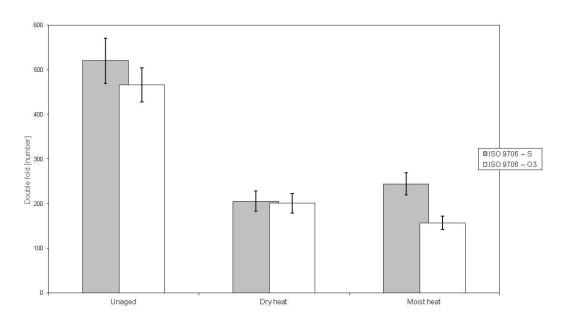
Figs. 2 to 11 depict the dependence of the effect of ozonization and artificial ageing by dry and damp heat on the folding endurance of various kinds of paper. The negligible effect of ozonization on this mechanical property is apparent from the histograms.



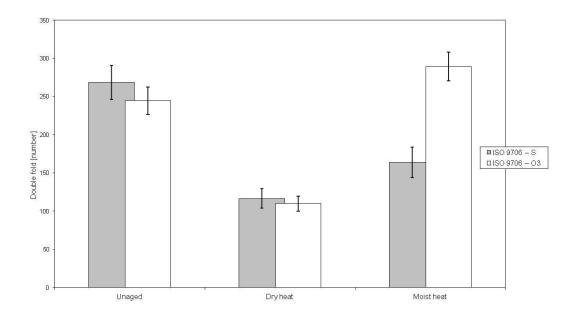
*Fig. 2* Effect of ozonization and artificial ageing on the folding endurance of Whatman No. 1 filter paper in the machine direction



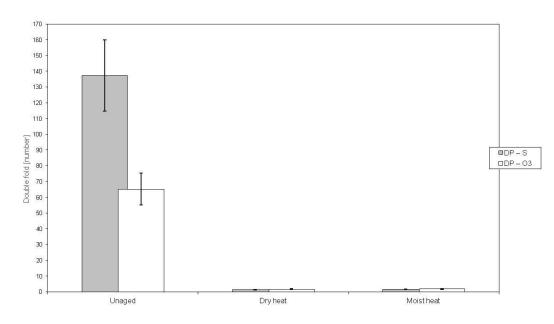
*Fig. 3* Effect of ozonization and artificial ageing on the folding endurance of Whatman No. 1 filter paper in the cross direction



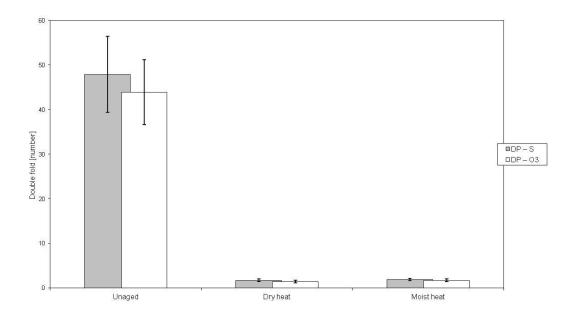
*Fig. 4* Effect of ozonization and artificial ageing on the folding endurance of paper ISO 9706 in the machine direction



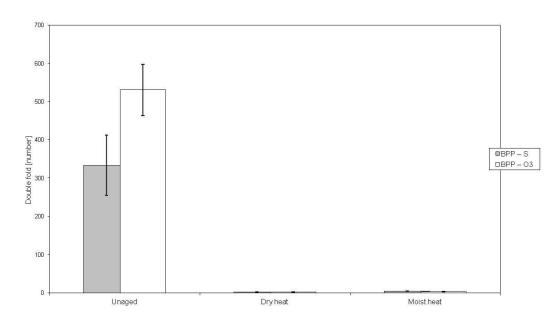
*Fig.* 5 Effect of ozonization and artificial ageing on the folding endurance of paper ISO 9706 in the cross direction



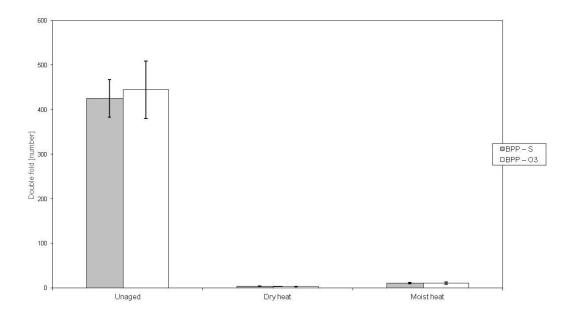
*Fig. 6* Effect of ozonization and artificial ageing on the folding endurance of groundwood paper in the machine direction



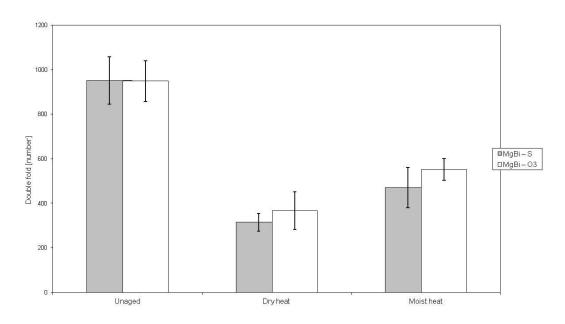
*Fig.* 7 Effect of ozonization and artificial ageing on the folding endurance of groundwood paper in the cross direction



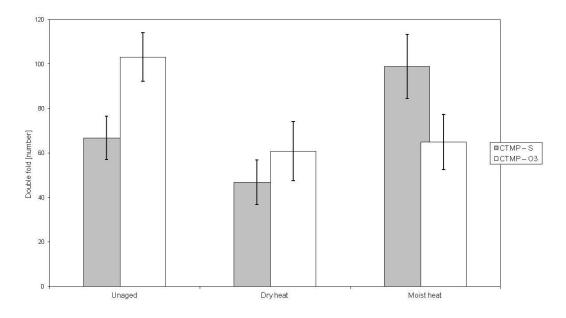
*Fig. 8* Effect of ozonization and artificial ageing on the folding endurance of wood-free writing paper in the machine direction



*Fig. 9* Effect of ozonization and artificial ageing on the folding endurance of wood-free writing paper in the cross direction



*Fig. 10* Effect of ozonization and artificial ageing on the folding endurance of bleached sulphite pulp

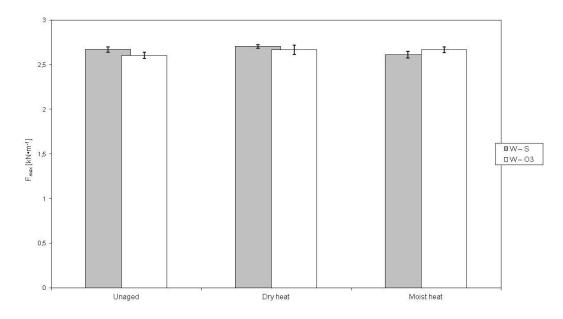


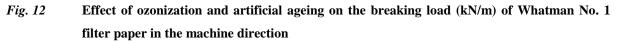
*Fig. 11* Effect of ozonization and artificial ageing on the folding endurance of chemothermomechanical pulp

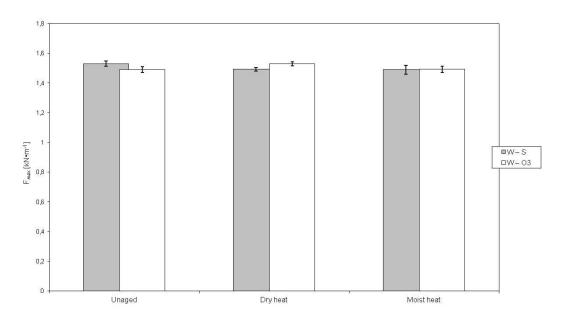
# 3.2 Tensile strength

# 3.2.1 Breaking load

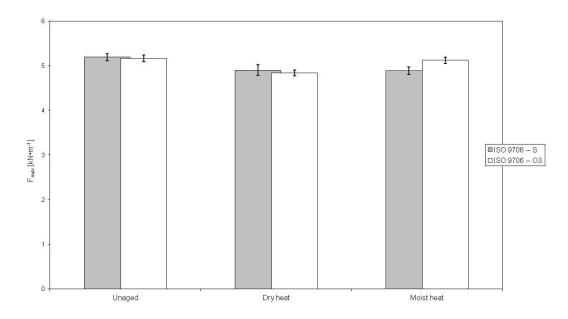
Figs. *12 to 21* depict the dependence of the effect of ozonization and artificial ageing by dry and damp heat on the breaking load (kN/m) of various kinds of paper. The negligible effect of ozonization on this mechanical property is apparent from the histograms.



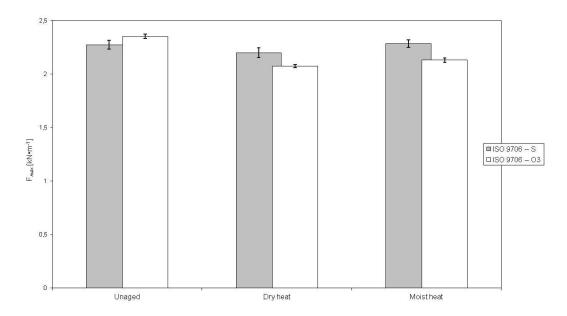




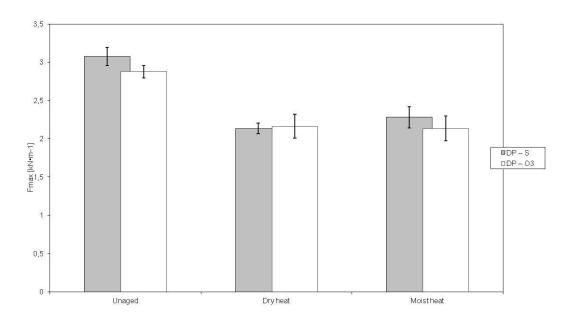
# *Fig. 13* Effect of ozonization and artificial ageing on the breaking load (kN/m) of Whatman No. 1 filter paper in the cross direction



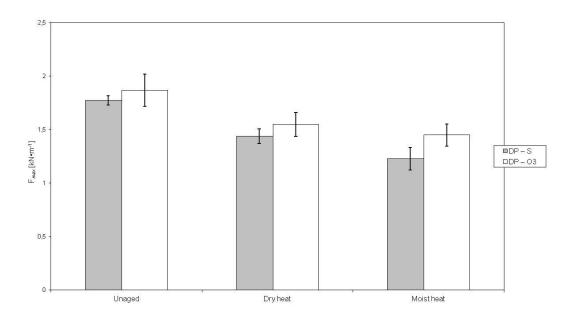
*Fig. 14* Effect of ozonization and artificial ageing on the breaking load (kN/m) of paper ISO 9706 in the machine direction



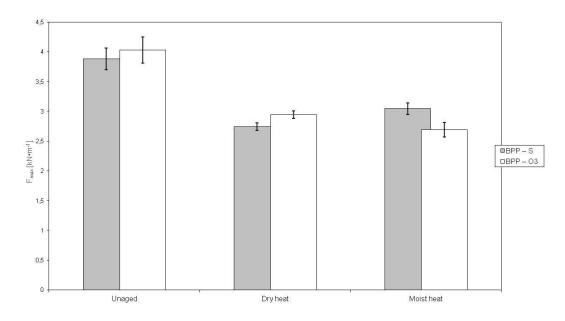
*Fig. 15* Effect of ozonization and artificial ageing on the breaking load (kN/m) of paper ISO 9706 in the cross direction



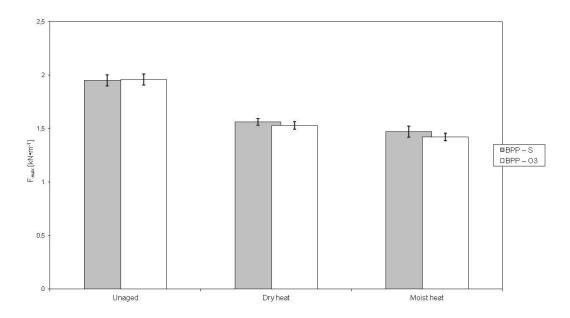
*Fig. 16* Effect of ozonization and artificial ageing on the breaking load (kN/m) of groundwood paper in the machine direction



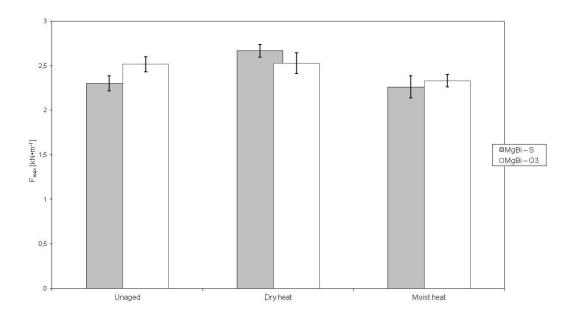
*Fig. 17* Effect of ozonization and artificial ageing on the breaking load (kN/m) of groundwood paper in the cross direction



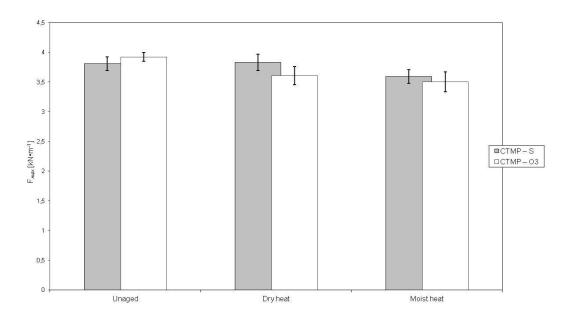
*Fig. 18* Effect of ozonization and artificial ageing on the breaking load (kN/m) of wood-free writing paper in the machine direction



*Fig. 19* Effect of ozonization and artificial ageing on the breaking load (kN/m) of wood-free writing paper in the cross direction



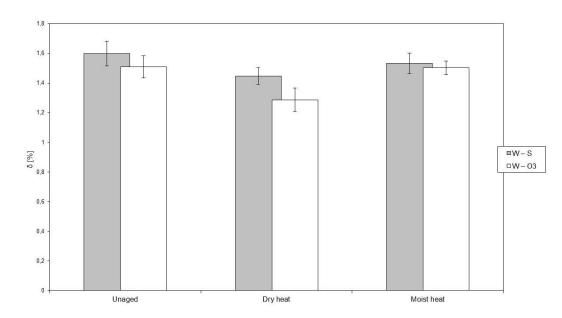
*Fig. 20* Effect of ozonization and artificial ageing on the breaking load (kN/m) of bleached sulphite pulp



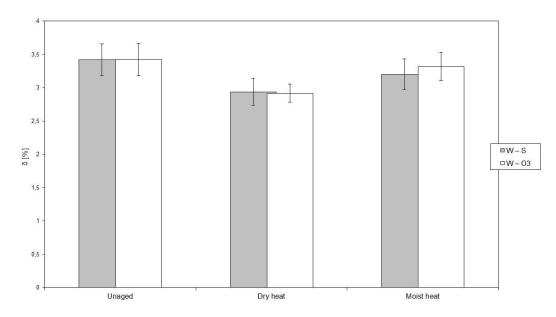
*Fig. 21* Effect of ozonization and artificial ageing on the breaking load (kN/m) of chemothermomechanical pulp

# 3.2.2 Elongation at break

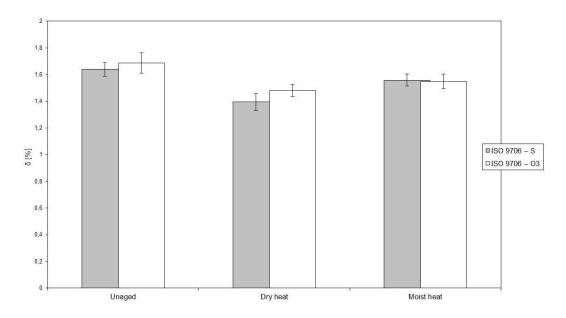
The histograms in Figs 22 to 31 depict the dependence of the effect of ozonization and artificial ageing by dry and damp heat on the elongation at break (%) of various kinds of paper. Ozonization does not affect this mechanical property.



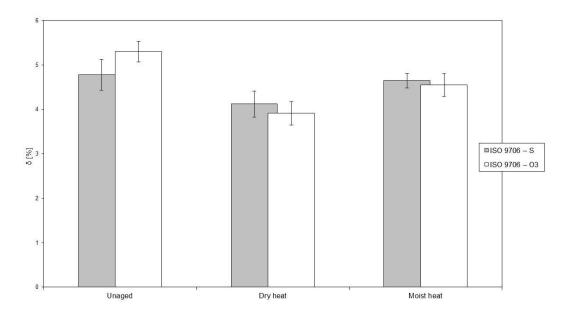
*Fig. 22* Effect of ozonization and artificial ageing on the elongation at break (%) of Whatman No. 1 paper in the machine direction



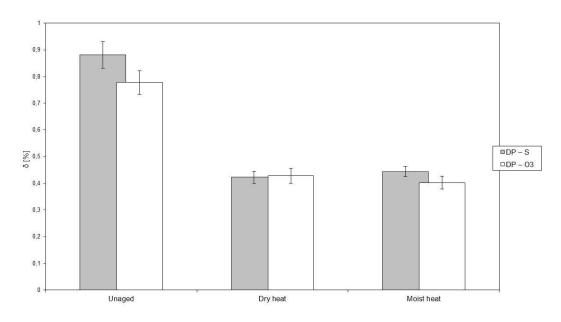
*Fig. 23* Effect of ozonization and artificial ageing on the elongation at break (%) of Whatman No. 1 paper in the cross direction



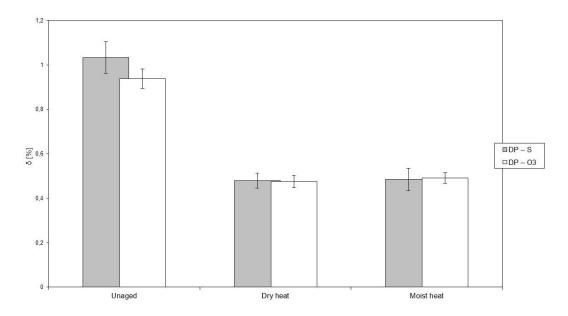
*Fig. 24* Effect of ozonization and artificial ageing on the elongation at break (%) of paper ISO 9706 in the machine direction



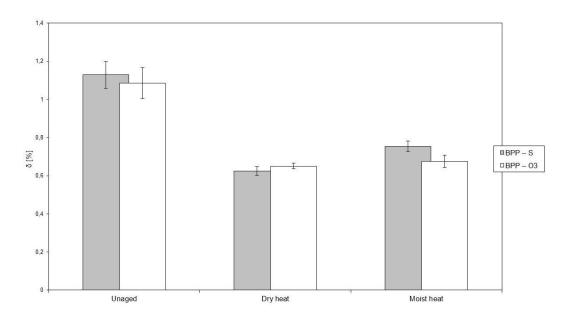
*Fig. 25* Effect of ozonization and artificial ageing on the elongation at break (%) of paper ISO 9706 in the cross direction



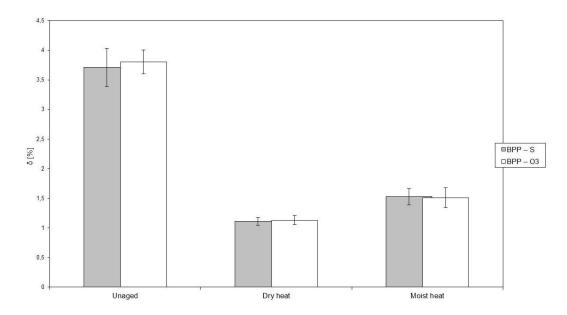
*Fig. 26* Effect of ozonization and artificial ageing on the elongation at break (%) of groundwood paper in the machine direction



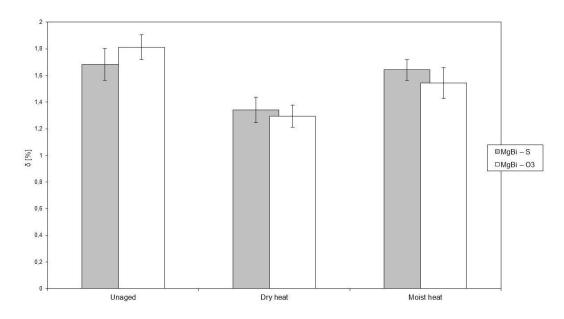
*Fig. 27* Effect of ozonization and artificial ageing on the elongation at break (%) of groundwood paper in the cross direction



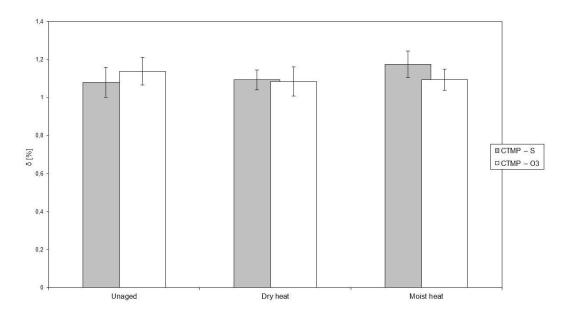
*Fig. 28* Effect of ozonization and artificial ageing on the elongation at break (%) of wood-free writing paper in the machine direction



*Fig. 29* Effect of ozonization and artificial ageing on the elongation at break (%) of wood-free writing paper in the cross direction



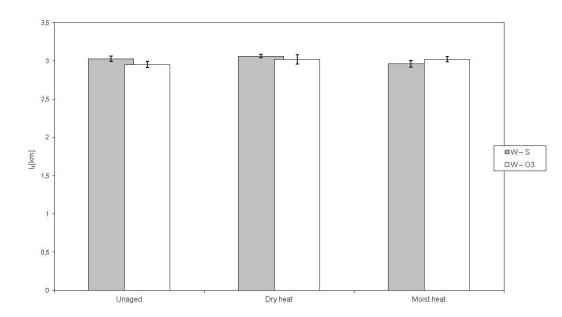
*Fig. 30* Effect of ozonization and artificial ageing on the elongation at break (%) of bleached sulphite pulp



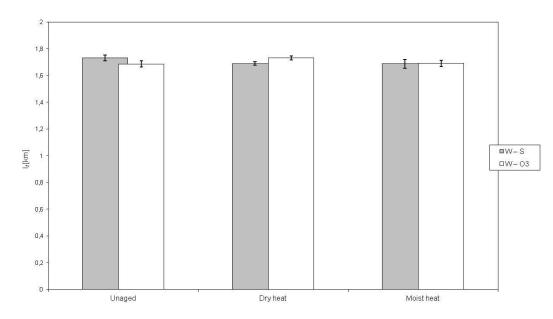
*Fig. 31* Effect of ozonization and artificial ageing on the elongation at break (%) of chemothermomechanical pulp

# 3.2.3 Breaking length

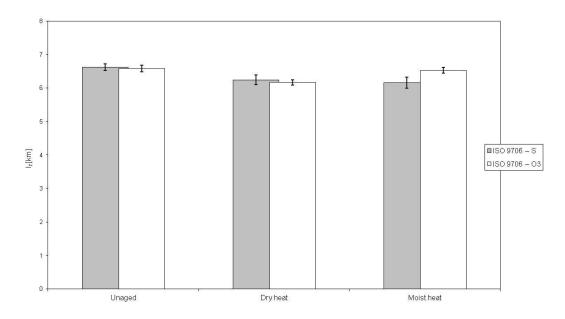
Figs. *32 to 41* depict the dependence of the effect of ozonization and artificial ageing by dry and damp heat on the breaking length (km) of various kinds of paper. Ozonization has practically a negligible effect on this mechanical property.



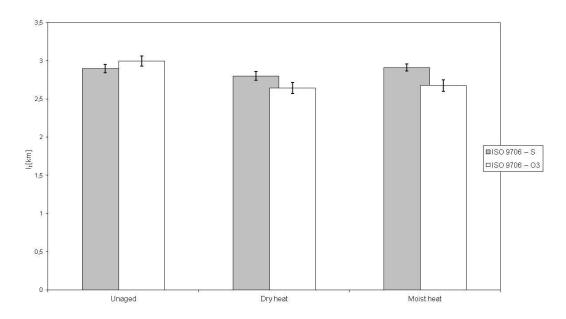
*Fig. 32* Effect of ozonization and artificial ageing on the breaking length (km) of Whatman No. 1 paper in the machine direction



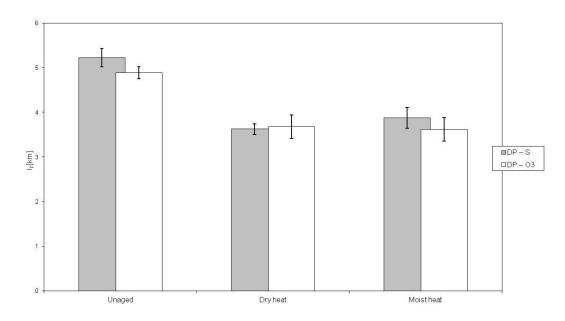
*Fig. 33* Effect of ozonization and artificial ageing on the breaking length (km) of Whatman No. 1 paper in the cross direction



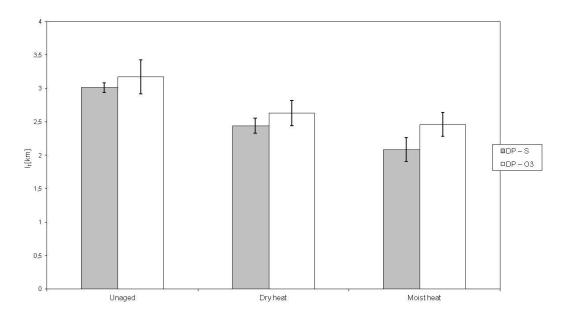
*Fig. 34* Effect of ozonization and artificial ageing on the breaking length (km) of paper ISO 9706 in the machine direction



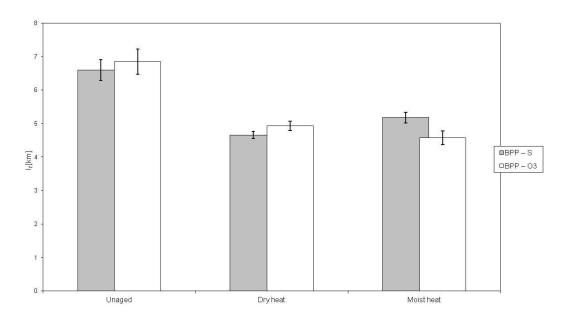
*Fig. 35* Effect of ozonization and artificial ageing on the breaking length (km) of paper ISO 9706 in the cross direction



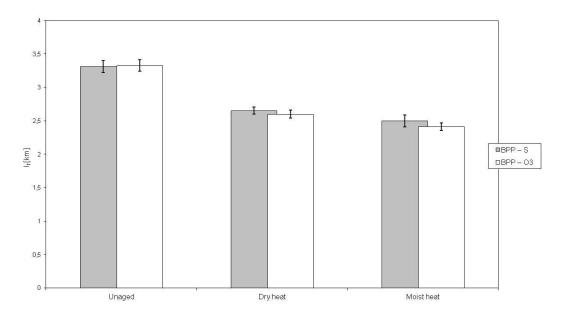
*Fig. 36* Effect of ozonization and artificial ageing on the breaking length (km) of groundwood paper in the machine direction



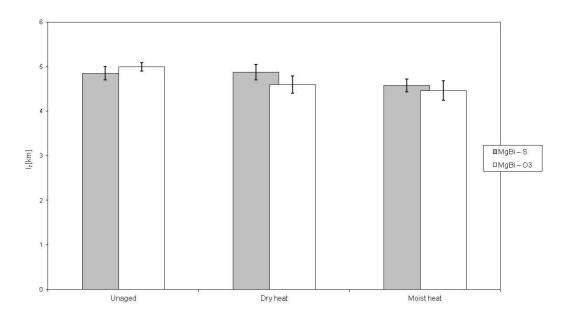
*Fig. 37* Effect of ozonization and artificial ageing on the breaking length (km) of groundwood paper in the cross direction



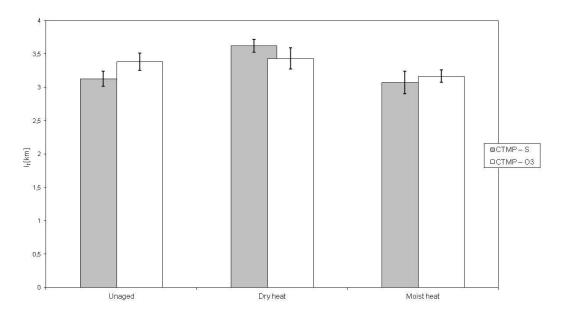
*Fig. 38* Effect of ozonization and artificial ageing on the breaking length (km) of wood-free writing paper in the machine direction



*Fig. 39* Effect of ozonization and artificial ageing on the breaking length (km) of wood-free writing paper in the cross direction



*Fig. 40* Effect of ozonization and artificial ageing on the breaking length (km) of bleached sulphite pulp



*Fig. 41* Effect of ozonization and artificial ageing on the breaking length (km) of chemothermomechanical pulp

# 3.3 Total colour difference $\Delta E*$

*Tab. 1* gives the values of L\*, a\* and b\*, their differences and the total colour differences  $\Delta E*$  of the individual kinds of tested papers. It follows from the given values of the total colour difference that ozonization has practically no effect on the colour of documents.

Paper sample	L*	a*	b*	ΔL*	∆a*	Δb*	ΔE*
DP – unaged	85.71	3.56	18.62				
DP – moist heat	76.23	7.38	22.34	-9.48	3.82	3.72	10.88
DP – dry heat	69.11	9.77	24.73	-16.6	6.21	6.11	18.75
$DP - O_3 - unaged$	84.04	4.40	19.00	-1.67	0.84	0.38	1.91
DP – O3 – moist heat	77.31	7.27	23.17	-8.40	3.71	4.55	10.25
DP – O3 – dry heat	75.05	8.81	26.28	-10.66	5.25	7.66	14.14
BPP – unaged	94.87	0.04	6.25				
BPP – moist heat	90.33	1.72	13.20	-4.54	1.68	6.95	8.47
BPP – dry heat	90.64	1.33	17.43	-4.23	1.29	11.18	12.02
$BPP - O_3 - unaged$	94.96	-0.05	5.99	0.09	-0.09	-0.26	0.29
BPP – O3 – moist heat	90.17	1.76	12.71	-4.70	1.72	6.46	8.17
BPP – O3 – dry heat	91.09	0.98	16.73	-3.78	0.94	10.48	11.18
W – unaged	97.33	0.13	2.10				
W – moist heat	94.92	0.70	6.08	-2.41	0.57	3.98	4.69
W – dry heat	96.45	-0.08	5.66	-0.88	-0.21	3.56	3.67
W – O <sub>3</sub> – unaged	97.40	0.14	2.11	0.07	0.01	0.01	0.07
W – O3 – moist heat	94.91	0.71	6.28	-2.42	0.58	4.18	4.86
W – O3 – dry heat	96.58	-0.07	5.22	-0.75	-0.2	3.12	3.22
ISO 9706 – unaged	96.53	-0.13	4.55				
ISO 9706 – moist heat	92.76	1.12	10.39	-3.77	1.25	5.84	7.06
ISO 9706 – dry heat	94.59	-0.22	10.94	-1.94	-0.09	6.39	6.68
ISO 9706 – O <sub>3</sub> – unaged	96.48	-0.18	4.62	-0.05	-0.05	0.07	0.03
ISO 9706 – O <sub>3</sub> – moist heat	93.09	1.00	9.73	-3.44	1.13	5.18	6.32
ISO 9706 – O <sub>3</sub> – dry heat	94.61	-0.11	10.65	-1.92	0.02	6.1	6.40
CTMP – unaged	93.32	-0.56	13.42				
CTMP – moist heat	84.63	4.08	21.50	-8.69	4.64	8.08	12.74
CTMP – dry heat	85.60	4.15	24.13	-7.72	4.71	10.71	14.02
CTMP – O <sub>3</sub> – unaged	93.03	-0.28	13.64	-0.29	0.28	0.22	0.46
CTMP – O3 – moist heat	84.12	4.32	21.66	-9.2	4.88	8.24	13.28
CTMP – O3 – dry heat	85.67	4.10	24.17	-7.65	4.66	10.75	13.99
MgBi – unaged	95.48	-0.03	6.36				
MgBi – moist heat	89.89	1.76	12.98	-5.59	1.79	6.62	8.85
MgBi – dry heat	93.30	-0.15	13.83	-2.18	-0.12	7.47	7.78
MgBi – O <sub>3</sub> – unaged	95.52	-0.11	6.65	0.04	-0.08	0.29	0.30
MgBi – O3 – moist heat	89.92	1.69	12.83	-5.56	1.72	6.47	8.70
MgBi – O3 – dry heat	93.50	-0.18	13.73	-1.98	-0.15	7.37	7.63

Tab. 1.	Effect of ozonization on the total colour difference $\Delta E *$ of individual kinds of paper.
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# 3.4. Determination of the decoloration number DC<sub>457</sub>

*Tab.* 2 gives the reflectivity at critical sample thickness ( $R_{\infty}$ ), the ratio factor K/S calculated from the Kubelka-Munk equation and the decoloration number ( $DC_{457}$ ) of the samples following ozonization and artificial ageing. It follows from these data that ozonization does not cause substantial changes in this parameter.

Sample of paper	$\mathbf{R}_{\infty}$	K/S	DC <sub>457</sub>
DP – unaged	48.6	0.2718	
DP – moist heat	30.3	0.8017	-0.5299
DP – dry heat	23.2	1.2712	-0.9994
$DP - O_3 - unaged$	48.1	0.2800	-0.0082
DP – O3 – moist heat	32.8	0.6884	-0.4166
DP – O3 – dry heat	31.5	0.7448	-0.4730
BPP – unaged	79.3	0.0270	
BPP – moist heat	62.9	0.1094	-0.0824
BPP – dry heat	60.0	0.1333	-0.1063
<b>BPP</b> – $O_3$ – unaged	78.9	0.0282	-0.0012
BPP – O3 – moist heat	62.4	0.1133	-0.0863
BPP – O3 – dry heat	61.1	0.1238	-0.0968
W – unaged	93.0	0.0026	
W – moist heat	79.8	0.0256	-0.0230
W – dry heat	83.8	0.0157	-0.0131
$W - O_3 - unaged$	91.8	0.0037	-0.0011
W – O3 – moist heat	79.3	0.0270	-0.0244
W – O3 – dry heat	84.5	0.0142	-0.0116
ISO 9706 – unaged	86.5	0.0105	
ISO 9706 – moist heat	71.5	0.0568	-0.0543
ISO 9706 – dry heat	75.4	0.0401	-0.0296
ISO 9706 – O <sub>3</sub> – unaged	86.8	0.0100	+0.0005
ISO 9706 – O <sub>3</sub> – moist heat	73.1	0.0494	-0.0389
ISO 9706 – O <sub>3</sub> – dry heat	75.7	0.0390	-0.0285
CTMP – unaged	66.7	0.0831	
CTMP – moist heat	47.7	0.2867	-0.2036
CTMP – dry heat	45.2	0.3322	-0.2491
CTMP – O <sub>3</sub> – unaged	67.0	0.0813	+0.0018
CTMP – O3 – moist heat	46.3	0.3114	-0.2283
CTMP – O3 – dry heat	46.3	0.3114	-0.2283
MgBi – unaged	73.0	0.0499	
MgBi – moist heat	59.2	0.1406	-0.0907
MgBi – dry heat	60.9	0.1255	-0.0756
$MgBi - O_3 - unaged$	73.1	0.0495	+0.0004
MgBi – O3 – moist heat	58.6	0.1462	-0.0963
MgBi – O3 – dry heat	62.2	0.1149	-0.0650

*Tab. 2.* Effect of ozonization on the decoloration number DC<sub>457</sub> for the individual kinds of paper.

# 3.5 pH of an aqueous extract

*Tab.* 4 gives the pH values of an aqueous extract of samples of paper following ozonization and artificial ageing. Ozone has a practically negligible effect on the pH of a cold extract.

Tab. 3.	Effect of ozonization and artificial ageing on the overall pH of an aqueous extract	
	of the individual kinds of paper.	

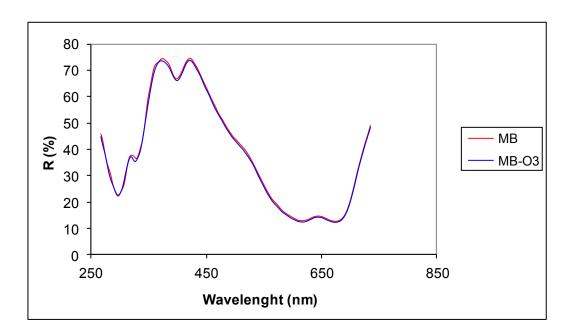
Sample of paper	Unaged	Moist heat	Dry heat
DP	4.57	4.29	3.95
$DP - O_3$	4.30	4.55	4.31
BPP	5.84	5.25	4.75
$BPP - O_3$	5.16	4.58	4.72
W	6.30	6.30	6.03
$W - O_3$	6.25	6.17	6.07
ISO 9706	8.75	8.57	8.55
ISO 9706 – O <sub>3</sub>	8.90	8.59	8.58
СТМР	6.60	6.23	6.14
$CTMP - O_3$	6.60	6.34	6.31
MgBi	7.45	6.70	6.53
$MgBi - O_3$	7.36	6.90	6.40

# 3.6 Effect of ozonization on the stability of aryl methane dyes

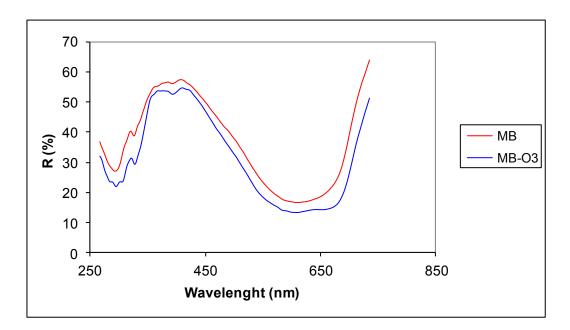
# 3.6.1 Reflection UV/VIS spectra

*Figs.* 42 to 56 give the reflectance spectra in the visible and ultraviolet regions (UV/VIS) of some aryl methane dyes following ozonization and artificial ageing by dry and moist heat. It is apparent from the figures that ozonization has no fundamental effect on the shapes of the curves of the reflectance spectra of the individual dyes.

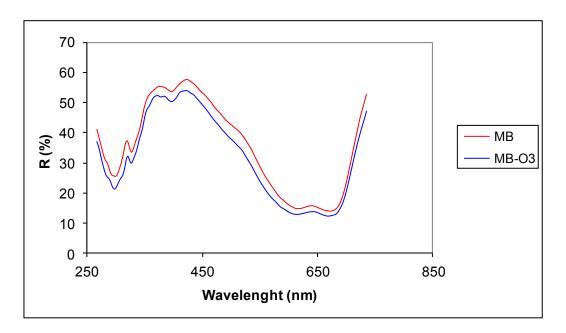
It can be stated that ozonization has a minimal or no effect on the stability of the studied aryl methane dyes.



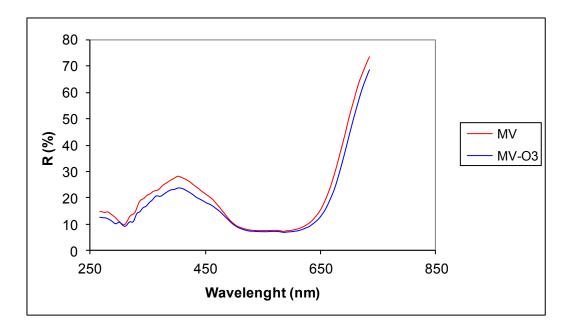
*Fig. 42* Effect of ozonization on the UV/VIS reflectance spectra of the dye Basic Blue 6



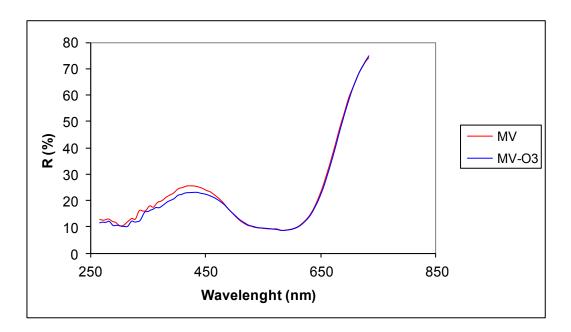
*Fig. 43* Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Blue 6



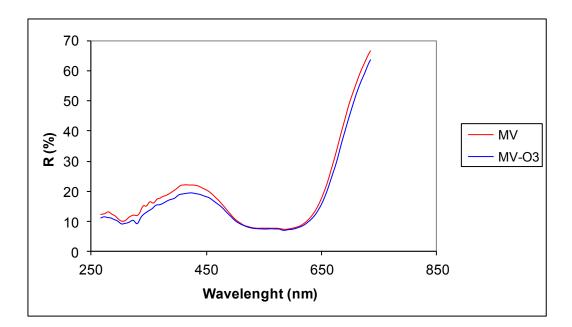
*Fig. 44* Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Blue 6



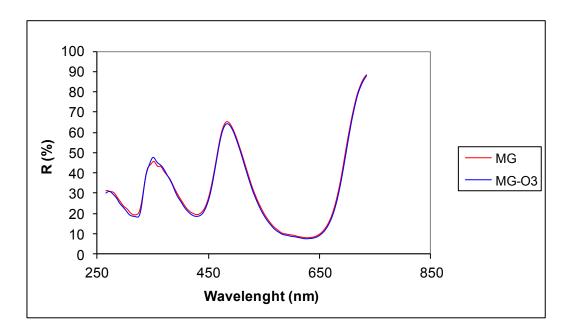
*Fig. 45* Effect of ozonization on the UV/VIS reflectance spectra of the dye Basic Violet 1



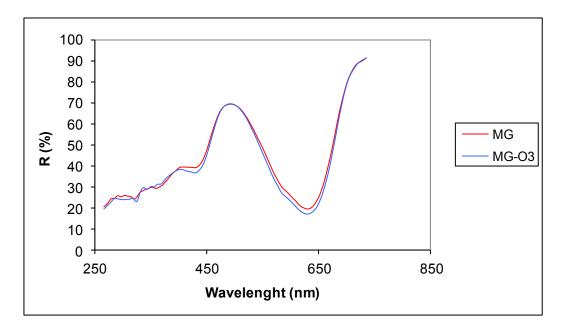
*Fig. 46* Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Violet 1



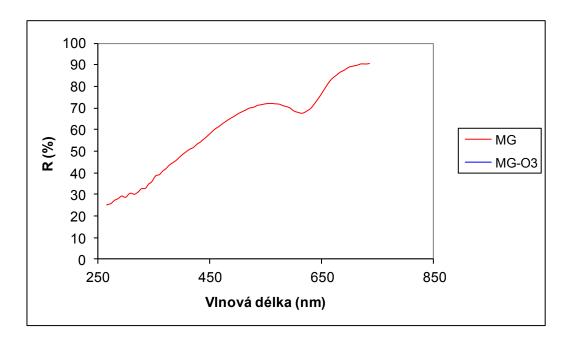
*Fig. 47* Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Violet 1



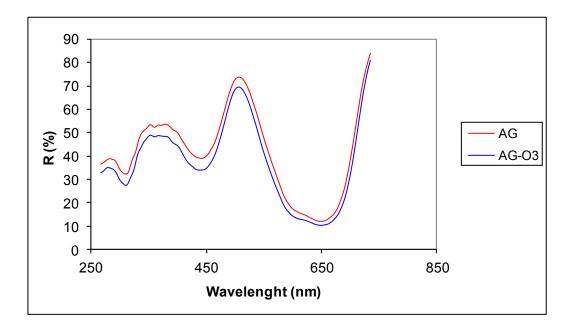
*Fig. 48* Effect of ozonization on the UV/VIS reflectance spectra of the dye Malachite Green



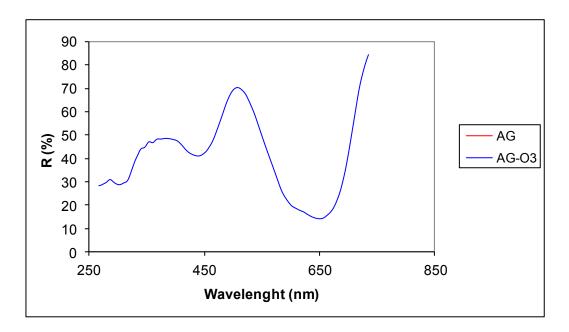
*Fig. 49* Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Malachite Green



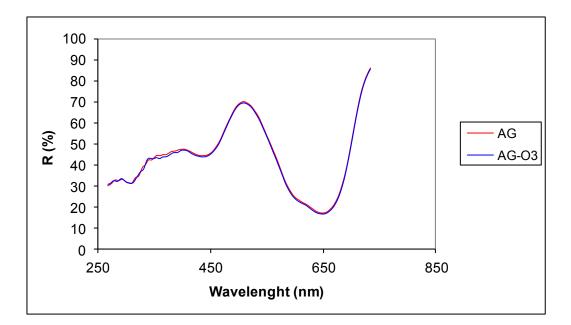
*Fig. 50* Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Malachite Green



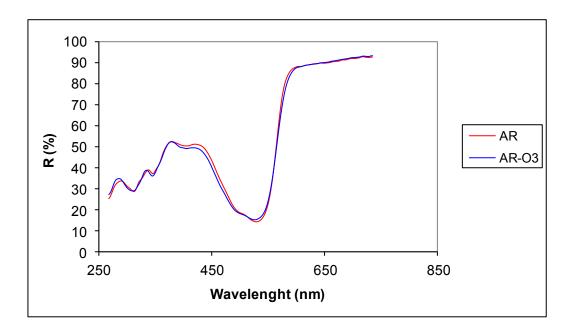
*Fig. 51* Effect of ozonization on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16



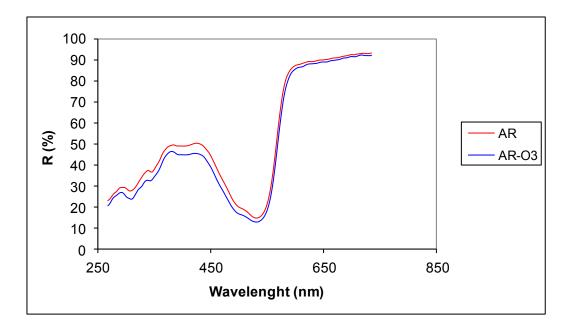
*Fig.* 52 Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16



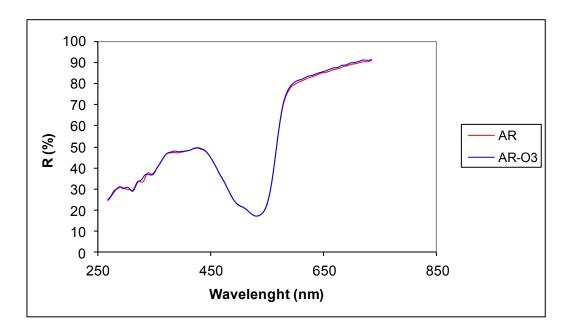
*Fig. 53* Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16



*Fig. 54* Effect of ozonization on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87



*Fig. 55* Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87



*Fig. 56* Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87

# 3.6.2 Total colour difference $\Delta E *$

It follows from the data on the total colour difference  $\Delta E^*$  of any methane dyes after ozonization and artificial ageing in *Tab. 3* that ozonization has no effect on the individual dyes.

Tab. 4.	Effect of ozonization and artificial ageing on the total colour difference $\Delta E^*$ of the individual
	kinds of aryl methane dyes.

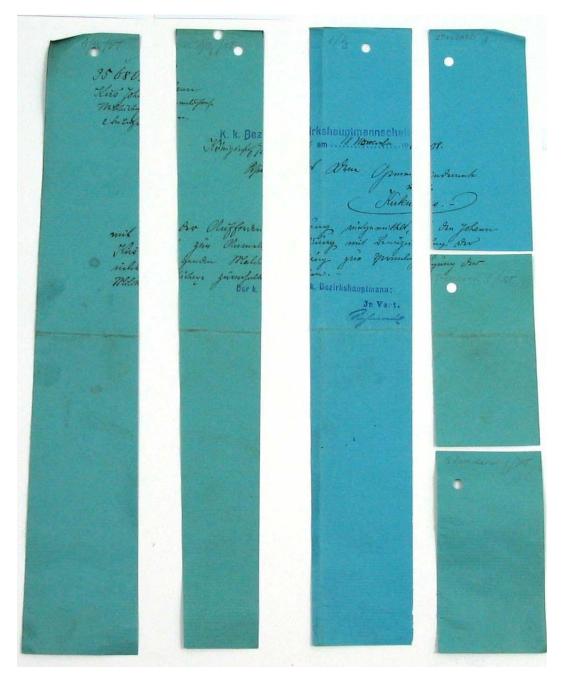
Paper sample	$\Delta E^*$
Basic Blue 6 – moist heat	9.58
Basic Blue 6 – O3 – moist heat	9.20
Basic Blue 6 – dry heat	9.07
Basic Blue 6 – O3 – dry heat	9.10
Basic Violet 1 – moist heat	6.60
Basic Violet 1 – O3 – moist heat	9.30
Basic Violet 1 – dry heat	10.09
Basic Violet 1 – O3 – dry heat	9.84
Malachite Green – moist heat	59.19
Malachite Green – O3 – moist heat	60.39
Malachite Green – dry heat	23.11
Malachite Green – O3 – dry heat	23.72
Acid Green 16 – moist heat	11.33
Acid Green 16 – O3 – moist heat	10.36
Acid Green 16 – dry heat	5.21
Acid Green 16 – O3 – dry heat	4.98
Acid Red 87 – moist heat	5.96
Acid Red 87 – O3 – moist heat	5.97
Acid Red 87 – dry heat	2.24
Acid Red 87 – O3 – dry heat	2.58

## 3.7 Visual evaluation of changes in the colours of archive documents

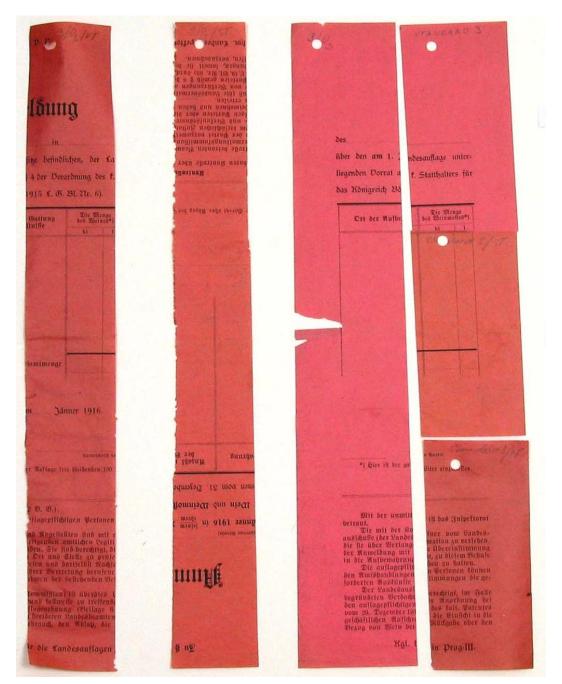
## 3.7.1 Visual evaluation of changes in the colours of archive documents

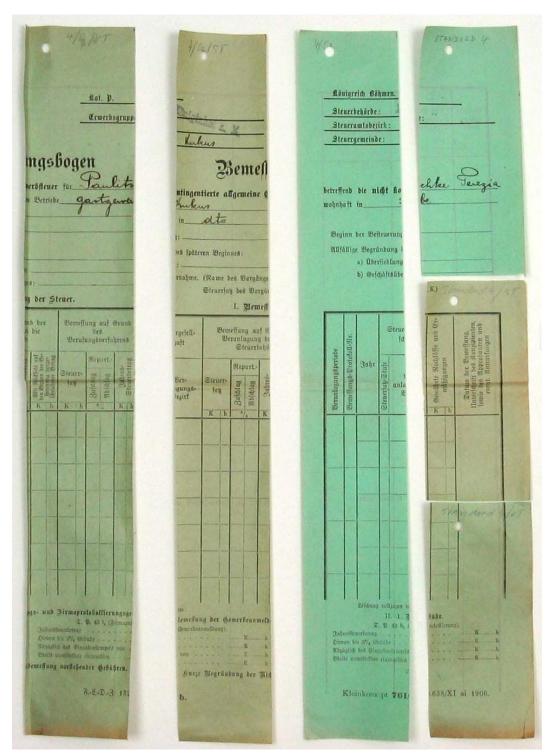
Visual comparison of the effect of ozonization and artificial ageing on archive documents from the 19th and 20th centuries was performed by ordering these documents according to the following scheme and were then photographed (*samples No. 1 to 14*):

1	2	3	4
ozonization, moist heat ageing	ozonization, dryheat ageing	ozonization, unaged	standard, unaged
			5 standard,
			dry heat ageing
			6 standard, moist heat ageing

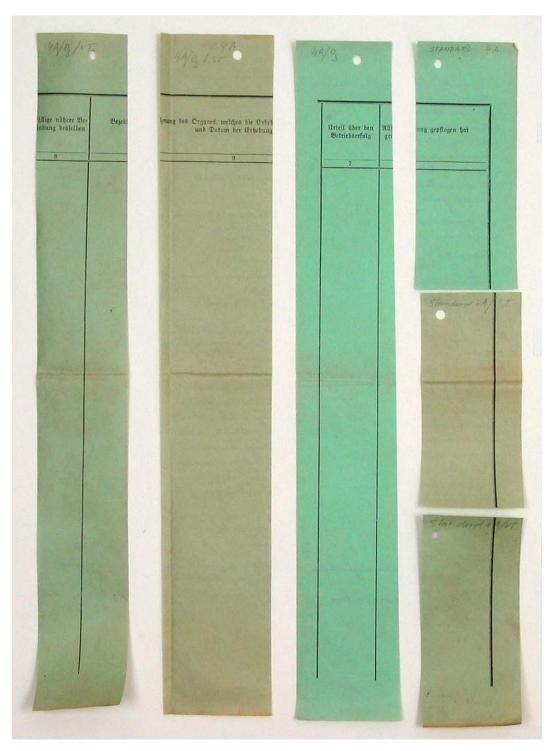








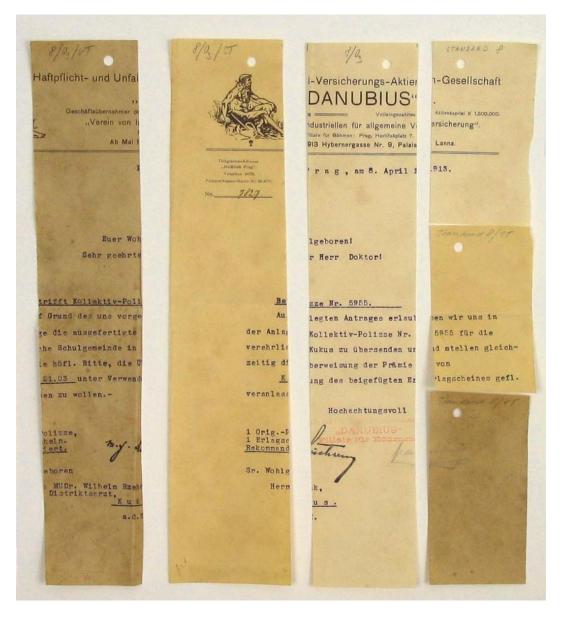
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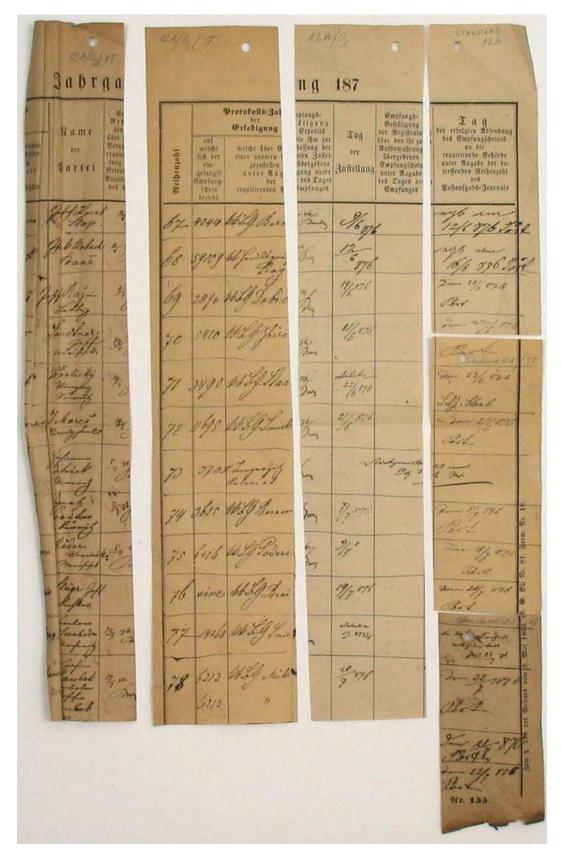
59 164 Cđ Okresni sou v Sablonci n. biu., 9.1964. dres 1. a ubuon b0 Od otren. se na předvolání , nar. dne 23.1. , okr. Jbc n.Nis., bytem Velké Hamry destření věci udal : Kopslova . 2413. Destavil Karel F o t r 1903 v Zásadě -učitel v.v., čp.45 a po pře Ing. 1 Státní léčeh Horních Beřki Dne 2 til domi ke i opět doprave Opatre V Jellonci n.! právnosti pre Opatre trovaný "je m yšeti trovaný "je m yšeti normálně . V žival slkohoj trovaného byl Poelec nocíci bylo v Bohuslav Seidl t., y psychiatrické i bvicích . J.května 1954 z. le tvé makce . Asi i h do SLP v Kosmosi bvnictvi ohledně (is. pod č.j. P le h duševné chorobu prníkem vyšetřovani mného jsem opatra m švagrem . Vyšet iovaný pocházi ze pozdějších letech ické nápoje a ner l zdráví . Vyšetř thí bydliště vyšet e Velkých Hamrech j. vyšetřovaný je již Kosmonosích – před řadu let v léčení tím byl i ve SLP v tents den se vrá ohuslav Seidl mnou tomto ústavě. e u chresního soudu e zcela zbaven svěičebny uprchl , resp. itvrtý den byl ing. B ich a od té doby je v vyšetřovaného se ved 19/50 a vyšetřovaný j cho byl původně jeho vníkem ing. Bohuslav, rovaný jev Kosmonos dvou dětí ; v niádí při studich vedl n vové anemocněl . Rod ovaný je kuřákem . rovaného před dodání čp.254 , okr. Jablo otec a po sarti a Seidla Aá . Vyše-ich Aiž od r.1956. se choval a učil epořádný život , po-iče a sestra vyšea do SLP v Kosmo-nec n.Nis. ení podepsáno. Po přečt NI SOUD Skene . a pod. Haver BOLESLAY VMLADE N. 1964 0 9400 RUBRIK Hlad é Boleslavi po vyhovění tionein.M. Okresni send v Ja 4.4 dne 1 .9.196 ca! B189150 rd An Kone : midn r Jacobional Mas 1. 64 Mayilez 18 X 1964 14. IX. 19

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Ozonization has no effect on the colour of archive documents. Changes in the colour of the recording media of archive documents were not measured; photographic documentation was acquired and any changes will be progressively monitored. Based on visual evaluation, ozonization does not have a demonstrable effect on changes in the colour of recording media.

## 3.7.2 Changes in the total colour difference $\Delta E * of$ archive documents

It was found by comparison of the colour differences of all the measured values of selected types of archive documents that ozonization does not have a significant effect on colour changes. The measured values of the total colour difference following ageing (in both a moist heat and a dry heat atmosphere) of samples of paper following ozonization and without ozonization are very similar (see *Tab. 5*).

Paper sample	L*	a*	b*	ΔL*	∆a*	∆b*	ΔE*
1 – unaged	63.93	-10.08	-17.37				
1 – moist heat	62.72	-12.49	-6.91	-1.17	-2.43	10.4	10.8
1 – dry heat	62.68	-13.40	-5.53	-1.21	-3.34	11.8	12.3
1 – ozonization – unaged	62.27	-10.28	-16.21	-1.62	-0.22	1.10	1.97
1 – ozonization – moist heat	62.59	-12.42	-6.53	-1.30	-2.36	10.8	11.1
1 - ozonization - dry heat	62.39	-13.22	-5.85	-1.50	-3.17	11.5	12.0
2 – unaged	70.67	-12.78	-0.71				
2 – moist heat	67.81	-8.14	9.35	-2.85	4.64	10.1	11.4
2 – dry heat	67.99	-10.44	10.50	-2.68	2.35	11.2	11.8
2 – ozonization – unaged	69.95	-12.60	-0.07	-0.71	0.19	0.64	0.97
2 – ozonization – moist heat	69.38	-8.36	8.97	-1.29	4.42	9.68	10.7
2 – ozonization – dry heat	68.43	-10.99	9.09	-2.24	1.79	9.79	10.2
3 – unaged	68.11	24.84	7.03				
3 – moist heat	65.24	18.75	12.85	-2.87	-6.08	5.82	8.89
3 – dry heat	66.87	19.88	14.86	-1.24	-4.96	7.83	9.35
3 – ozonization – unaged	68.18	25.26	7.47	0.07	0.42	0.44	0.24
3 – ozonization – moist heat	65.35	19.04	12.98	-2.76	-5.80	5.95	8.75
3 – ozonization – dry heat	66.96	20.55	14.61	-1.15	-4.29	7.57	8.78
4 – unaged	75.20	-16.03	9.77				
4 – moist heat	72.46	-8.54	15.61	-2.74	7.49	5.85	9.89
4 – dry heat	73.69	-5.94	17.91	-1.51	10.1	8.15	13.1
4 – ozonization – unaged	75.41	-17.94	8.91	0.21	-1.91	-0.85	2.10
4 – ozonization – moist heat	72.88	-8.36	14.92	-2.33	7.67	5.16	9.53
4 – ozonization – dry heat	73.92	-6.79	17.36	-1.29	9.25	7.60	12.0
5 – unaged	83.56	1.42	17.48				
5 – moist heat	74.63	4.87	21.91	-8.93	3.44	4.43	10.6
5 – dry heat	77.38	4.27	25.57	-6.19	2.85	8.08	10.6
5 – ozonization – unaged	82.21	2.19	19.17	-1.36	0.77	1.69	2.30
5 – ozonization – moist heat	74.08	4.86	23.48	-9.48	3.44	6.00	11.7
5 – ozonization – dry heat	77.78	4.47	26.83	-5.78	3.05	9.35	11.4
6 – unaged	87.29	-0.01	14.63				
6 – moist heat	77.57	4.01	21.14	-9.72	4.01	6.51	12.4
6 – dry heat	82.38	2.22	24.98	-4.91	2.23	10.4	11.7
6 – ozonization – unaged	87.43	-0.04	15.01	0.14	-0.04	0.38	0.41
6 – ozonization – moist heat	77.62	3.84	21.08	-9.66	3.85	6.45	12.2
6 – ozonization – dry heat	82.13	2.37	24.81	-5.16	2.37	10.2	11.7

*Tab. 5.* Effect of ozonization and artificial ageing on the overall colour difference of archive documents.

Tab. 5 continued

7         unaged         88.47         -0.17         14.56           7         -mois heat         79.85         3.56         19.85         -8.62         3.73         5.29         10.8           7         -dry heat         88.38         1.60         22.71         -4.64         1.77         8.15         9.54           7         -ozonization - mois heat         80.69         3.54         19.97         -7.78         3.72         5.41         10.2           7         -ozonization - dry heat         84.29         1.99         23.88         -4.18         2.16         9.32         10.4           8<-moist heat         66.06         6.43         20.78         -18.0         3.61         2.48         18.5           8 - ozonization - maged         84.43         2.67         1.75         0.38         -0.14         -0.34         0.53           8 - ozonization - mist heat         67.18         5.99         19.99         -16.9         3.17         1.7         17.3           9         -unaged         72.91         7.01         26.36         9         -0.34         12.3           9         -ozonization - maged         72.54         6.61         27.62         -3.41	Paper sample	L*	a*	b*	ΔL*	∆a*	Δb*	ΔΕ*
7 - most heat         79.85         3.56         19.85         -8.62         3.73         5.29         10.8           7 - dy heat         83.83         1.60         22.71         -4.64         1.77         8.15         9.43           7 - ozonization - moist heat         80.69         3.54         19.97         -7.78         3.72         5.41         10.2           7 - ozonization - dry heat         84.29         1.99         23.88         -4.18         2.16         9.32         10.4           8 - unaged         84.20         1.99         23.84         -4.18         2.16         9.31         10.4           8 - moist heat         66.06         6.43         2.078         -18.0         3.61         2.48         18.5           8 - ozonization - maged         84.34         2.67         17.95         0.38         -0.04         -0.03           9 - unaged         72.91         7.01         23.22         -3.11         12.8         9           9 - unaged         72.91         7.01         23.22         -11.9         0.59         -3.14         12.8           9 - ozonization - moist heat         61.63         7.42         2.18         -11.3         0.40         0.84		88.47	-0.17	14.56				_
7 - dry heat         83.83         1.60         22.71         -4.64         1.77         8.15         9.54           7 - ozonization - moist heat         88.96         -0.56         13.50         0.49         -0.38         -1.06         1.23           7 - ozonization - moist heat         84.05         2.82         18.97         -7.78         3.72         5.41         10.2           8 - maged         64.05         2.82         18.29         -         -         -         4.18         2.16         9.32         10.4           8 - maged         68.43         2.078         -18.0         3.61         2.48         18.53           8 - ozonization - maged         84.43         2.67         17.95         0.38         -0.14         -0.34         0.53           8 - ozonization - moist heat         60.62         7.53         22.95         -12.3         0.52         -3.41         12.8           9 - dry heat         61.03         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - moist heat         73.37         5.90         24.06         -6.67         7.8         8.94           10 - unaged         80.04         4.12         22.47 <th>0</th> <th></th> <th></th> <th></th> <th>-8.62</th> <th>3 73</th> <th>5 29</th> <th>10.8</th>	0				-8.62	3 73	5 29	10.8
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7 - ozonization - dry heat         84.29         1.99         23.88         -4.18         2.16         9.32         10.4           8 - moist heat         66.06         6.43         20.78         -18.0         3.61         2.48         18.5           8 - moist heat         78.78         4.91         23.45         -5.27         2.09         7.15         9.13           8 - ozonization - unaged         84.43         2.67         17.95         0.38         -0.14         -0.34         0.53           8 - ozonization - unoist heat         67.18         5.99         19.99         -16.9         3.17         1.7         17.3           8 - ozonization - unaged         72.91         7.01         26.36	0							
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8 - dry heat         78.78         4.91         23.45         -5.27         2.09         7.15         9.13           8 - ozonization - unoist heat         67.18         5.90         17.95         0.38         -0.14         -0.34         0.53           8 - ozonization - dry heat         60.31         4.53         25.17         -3.73         1.71         6.80         8.01           9 - unaged         72.91         7.01         26.36         -         -         -         -         -         -3.14         12.3           9 - dry heat         61.03         7.61         23.22         -11.9         0.59         -3.14         12.3           9 - ozonization - unaged         7.254         6.61         25.76         -0.37         -0.40         -0.60         0.81           9 - ozonization - moist heat         61.63         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - unaged <th></th> <th></th> <th></th> <th></th> <th>-18.0</th> <th>3.61</th> <th>2 48</th> <th>18 5</th>					-18.0	3.61	2 48	18 5
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8 - ozonization - moist heat       67.18       5.99       19.99       -16.9       3.17       1.7       17.3         8 - ozonization - dry heat       80.31       4.53       25.17       -3.73       1.71       6.80       8.01         9 - moist heat       60.62       7.53       22.95       -12.3       0.52       -3.41       12.3         9 - ozonization - unaged       72.54       6.61       23.22       -11.9       0.59       -3.14       12.3         9 - ozonization - unaged       72.54       6.61       25.76       -0.37       -0.40       -0.60       0.81         9 - ozonization - unaged       80.04       4.12       22.47       0.41       -3.18       11.7         9 - ozonization - unaged       80.42       3.98       22.47       0.37       -0.13       0.01       0.40         10 - ozonization - unaged       80.42       3.98       22.47       0.37       -0.13       0.01       0.40         10 - ozonization - unaged       86.29       0.44       15.15       11       unaged       86.29       0.44       15.15       11       unaged       86.74       0.07       14.06       0.45       -0.38       -1.09       1.24       11 - ozonization - unaged								
8 - ozonization - dry heat         80.31         4.53         25.17         -3.73         1.71         6.80         8.01           9 - unaged         72.91         7.01         26.36								
9 - unaged         72.91         7.01         26.36           9 - moist heat         60.62         7.53         22.95         -12.3         0.52         -3.11         12,8           9 - dry heat         61.03         7.61         23.22         -11.9         0.59         -3.14         12,3           9 - ozonization - unaged         72.54         6.61         25.76         -0.37         -0.40         -0.60         0.81           9 - ozonization - moist heat         61.63         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - dry heat         64.59         9.21         20.0         -8.32         2.20         2.43         8.94           10 - unaged         80.04         4.12         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.25         6.13         24.44         -6.77         2.65         5.83         9.32           11 - unaged         80.47         3.30         20.84         -5.82         2.86         5.69         8.62           11 - unosit heat         80.47         3.30         20.84         -5.82         2.86         5.69         8.62								
9 - moist heat       60.62       7.53       22.95       -12.3       0.52       -3.41       12,8         9 - dry heat       61.03       7.61       23.22       -11.9       0.59       -3.14       12.3         9 - ozonization - unaged       72.54       6.61       25.76       -0.37       -0.40       -0.60       0.81         9 - ozonization - moist heat       61.63       7.42       23.18       -11.3       0.41       -3.18       11.7         9 - ozonization - dry heat       64.59       9.21       20.0       -8.32       2.20       2.43       8.94         10 - unaged       80.04       4.12       22.47        -       -       -       -       -       -       -       0.01       0.41       -5.83       9.09       10       0.01       0.01       0.04       0.10       0.93       -       0.37       -0.13       0.01       0.40       0.51       1.98       7.35         10 - ozonization - moist heat       73.27       6.76       28.30       -6.77       2.65       5.83       9.32         11 - unaged       86.29       0.44       15.15       11       -0.90       9.08       10.00         11 - ozonization - una					5.15	1.71	0.00	0.01
9 - dry heat         61.03         7.61         23.22         -11.9         0.59         -3.14         12.3           9 - ozonization - unaged         72.54         6.61         25.76         -0.37         -0.40         -0.60         0.81           9 - ozonization - moist heat         61.63         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - dry heat         64.59         9.21         20.0         -8.32         2.20         2.43         8.94           10 - unaged         80.04         4.12         22.47          1.59         7.09           10 - ozonization - moist heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - moist heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11 - unaged         86.29         0.44         15.15         11         naged         86.74         0.07         14.06         0.45         -0.38         -1.09         1.24           11 - ozonization - mised heat         81.23         3.17         20.89         -5.06         2.73         5.74         8.12					-123	0.52	-341	12.8
9 - ozonization - unaged         72.54         6.61         25.76         -0.37         -0.40         -0.60         0.81           9 - ozonization - moist heat         61.63         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - dry heat         64.59         9.21         20.0         -8.32         2.20         2.43         8.94           10 - unaged         80.04         4.12         22.47								-
9 - ozonization - moist heat         61.63         7.42         23.18         -11.3         0.41         -3.18         11.7           9 - ozonization - dry heat         64.59         9.21         20.0         -8.32         2.20         2.43         8.94           10 - unaged         80.04         4.12         22.47         7.83         7.09           10 - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.25         6.13         24.44         -6.79         2.01         1.98         7.35           10 - ozonization - dry heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11 - unaged         86.29         0.44         15.15         11         moist heat         80.47         3.30         20.84         -5.82         2.86         5.69         8.62           11 - ozonization - unaged         86.74         0.07         14.06         0.45         -0.38         -1.09         1.24           11 - ozoni	· · ·							
9 - ozonization - dry heat         64.59         9.21         20.0         -8.32         2.20         2.43         8.94           10 - unaged         80.04         4.12         22.47            7.337         5.90         24.06         -6.67         1.78         1.59 <b>7.09</b> 10 - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45 <b>8.99</b> 10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.27         6.76         28.30         -6.77         2.65         5.83 <b>9.32</b> 11 - unaged         86.29         0.44         15.15             1.44         -6.79         2.01         1.98         7.35            9.08         10.0           11 - unaged         86.29         0.44         15.15              8.62         11-         4.23         -0.07         14.06         0.45         -0.38         -1.09         1.24          1.24         <	0							
10 - unaged         80.04         4.12         22.47           10 - moist heat         73.37         5.90         24.06         -6.67         1.78         1.59         7.09           10 - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.25         6.13         24.44         -6.79         2.01         1.98         7.35           10 - ozonization - dry heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11 - unaged         86.29         0.44         15.15         11								
10 - moist heat         73.37         5.90         24.06         -6.67         1.78         1.59         7.09           10 - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.25         6.13         24.44         -6.79         2.01         1.98         7.35           10 - ozonization - dry heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11 - unaged         86.29         0.44         15.15					0.52	2.20	2.13	512 T
10 - dry heat         73.35         6.56         27.95         -6.69         2.44         5.45         8.99           10 - ozonization - unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10 - ozonization - moist heat         73.25         6.13         24.44         -6.79         2.01         1.98         7.35           10 - ozonization - dry heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11 - unaged         86.29         0.44         15.15         -         -         -         -         -         5.82         2.86         5.69         8.62           11 - dry heat         82.40         2.24         24.23         -3.89         1.79         9.08         10.0           11 - ozonization - unaged         86.74         0.07         14.06         0.45         -0.38         -1.09         1.24           11 - ozonization - dry heat         82.70         2.34         24.29         -3.59         1.90         9.14         10.0           12 - unaged         75.02         3.83         21.03	8				-6.67	1 78	1 59	7 09
10         - zonization – unaged         80.42         3.98         22.47         0.37         -0.13         0.01         0.40           10         - zonization – moist heat         73.25         6.13         24.44         -6.79         2.01         1.98         7.35           10         - zonization – dry heat         73.27         6.76         28.30         -6.77         2.65         5.83         9.32           11         - moist heat         86.29         0.44         15.15								
10 - ozonization - moist heat       73.25       6.13       24.44       -6.79       2.01       1.98       7.35         10 - ozonization - dry heat       73.27       6.76       28.30       -6.77       2.65       5.83       9.32         11 - unaged       86.29       0.44       15.15								
10 - ozonization - dry heat73.276.7628.30-6.772.655.839.3211 - unaged86.290.4415.1511 - moist heat80.473.3020.84-5.822.865.698.6211 - dry heat82.402.2424.23-3.891.799.0810.011 - ozonization - unaged86.740.0714.060.45-0.38-1.091.2411 - ozonization - moist heat81.233.1720.89-5.062.735.748.1211 - ozonization - dry heat82.702.3424.29-3.591.909.1410.012 - unaged75.023.8321.03	-							
11 - unaged         86.29         0.44         15.15           11 - moist heat         80.47         3.30         20.84         -5.82         2.86         5.69         8.62           11 - dry heat         82.40         2.24         24.23         -3.89         1.79         9.08         10.0           11 - ozonization - unaged         86.74         0.07         14.06         0.45         -0.38         -1.09         1.24           11 - ozonization - moist heat         81.23         3.17         20.89         -5.06         2.73         5.74         8.12           11 - ozonization - dry heat         82.70         2.34         24.29         -3.59         1.90         9.14         10.0           12 - unaged         75.02         3.83         21.03								
11 - mois heat       80.47       3.30       20.84       -5.82       2.86       5.69       8.62         11 - dry heat       82.40       2.24       24.23       -3.89       1.79       9.08       10.0         11 - ozonization - unaged       86.74       0.07       14.06       0.45       -0.38       -1.09       1.24         11 - ozonization - moist heat       81.23       3.17       20.89       -5.06       2.73       5.74       8.12         11 - ozonization - dry heat       82.70       2.34       24.29       -3.59       1.90       9.14       10.0         12 - unaged       75.02       3.83       21.03       -       -       -       -       -       -       -       -       -       -       5       10.2       1.2       -       -       -       -       -       -       -       5       10.2       1.2       -       -       -       0.51       0.1       0.05       10.2       -       -       -       0.51       0.1       0.53       6.57       12       -       -       0.29       -1.22       9.37       -       12       -       0.29       -1.22       9.37       12       -       0.29<	-				0.77	2.05	5.65	7.02
11 - dry heat82.402.2424.23-3.891.799.0810.011 - ozonization - unaged86.740.0714.060.45-0.38-1.091.2411 - ozonization - moist heat81.233.1720.89-5.062.735.748.1211 - ozonization - dry heat82.702.3424.29-3.591.909.1410.012 - unaged75.023.8321.03					-5.82	2 86	5 69	8.62
11 - ozonization - unaged86.740.0714.060.45-0.38-1.091.2411 - ozonization - moist heat81.233.1720.89-5.062.735.748.1211 - ozonization - dry heat82.702.3424.29-3.591.909.1410.012 - unaged75.023.8321.03								
11 - ozonization - moist heat81.233.1720.89-5.062.735.748.1211 - ozonization - dry heat82.702.3424.29-3.591.909.1410.012 - unaged75.023.8321.0312-12 - moist heat64.975.2920.49-10.11.46-0.5510.212 - dry heat70.345.6824.40-4.691.863.386.0612 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - unaged70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613.7611.213-noist heat11.213 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged85.48-0.3610.48-1.170.380.291.2614 - unaged85.48-0.3610.48-1.170.380.292.752.7714 - unaged85.48-0.3610.48-1.42<	-							
11 - ozonization - dry heat82.702.3424.29-3.591.909.1410.012 - unaged75.023.8321.0321.0312 - moist heat64.975.2920.49-10.11.46-0.5510.212 - dry heat70.345.6824.40-4.691.863.386.0612 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - moist heat65.825.1119.81-9.201.29-1.229.3712 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613.7611.213 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - dry heat85.48-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814-0.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.68 <th>8</th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>	8							
12 - unaged       75.02       3.83       21.03         12 - moist heat       64.97       5.29       20.49       -10.1       1.46       -0.55       10.2         12 - dry heat       70.34       5.68       24.40       -4.69       1.86       3.38       6.06         12 - ozonization - unaged       74.94       4.34       21.13       -0.09       0.51       0.1       0.53         12 - ozonization - moist heat       65.82       5.11       19.81       -9.20       1.29       -1.22       9.37         12 - ozonization - dry heat       70.64       6.26       25.29       -4.38       2.43       4.25       6.57         13 - unaged       87.37       0.76       13.76       11.2       13-       11.2       13-       11.2       13-       11.2       13-       11.2       13-       11.2       13-       13-       13.4       3.82       13.76       11.2       13-       13-       11.2       13-       13-       11.2       13-       13-       11.2       13-       13-       0.04       3.34       3.82       13-       11.2         13 - ozonization - unaged       86.20       1.14       14.04       -1.17       0.38       0.29								
12 - moist heat64.975.2920.49-10.11.46-0.5510.212 - dry heat70.345.6824.40-4.691.863.386.0612 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - moist heat65.825.1119.81-9.201.29-1.229.3712 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7611.213 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged85.48-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.481.46-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80								
12 - dry heat70.345.6824.40-4.691.863.386.0612 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - moist heat65.825.1119.81-9.201.29-1.229.3712 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613.7611.213 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged86.201.1414.04-10.32.754.6511.613 - ozonization - unaged85.48-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814-14.04-1.032.426.5810.614 - moist heat77.582.0617.06-7.892.426.5810.614 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged7					-10.1	1.46	-0.55	10.2
12 - ozonization - unaged74.944.3421.13-0.090.510.10.5312 - ozonization - moist heat65.825.1119.81-9.201.29-1.229.3712 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613.7611.213 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - unaged86.201.1414.04-10.32.754.6511.613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.614 - unaged85.48-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814-0.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - moist heat78.441.9816.41-7.032.345.939.49								
12 - ozonization - moist heat65.825.1119.81-9.201.29-1.229.3712 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613.7613 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.614 - unaged85.48-0.3610.48-0.292.752.772.7714 - moist heat77.582.0617.06-7.892.426.5810.614 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - moist heat78.441.9816.41-7.032.345.939.49	· · · · · · · · · · · · · · · · · · ·							
12 - ozonization - dry heat70.646.2625.29-4.382.434.256.5713 - unaged87.370.7613.7613 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.613 - ozonization - dry heat84.54-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814-0.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.441.9816.41-7.032.345.939.49	8							
13 - unaged       87.37       0.76       13.76         13 - moist heat       77.39       3.65       18.07       -9.98       2.89       4.31       11.2         13 - dry heat       85.52       0.72       17.09       -1.85       -0.04       3.34       3.82         13 - ozonization - unaged       86.20       1.14       14.04       -1.17       0.38       0.29       1.26         13 - ozonization - moist heat       77.12       3.52       18.40       -10.3       2.75       4.65       11.6         13 - ozonization - dry heat       84.54       -0.65       13.23       0.05       -0.29       2.75       2.77         14 - unaged       85.48       -0.36       10.48       14-       -4ry heat       83.44       -0.32       13.61       -2.04       0.05       3.13       3.73         14 - ozonization - unaged       85.47       -0.46       9.80       -0.01       -0.1       -0.68       0.69         14 - ozonization - unaged       85.47       -0.46       9.80       -0.01       -0.1       -0.68       0.69         14 - ozonization - moist heat       78.44       1.98       16.41       -7.03       2.34       5.93       9.49 </th <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th> <th></th>								
13 - moist heat77.393.6518.07-9.982.894.3111.213 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.613 - ozonization - dry heat84.54-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4811.410.4811.210.4810.6514 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.69 <th></th> <th></th> <th></th> <th></th> <th></th> <th>-</th> <th></th> <th></th>						-		
13 - dry heat85.520.7217.09-1.85-0.043.343.8213 - ozonization - unaged86.201.1414.04-1.170.380.291.2613 - ozonization - moist heat77.123.5218.40-10.32.754.6511.613 - ozonization - dry heat84.54-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814 - moist heat77.582.0617.06-7.892.426.5810.614 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged78.441.9816.41-7.032.345.939.49	-				-9.98	2.89	4.31	11.2
13 - ozonization - unaged       86.20       1.14       14.04       -1.17       0.38       0.29       1.26         13 - ozonization - moist heat       77.12       3.52       18.40       -10.3       2.75       4.65       11.6         13 - ozonization - dry heat       84.54       -0.65       13.23       0.05       -0.29       2.75       2.77         14 - unaged       85.48       -0.36       10.48       14.4       -10.3       2.42       6.58       10.6         14 - moist heat       77.58       2.06       17.06       -7.89       2.42       6.58       10.6         14 - dry heat       83.44       -0.32       13.61       -2.04       0.05       3.13       3.73         14 - ozonization - unaged       85.47       -0.46       9.80       -0.01       -0.1       -0.68       0.69         14 - ozonization - unaged       78.44       1.98       16.41       -7.03       2.34       5.93       9.49								
13 - ozonization - moist heat       77.12       3.52       18.40       -10.3       2.75       4.65       11.6         13 - ozonization - dry heat       84.54       -0.65       13.23       0.05       -0.29       2.75       2.77         14 - unaged       85.48       -0.36       10.48       14-       14-       14-       17.58       2.06       17.06       -7.89       2.42       6.58       10.6         14 - dry heat       83.44       -0.32       13.61       -2.04       0.05       3.13       3.73         14 - ozonization - unaged       85.47       -0.46       9.80       -0.01       -0.1       -0.68       0.69         14 - ozonization - unaged       78.44       1.98       16.41       -7.03       2.34       5.93       9.49	-							
13 - ozonization - dry heat84.54-0.6513.230.05-0.292.752.7714 - unaged85.48-0.3610.4814 - moist heat77.582.0617.06-7.892.426.5810.614 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - unaged78.441.9816.41-7.032.345.939.49								
14 - unaged       85.48       -0.36       10.48         14 - moist heat       77.58       2.06       17.06       -7.89       2.42       6.58       10.6         14 - dry heat       83.44       -0.32       13.61       -2.04       0.05       3.13       3.73         14 - ozonization - unaged       85.47       -0.46       9.80       -0.01       -0.1       -0.68       0.69         14 - ozonization - moist heat       78.44       1.98       16.41       -7.03       2.34       5.93       9.49								
14 - moist heat77.582.0617.06-7.892.426.5810.614 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - moist heat78.441.9816.41-7.032.345.939.49								
14 - dry heat83.44-0.3213.61-2.040.053.133.7314 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - moist heat78.441.9816.41-7.032.345.939.49					-7.89	2.42	6.58	10.6
14 - ozonization - unaged85.47-0.469.80-0.01-0.1-0.680.6914 - ozonization - moist heat78.441.9816.41-7.032.345.939.49								
<b>14 – ozonization – moist heat</b> 78.44 1.98 16.41 –7.03 2.34 5.93 <b>9.49</b>	-							
	-							
17 - 0.00112a(1011 - 0.1)y   cat    05.54 - 0.05   15.25   0.05 - 0.29   2.75	14 – ozonization – dry heat	85.54	-0.65	13.23	0.05	-0.29	2.75	2.77

### 3.8 Effect of ozonization on selected microorganisms

*Tab.* 6 gives the results of microbiological tests The growth of mould was identical on all the samples and agreed with the control sample. Thus the performed ozonization method does not have any effect on the vitality and growth properties of the tested moulds.

Sample	A. niger	P. aurantiogriseum	T. koningii
1	+++	+++	+++
2	+++	+++	+++
3	+++	+++	+++
4	+++	+++	+++
5	+++	+++	+++
6	+++	+++	+++
7	+++	+++	+++
8	+++	+++	+++
9	+++	+++	+++
10	+++	+++	+++
Control	+++	+++	+++

Tab. 6.	Effect of ozonization on selected archive microorganisms.
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Evaluation: ++ strong growth (covers the entire surface of the paper square) and sporulation ++ growth (covers a major part of the surface of the paper square)

growth (covers a major part of the same of the paper square)
 weak growth (isolated colonies)

- no growth

## **4 CONCLUSIONS**

On the basis of the above results of measurements of the mechanical, optical and chemical properties of Whatman No. 1 filter paper, paper for documents pursuant to ISO 9706, groundwood paper, wood-free writing paper, bleached sulphite and chemothermomechanical pulp, it can be stated that ozonization performed by the method described in Chapter 2 **does not have an observable effect** on the monitored properties.

Similarly, study of the effect of ozonization on selected aryl methane dyes Acid Red 87, Acid Green 16, Basic Violet 1, Basic Blue 6, Basic Green 4 and actual archive materials from the 19th and 20th centuries confirmed that this technology **does not have a negative effect** on the colours.

However, ozonization **cannot** be considered to constitute effective disinfection of documents.