STUDY OF THE EFFECT OF OZONIZATION ON ARCHIVE MATERIALS

Prepared by:
Dr. Ing. Michal Ďurovič, Ing. Hana Paulusová,
Roman Straka, PhMr. Bronislava Bacílková

National Archives, Prague 2008

CONTENTS

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 g/m^2 *(W)*
- Paper for documents according to ISO 9706, 80 g/m^2 *(ISO 9706)*
- Groundwood paper, glazed on one side, 60 g/m^2 *(DP)*
- Wood-free writing paper CSN 502251, 60 g/m^2 *(BPP)*
- Bleached sulphite cellulose pulp, 80 g/m^2 *(MgBi)*
- Chemothermomechanical cellulose pulp, 75 g/m^2 *(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 μg/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 %.

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

	1 min prům.	*1 min prům.*		*1 min prům.*	*1 min prům.*
ČAS	O3* ul/m3	O3, ug/m3	ČAS	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	-	-	-
10:45	79,1	158	-	-	-
10:46	67,9	135	-	-	-
10:47	57,1	114	-	-	-
10:48	48,9	97,6	-	-	-
10:49	41,7	83,2	-	-	-
10:50	35,8	71,4	-	-	-
10:51	31,2	62,2	-	-	-
10:52	25,9	51,7	-	-	-
max.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**	-

* podmínky při měření a suchý vzduch

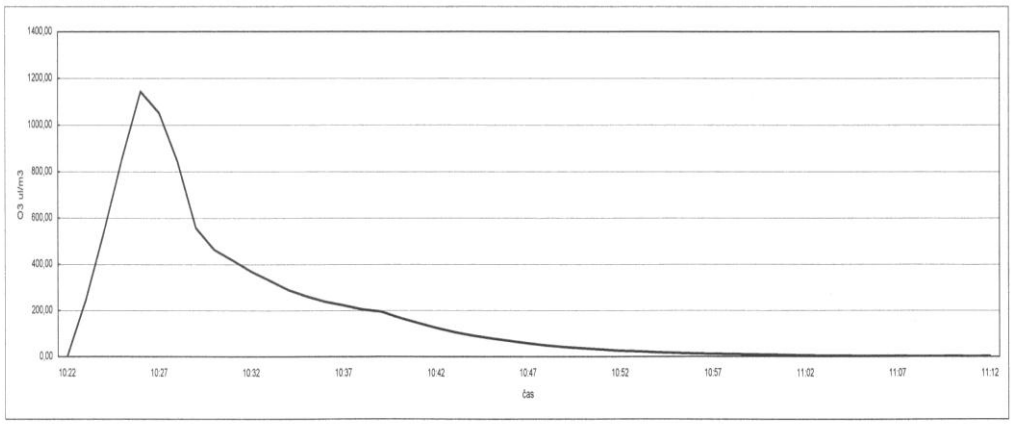


Fig. 1 **Progress of sample ozonization**

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 ± 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 ± 0.1 mm. 10 measurements were performed for each direction.

*2.4.4 Determination of the total colour difference ΔE**

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_{457}

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 2×2 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 ± 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.

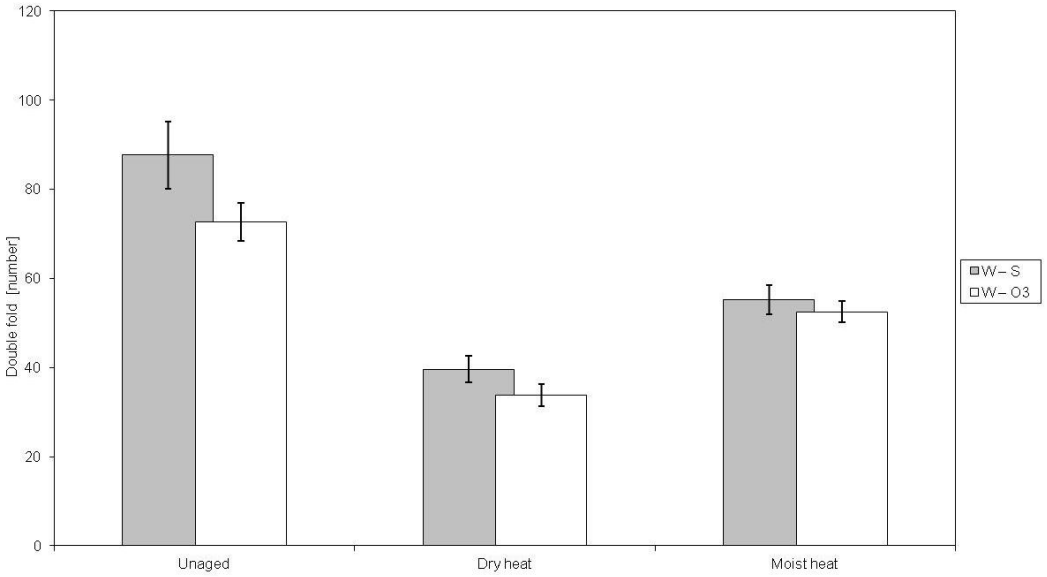


Fig. 2 **Effect of ozonization and artificial ageing on the folding endurance of Whatman No. 1 filter paper in the machine direction**

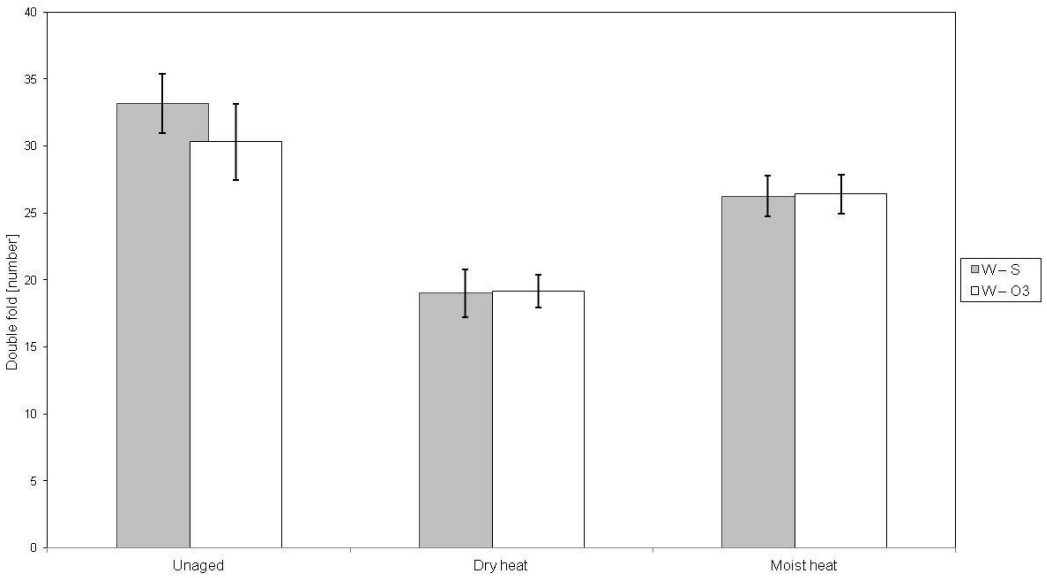


Fig. 3 **Effect of ozonization and artificial ageing on the folding endurance of Whatman No. 1 filter paper in the cross direction**

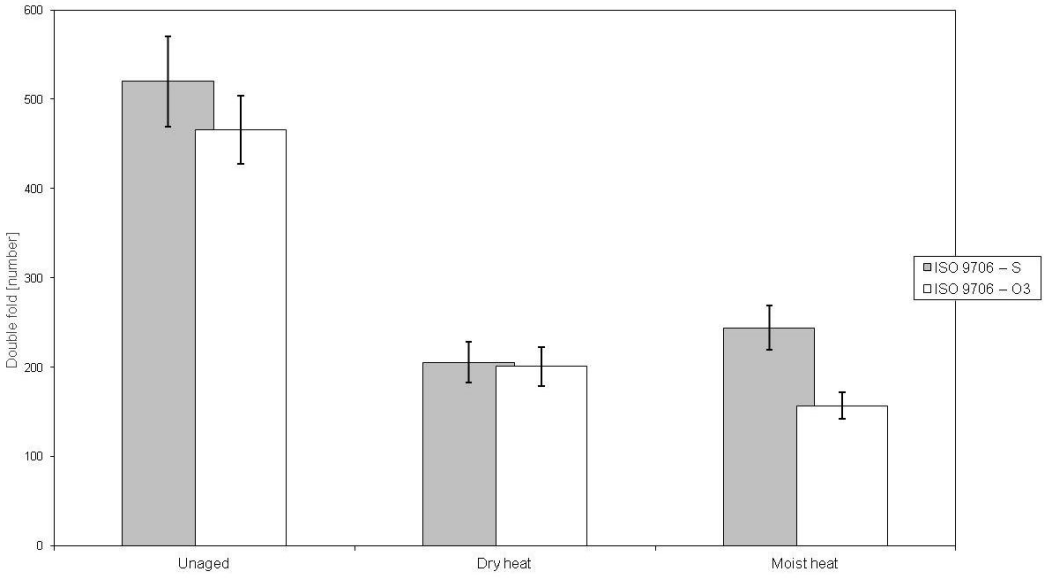


Fig. 4 **Effect of ozonization and artificial ageing on the folding endurance of paper ISO 9706 in the machine direction**

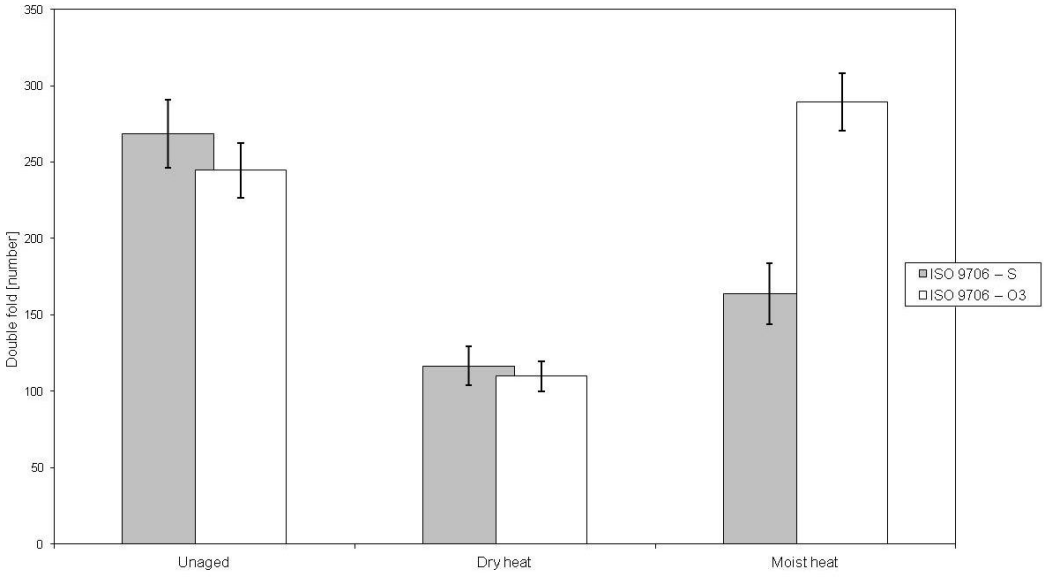


Fig. 5 **Effect of ozonization and artificial ageing on the folding endurance of paper ISO 9706 in the cross direction**

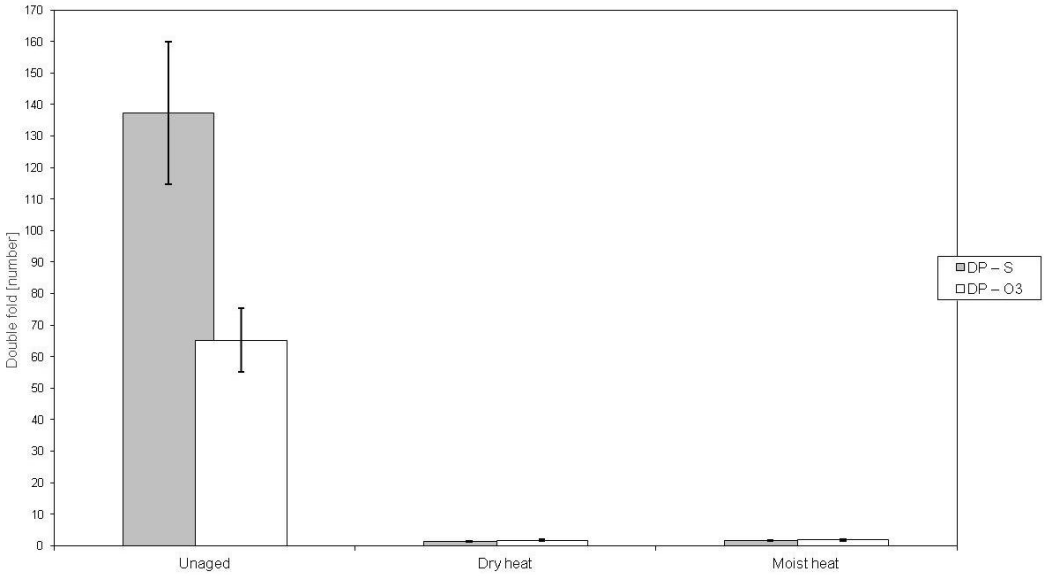


Fig. 6 **Effect of ozonization and artificial ageing on the folding endurance of groundwood paper in the machine direction**

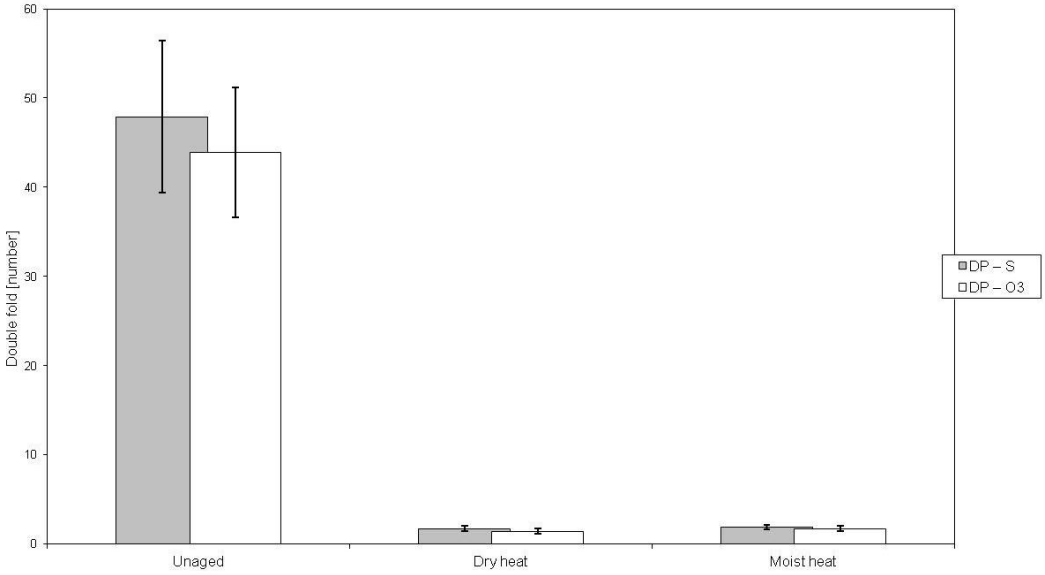


Fig. 7 **Effect of ozonization and artificial ageing on the folding endurance of groundwood paper in the cross direction**

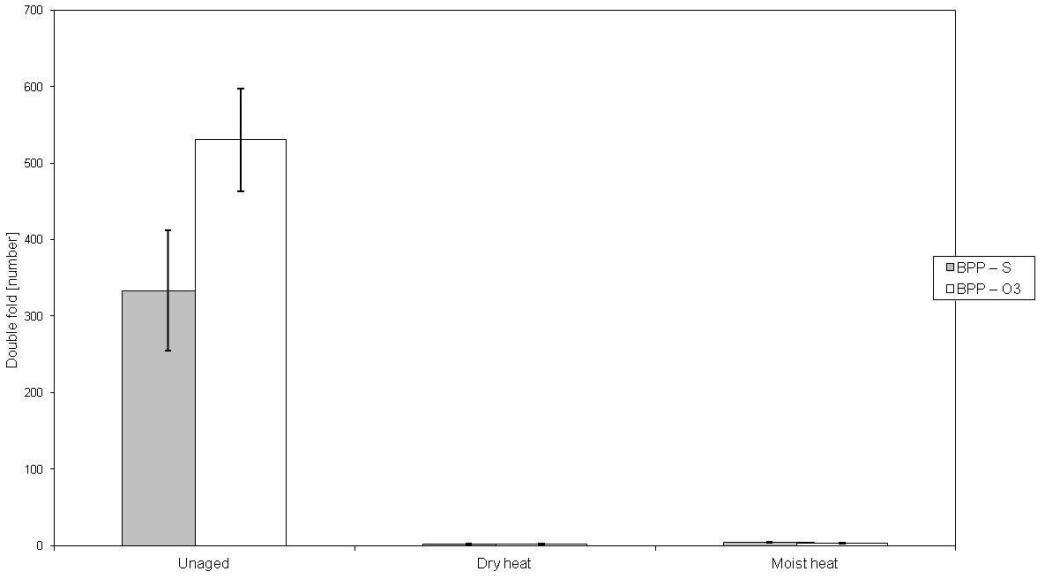


Fig. 8 **Effect of ozonization and artificial ageing on the folding endurance of wood-free writing paper in the machine direction**

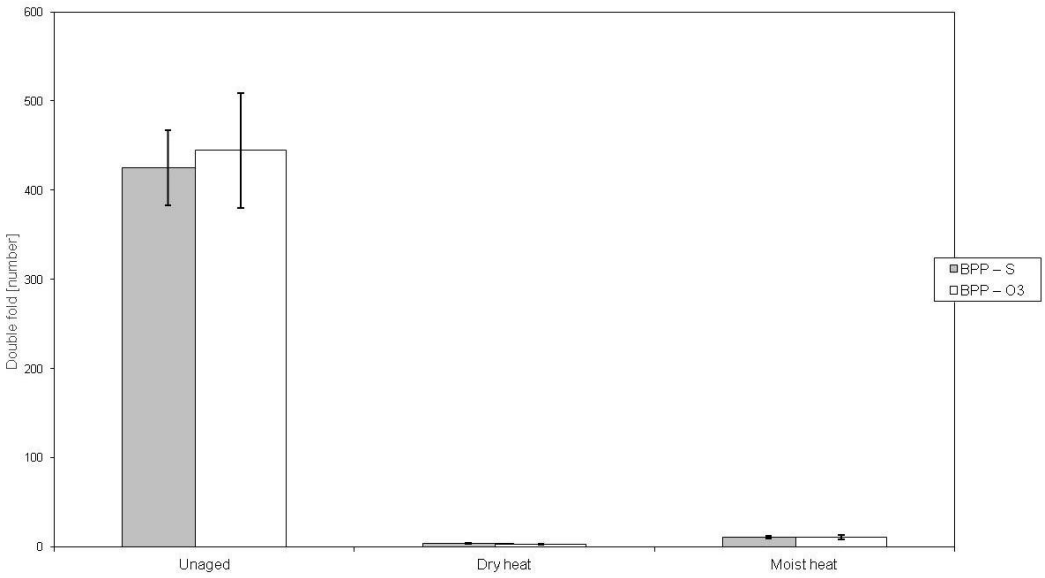


Fig. 9 **Effect of ozonization and artificial ageing on the folding endurance of wood-free writing paper in the cross direction**

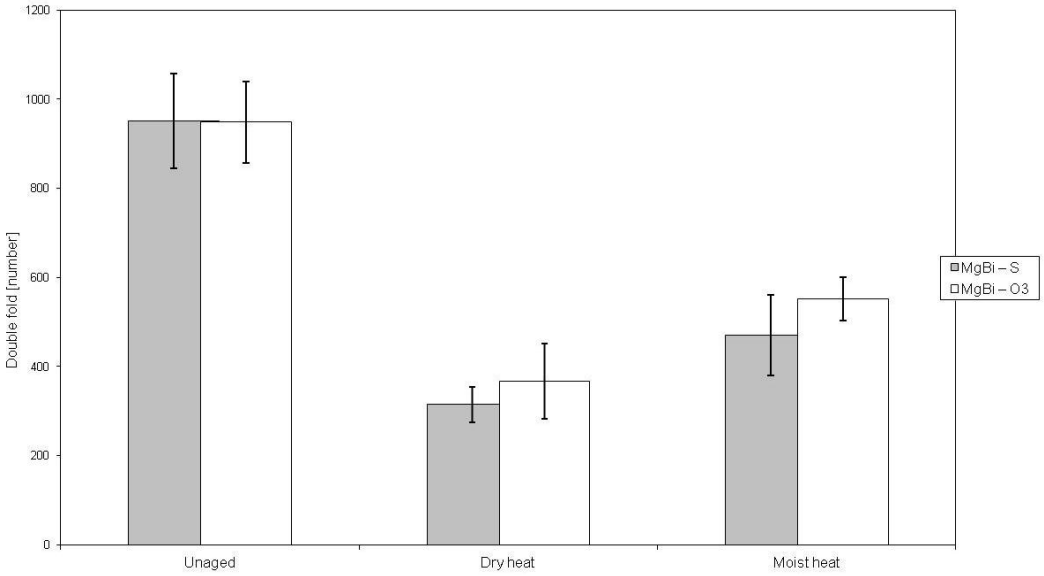


Fig. 10 **Effect of ozonization and artificial ageing on the folding endurance of bleached sulphite pulp**

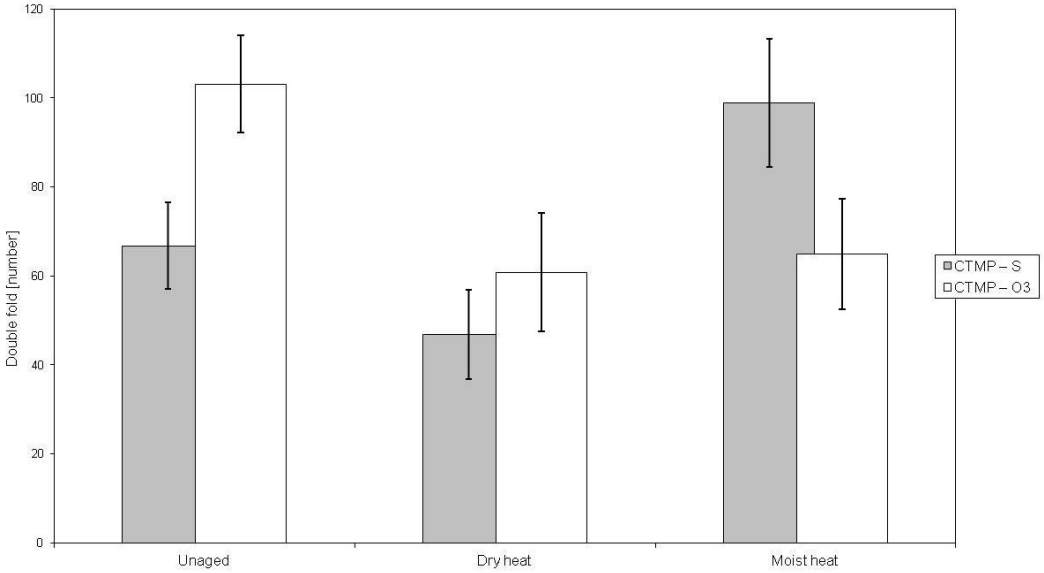


Fig. 11 **Effect of ozonization and artificial ageing on the folding endurance of chemothermomechanical pulp**

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.

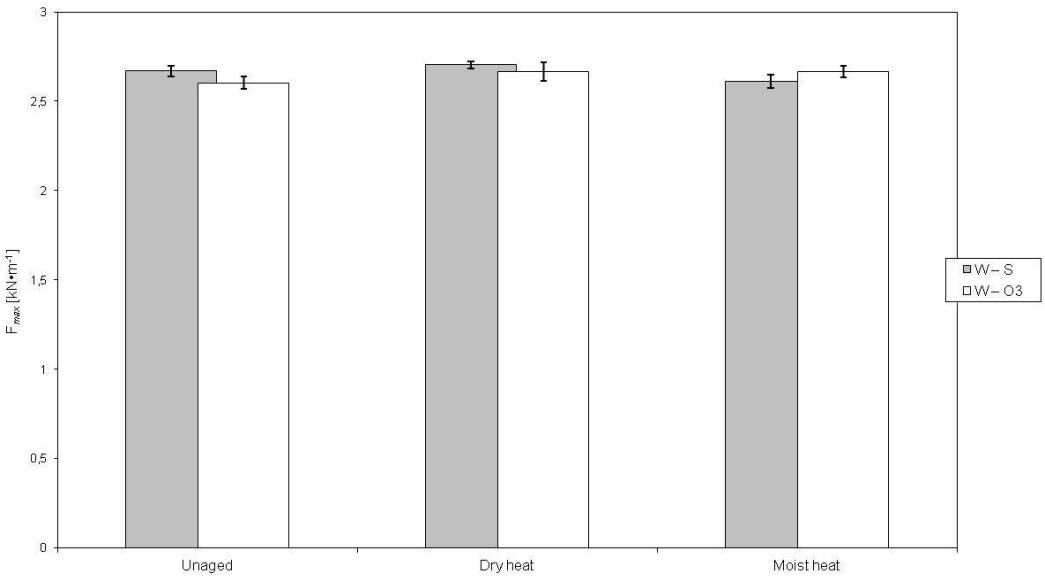


Fig. 12 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of Whatman No. 1 filter paper in the machine direction**

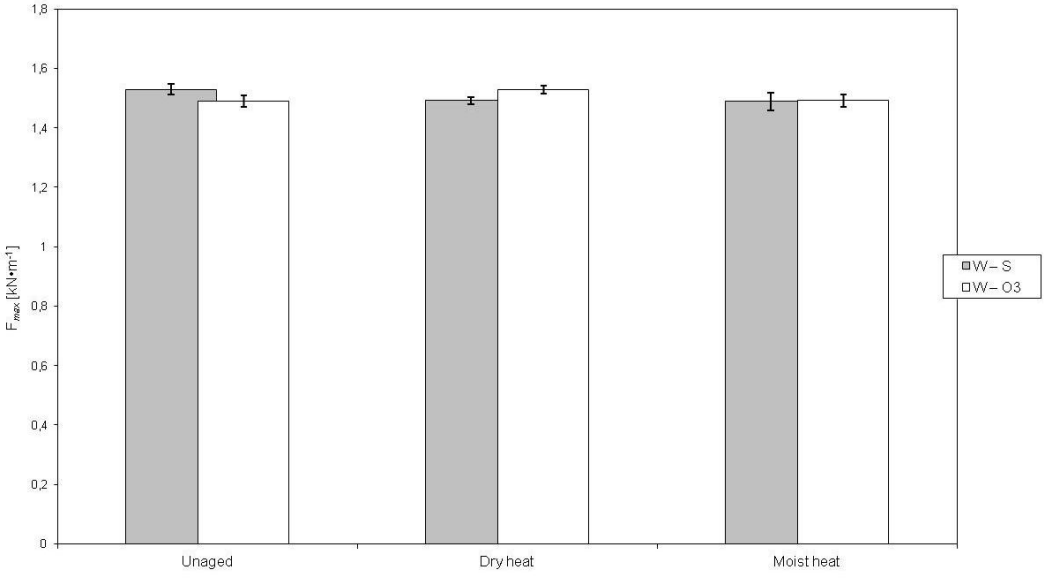


Fig. 13 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of Whatman No. 1 filter paper in the cross direction**

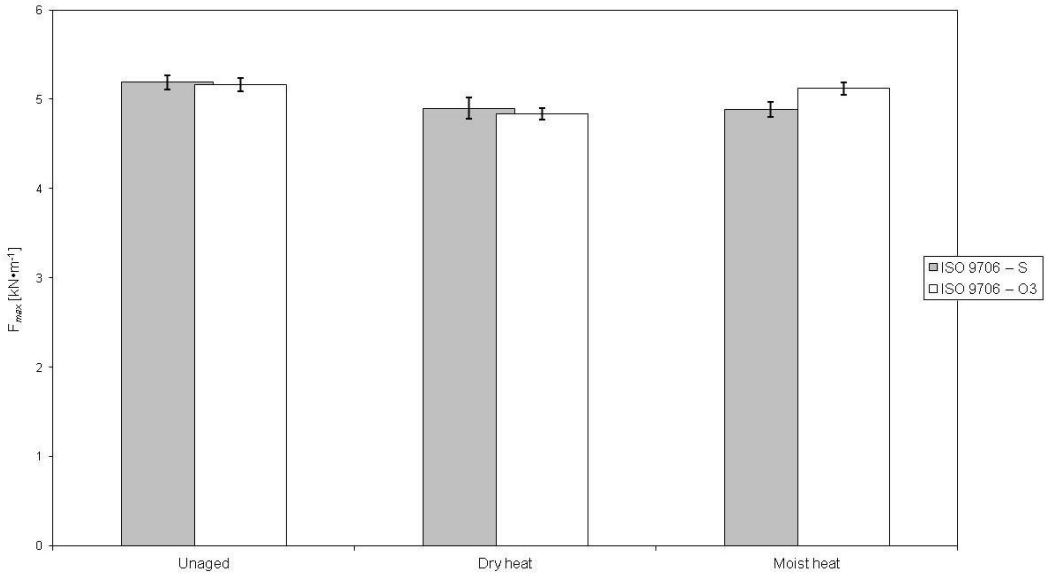


Fig. 14 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of paper ISO 9706 in the machine direction**

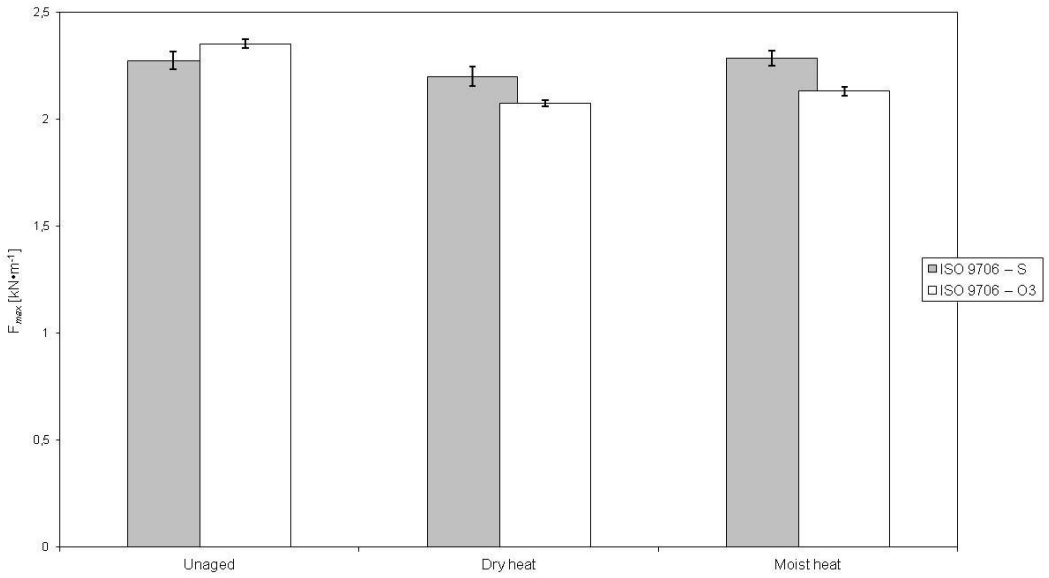


Fig. 15 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of paper ISO 9706 in the cross direction**

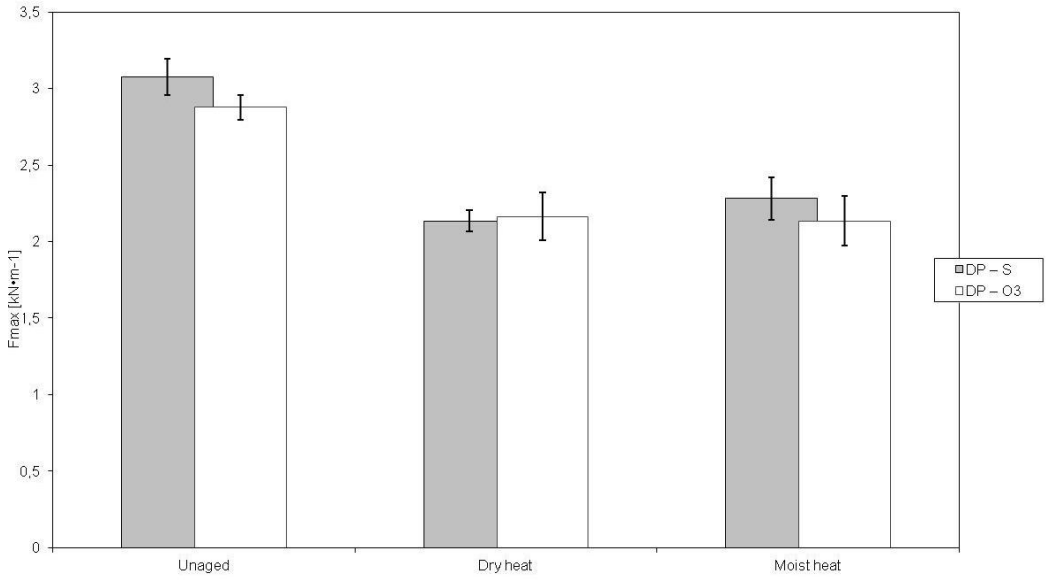


Fig. 16 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of groundwood paper in the machine direction**

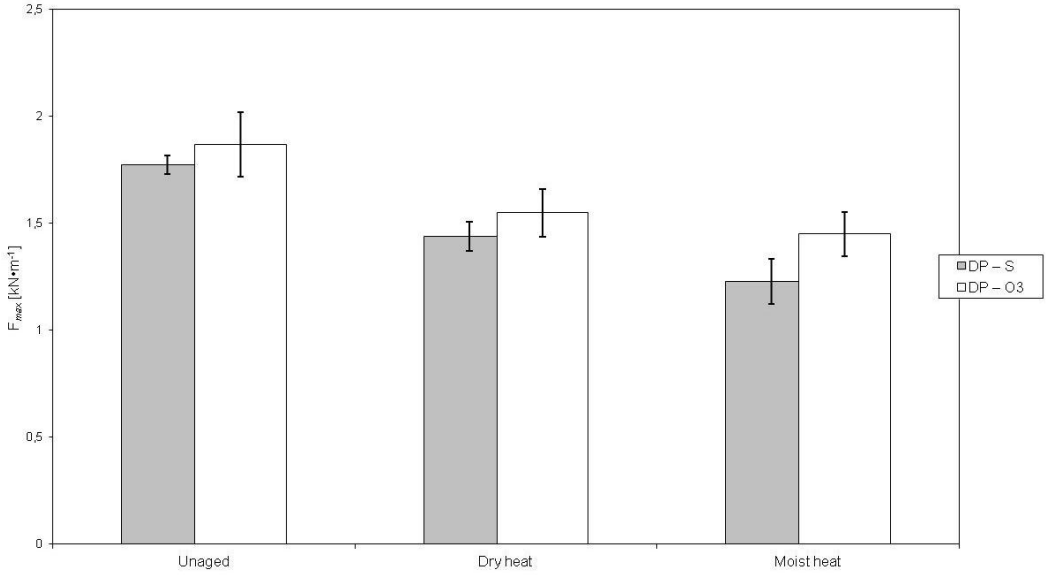


Fig. 17 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of groundwood paper in the cross direction**

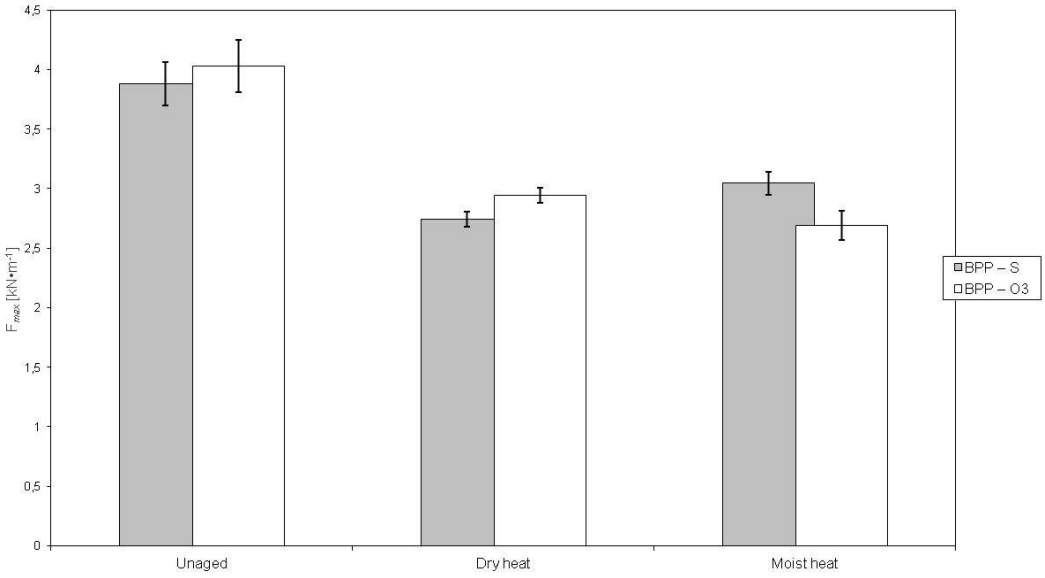


Fig. 18 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of wood-free writing paper in the machine direction**

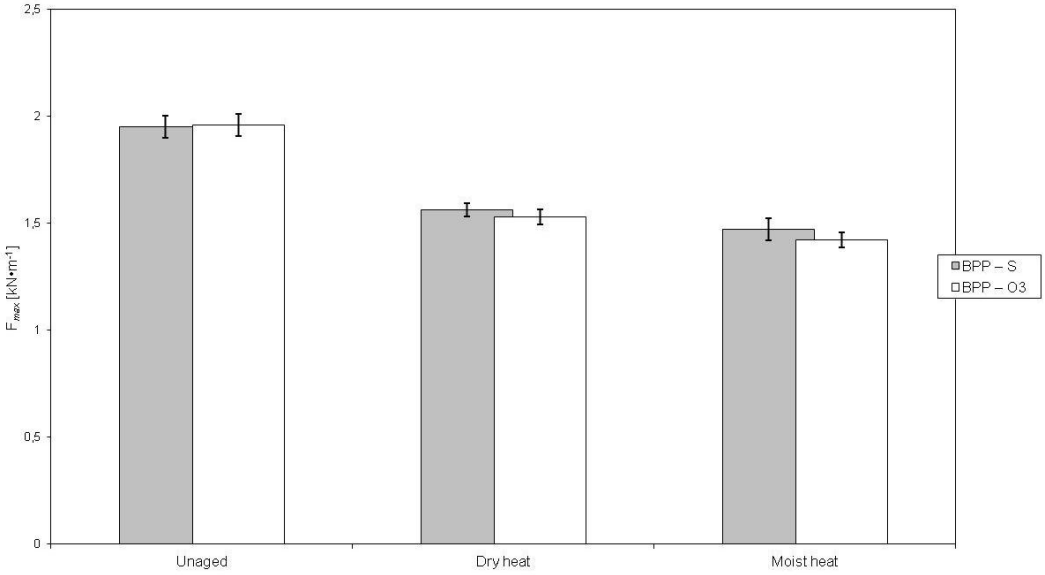


Fig. 19 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of wood-free writing paper in the cross direction**

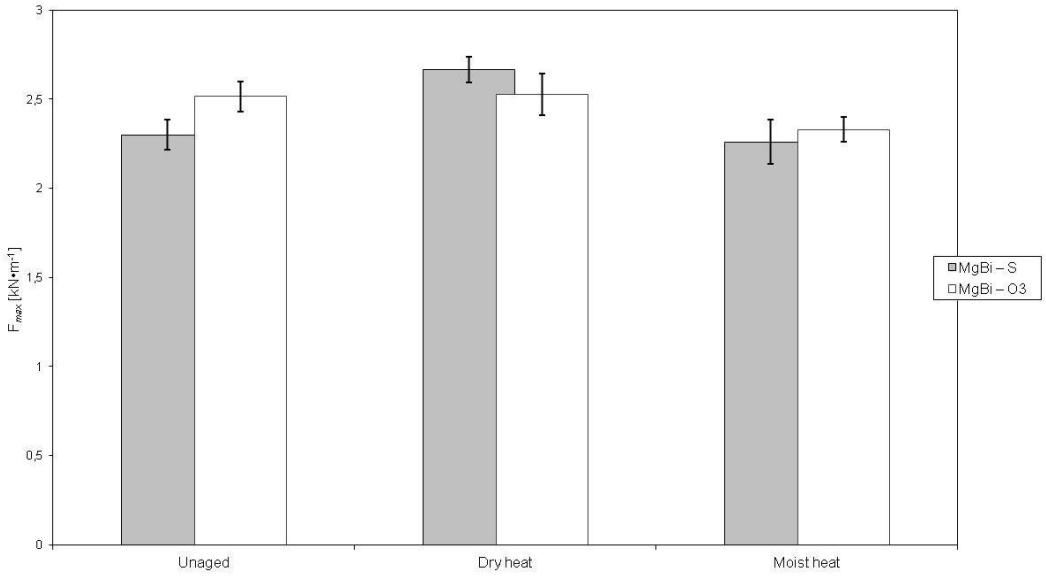


Fig. 20 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of bleached sulphite pulp**

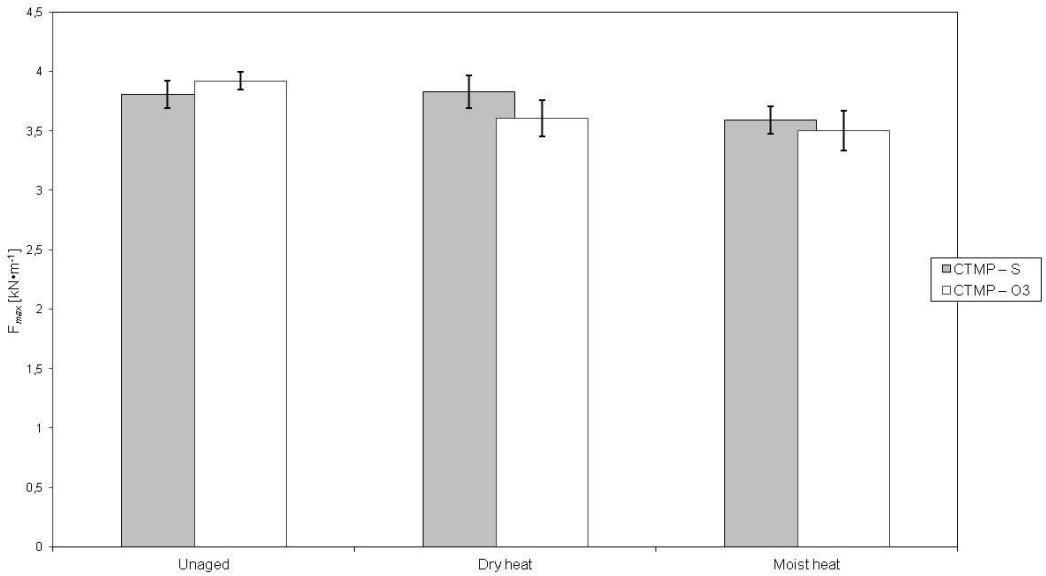


Fig. 21 **Effect of ozonization and artificial ageing on the breaking load (kN/m) of chemothermomechanical pulp**

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.

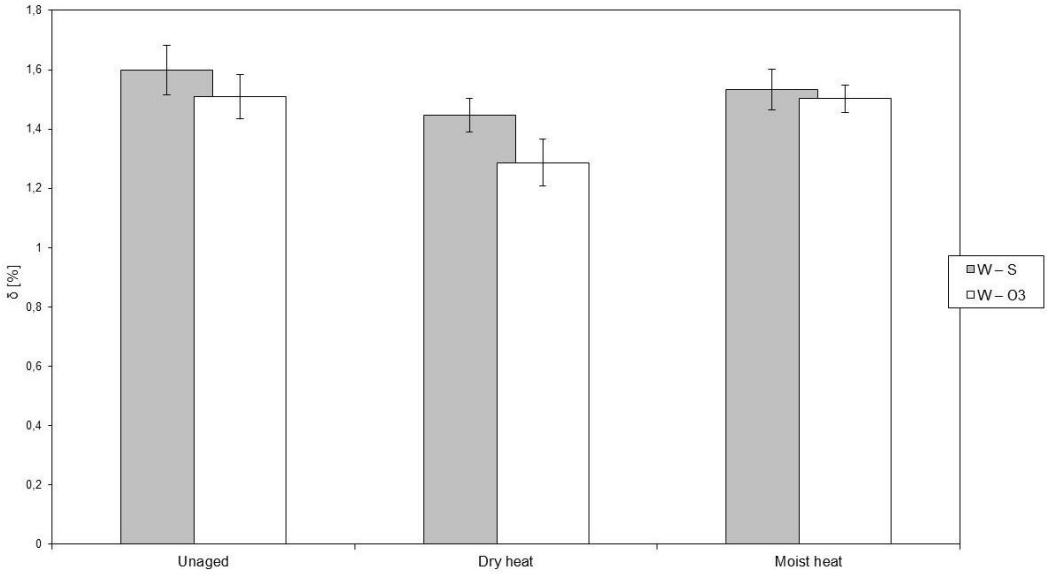


Fig. 22 **Effect of ozonization and artificial ageing on the elongation at break (%) of Whatman No. 1 paper in the machine direction**

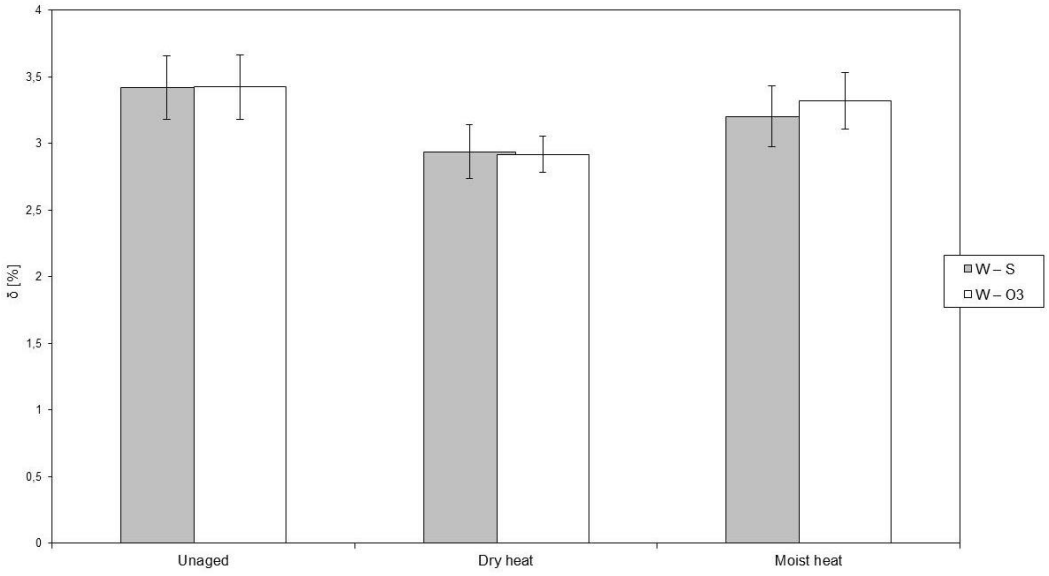


Fig. 23 **Effect of ozonization and artificial ageing on the elongation at break (%) of Whatman No. 1 paper in the cross direction**

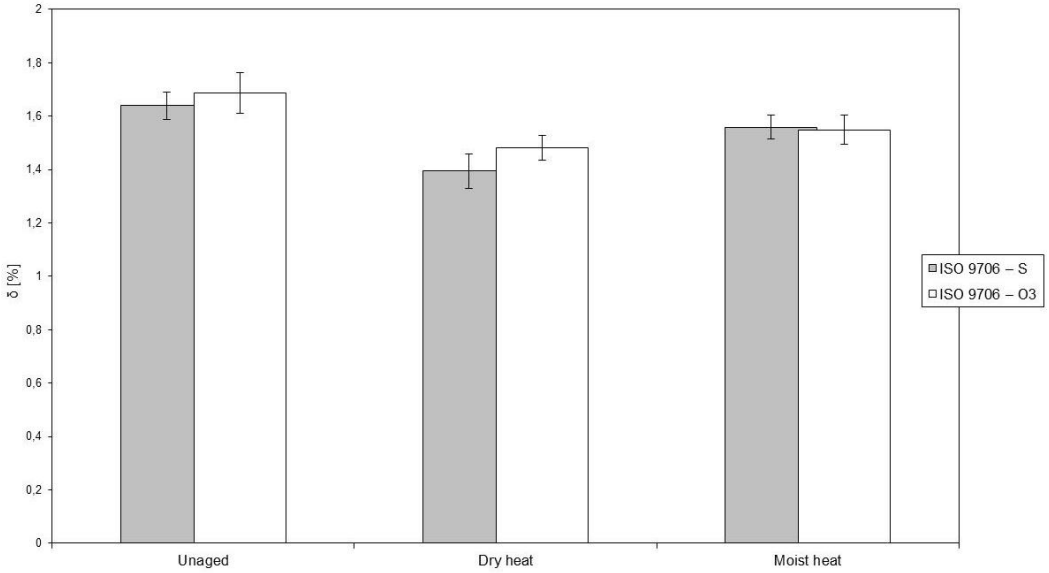


Fig. 24 **Effect of ozonization and artificial ageing on the elongation at break (%) of paper ISO 9706 in the machine direction**

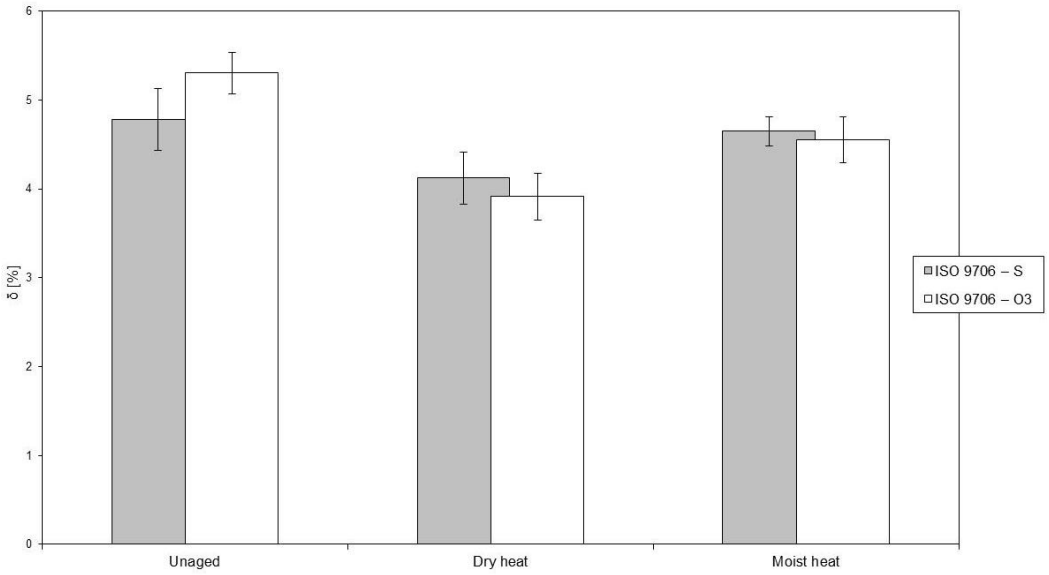


Fig. 25 **Effect of ozonization and artificial ageing on the elongation at break (%) of paper ISO 9706 in the cross direction**

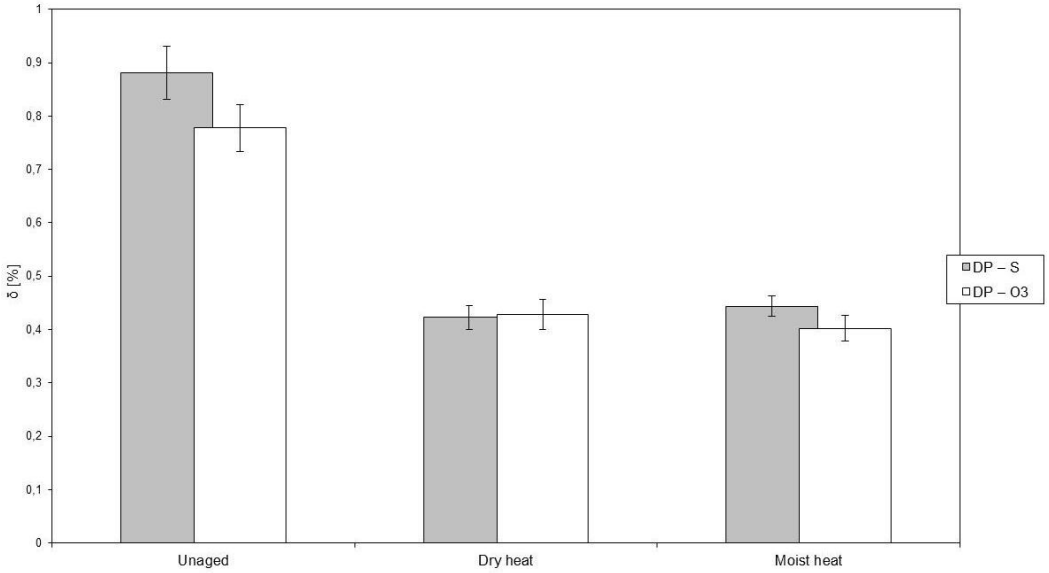


Fig. 26 **Effect of ozonization and artificial ageing on the elongation at break (%) of groundwood paper in the machine direction**

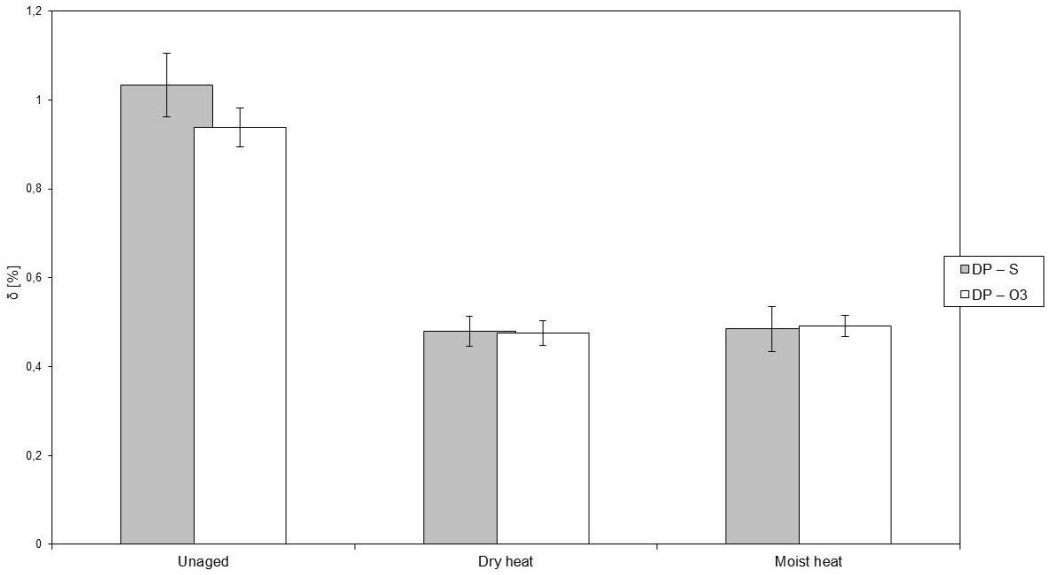


Fig. 27 **Effect of ozonization and artificial ageing on the elongation at break (%) of groundwood paper in the cross direction**

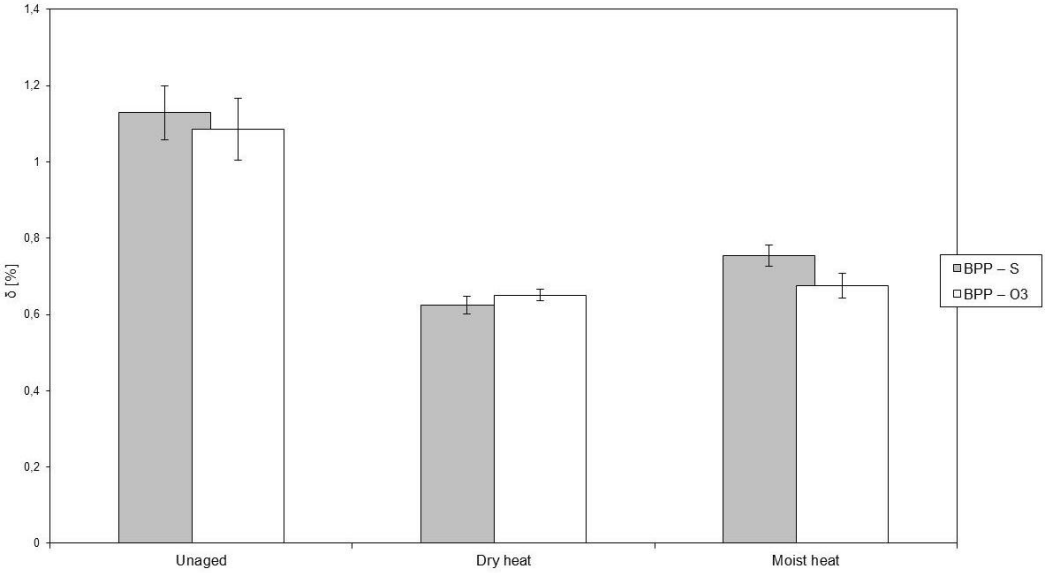


Fig. 28 **Effect of ozonization and artificial ageing on the elongation at break (%) of wood-free writing paper in the machine direction**

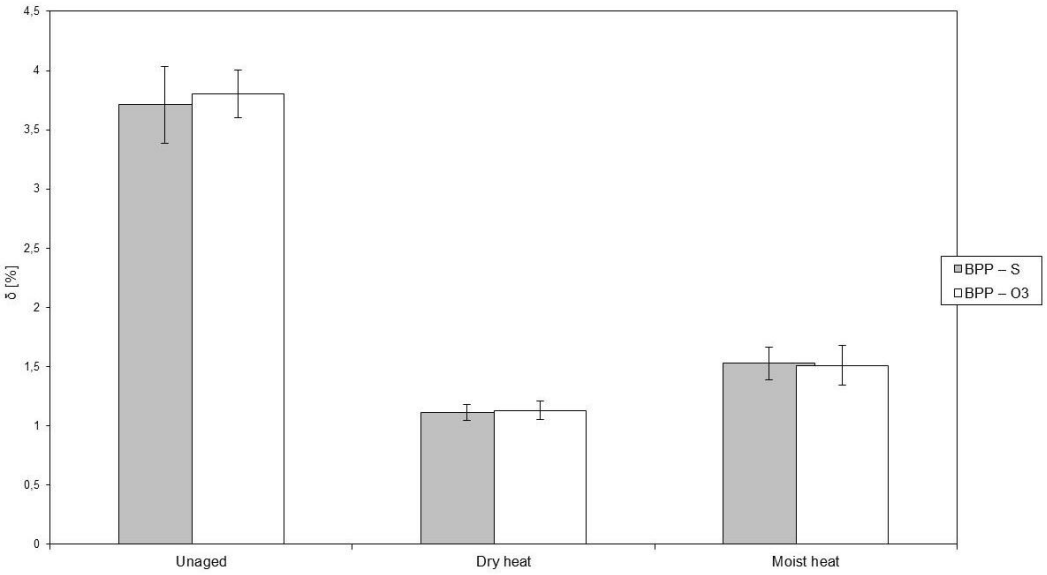


Fig. 29 **Effect of ozonization and artificial ageing on the elongation at break (%) of wood-free writing paper in the cross direction**

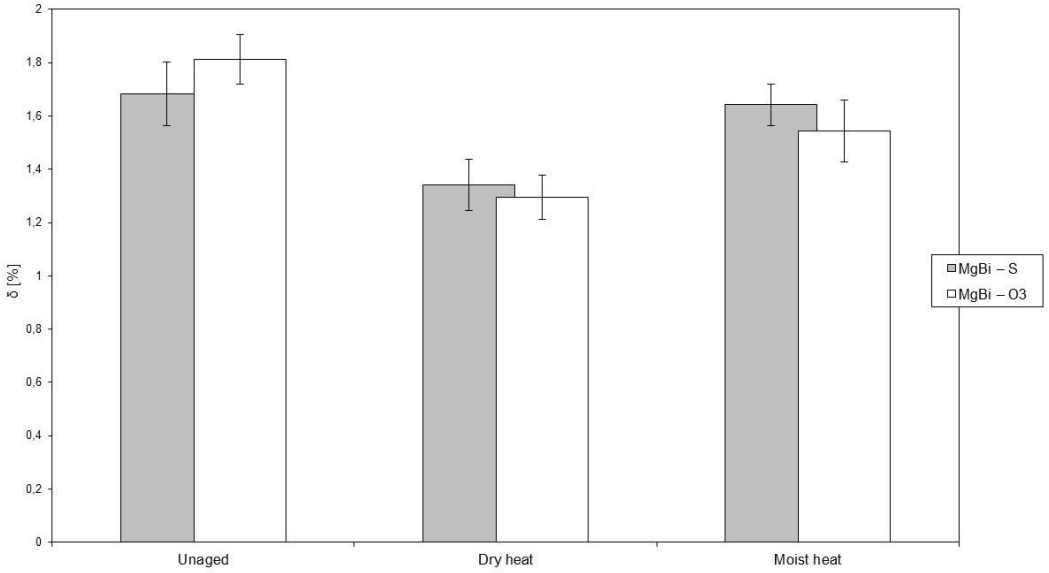


Fig. 30 **Effect of ozonization and artificial ageing on the elongation at break (%) of bleached sulphite pulp**

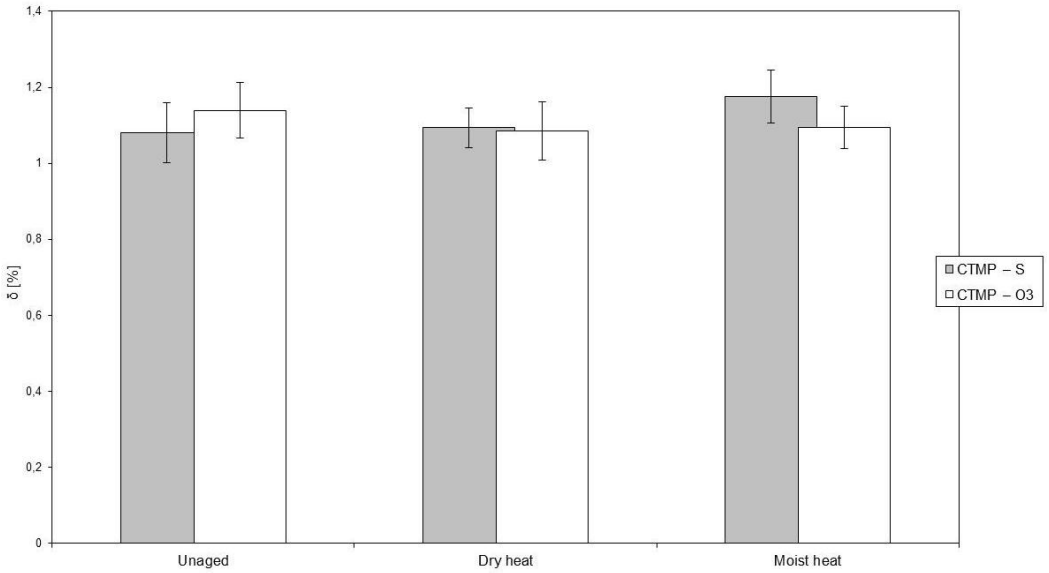


Fig. 31 **Effect of ozonization and artificial ageing on the elongation at break (%) of chemothermomechanical pulp**

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.

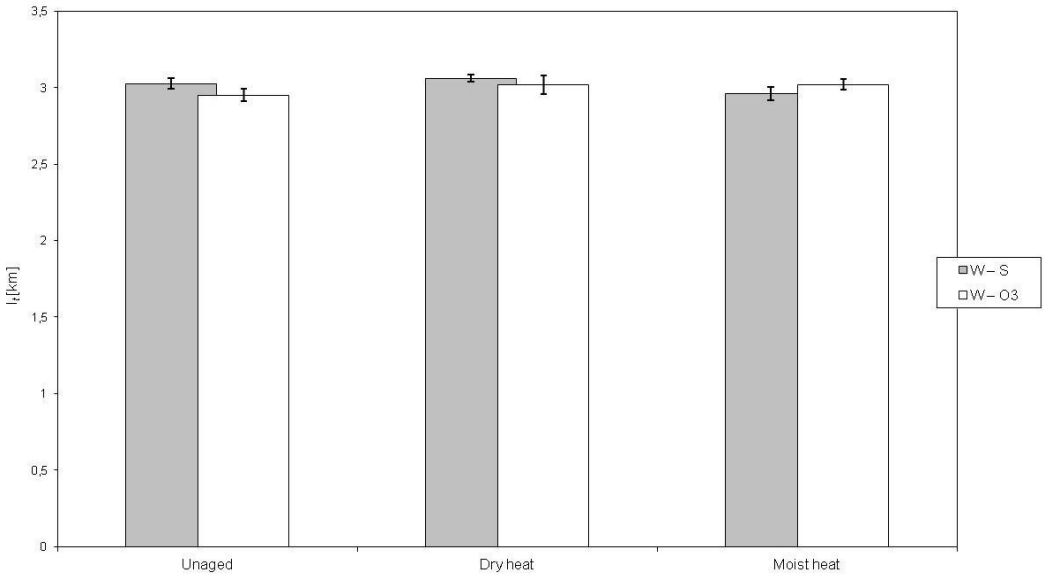


Fig. 32 **Effect of ozonization and artificial ageing on the breaking length (km) of Whatman No. 1 paper in the machine direction**

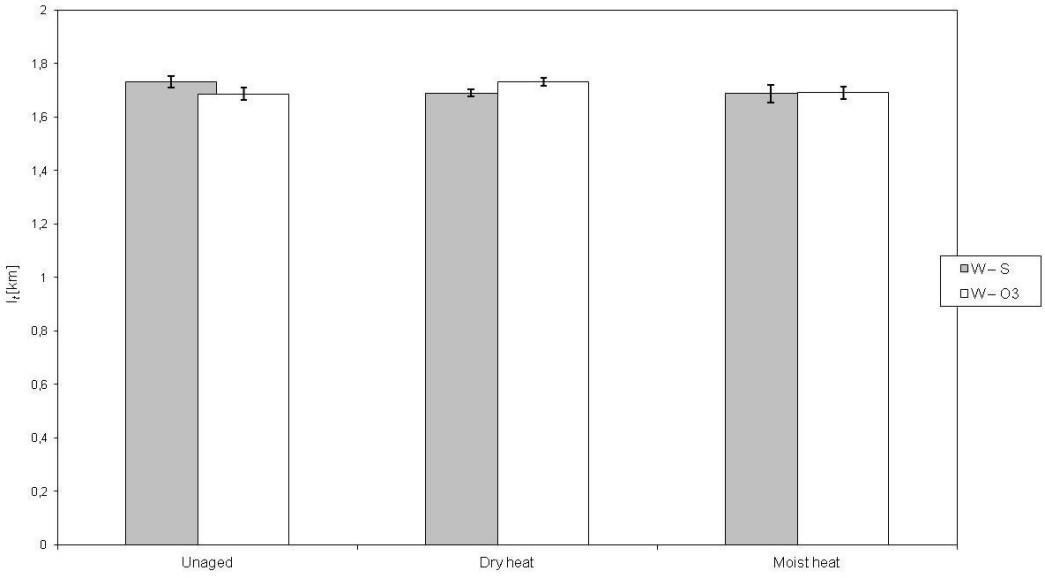


Fig. 33 **Effect of ozonization and artificial ageing on the breaking length (km) of Whatman No. 1 paper in the cross direction**

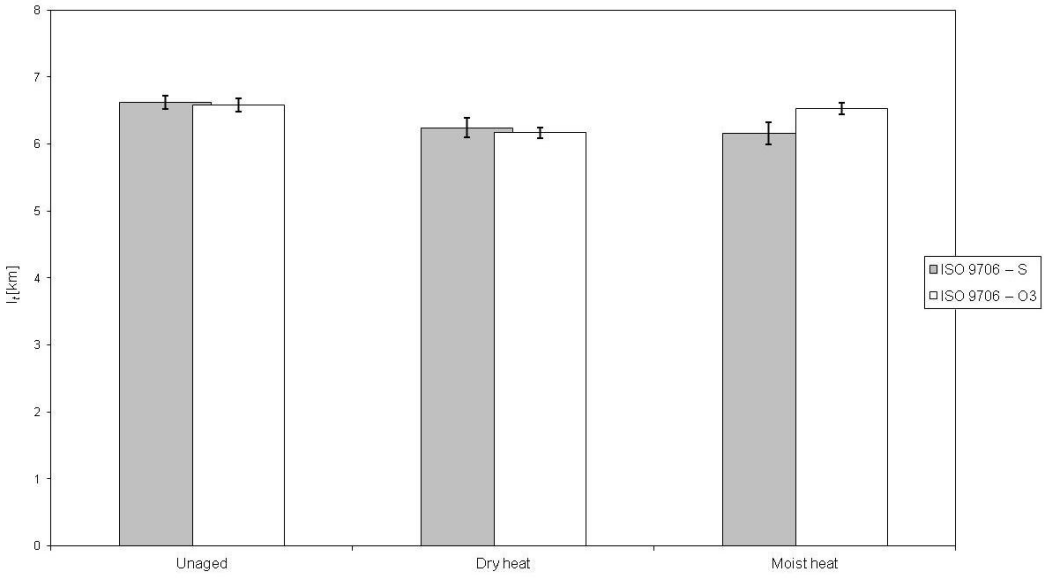


Fig. 34 **Effect of ozonization and artificial ageing on the breaking length (km) of paper ISO 9706 in the machine direction**

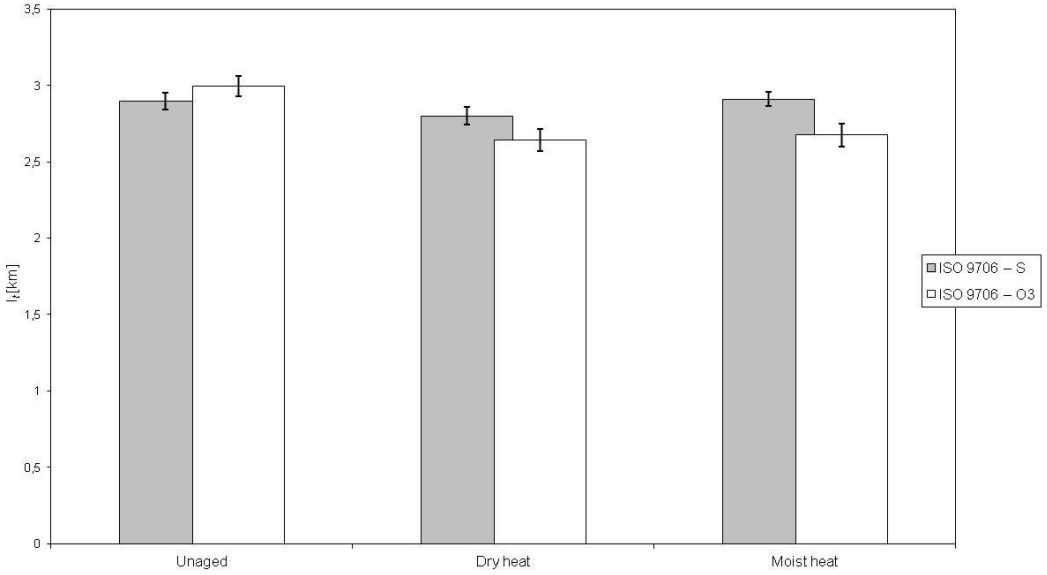


Fig. 35 **Effect of ozonization and artificial ageing on the breaking length (km) of paper ISO 9706 in the cross direction**

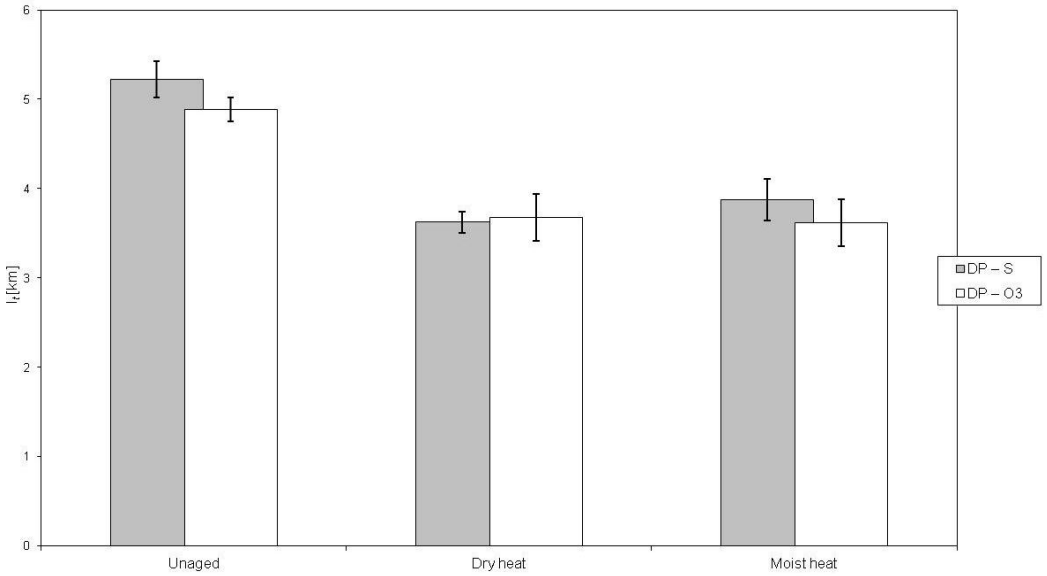


Fig. 36 **Effect of ozonization and artificial ageing on the breaking length (km) of groundwood paper in the machine direction**

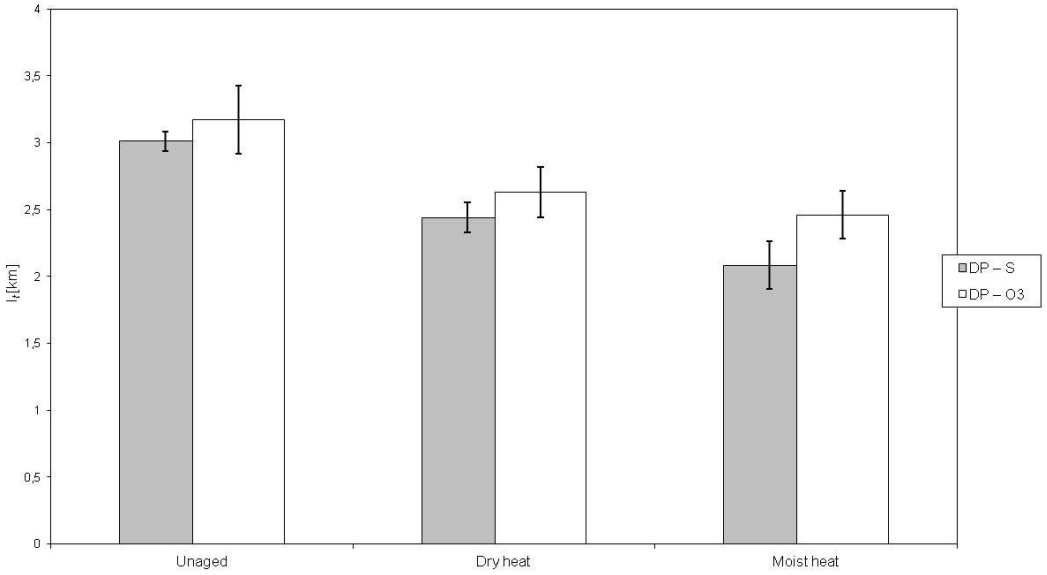


Fig. 37 **Effect of ozonization and artificial ageing on the breaking length (km) of groundwood paper in the cross direction**

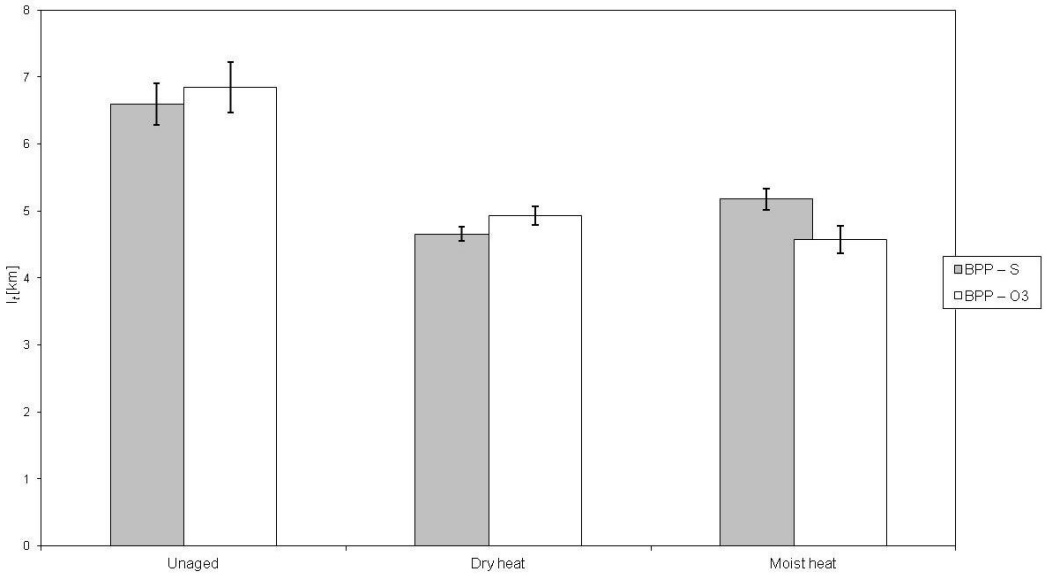


Fig. 38 **Effect of ozonization and artificial ageing on the breaking length (km) of wood-free writing paper in the machine direction**

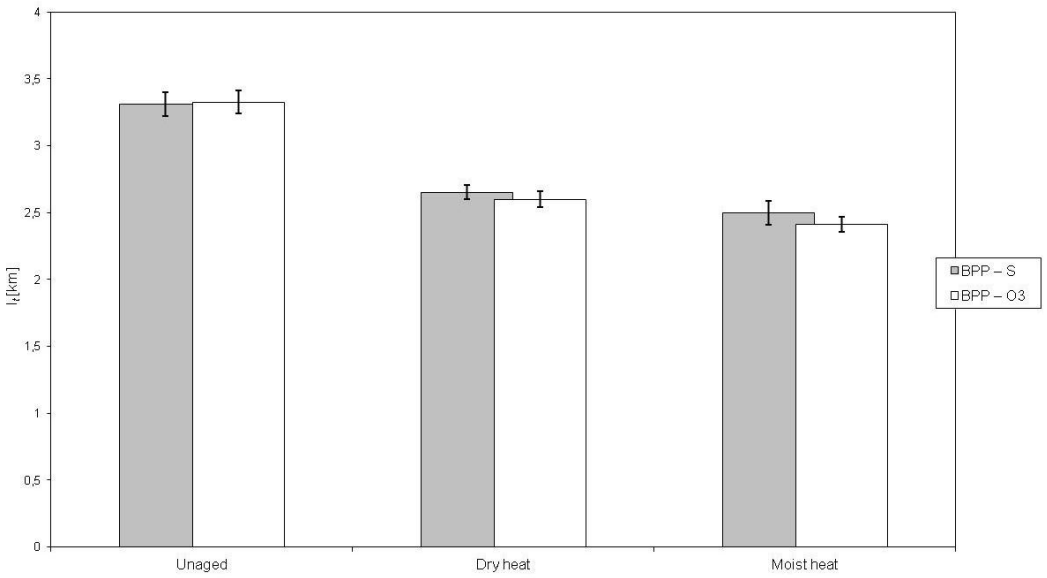


Fig. 39 **Effect of ozonization and artificial ageing on the breaking length (km) of wood-free writing paper in the cross direction**

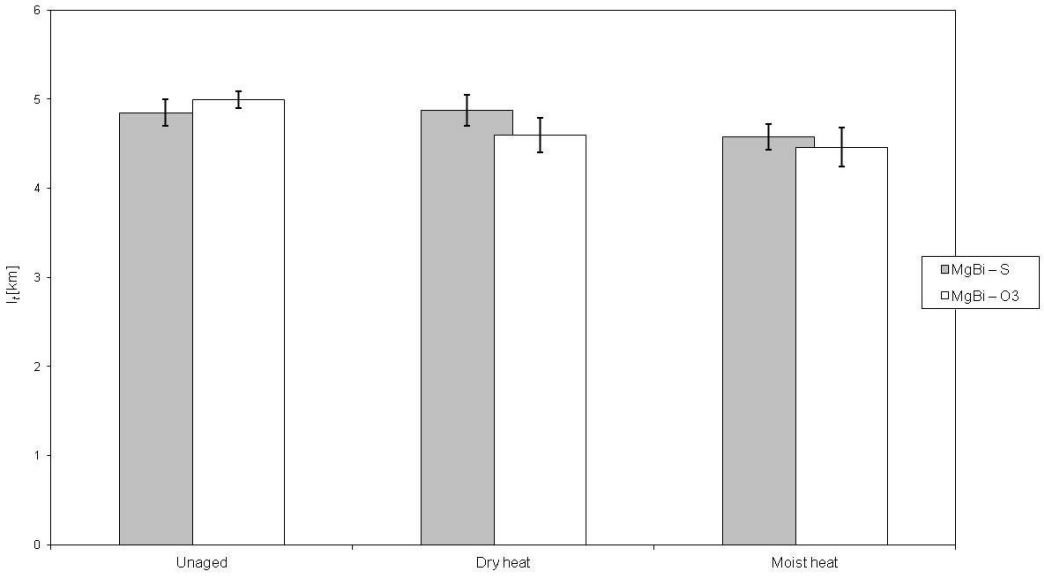


Fig. 40 **Effect of ozonization and artificial ageing on the breaking length (km) of bleached sulphite pulp**

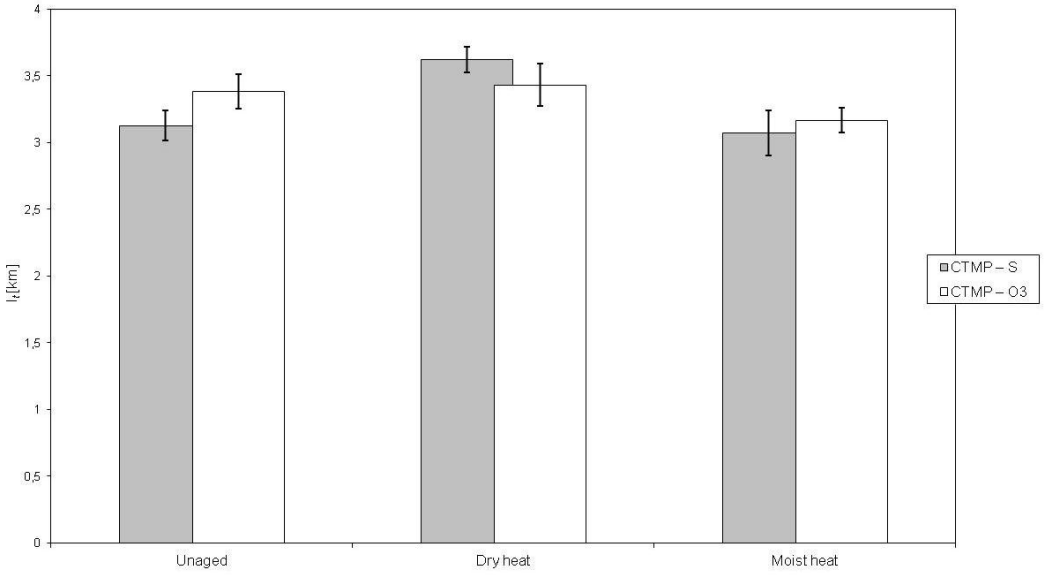


Fig. 41 **Effect of ozonization and artificial ageing on the breaking length (km) of chemothermomechanical pulp**

3.3 Total colour difference ΔE*

Tab. 1 gives the values of L*, a* and b*, their differences and the total colour differences ΔE* 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.

Tab. 1. **Effect of ozonization on the total colour difference ΔE* of individual kinds of paper.**

Paper sample	L*	a*	b*	ΔL*	Δa*	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_3 – 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_3 – unaged	96.48	−0.18	4.62	−0.05	−0.05	0.07	**0.03**
ISO 9706 – O_3 – moist heat	93.09	1.00	9.73	−3.44	1.13	5.18	**6.32**
ISO 9706 – O_3 – 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_3 – 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_3 – 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**

3.4. Determination of the decoloration number DC_{457}

Tab. 2 gives the reflectivity at critical sample thickness (R_∞), 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.

Tab. 2. **Effect of ozonization on the decoloration number DC_{457} for the individual kinds of paper.**

Sample of paper	R_∞	K/S	DC_{457}
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**
BPP – 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_3 – unaged	86.8	0.0100	**+0.0005**
ISO 9706 – O_3 – moist heat	73.1	0.0494	**–0.0389**
ISO 9706 – O_3 – 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_3 – 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**

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_3	8.90	8.59	8.58
CTMP	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.

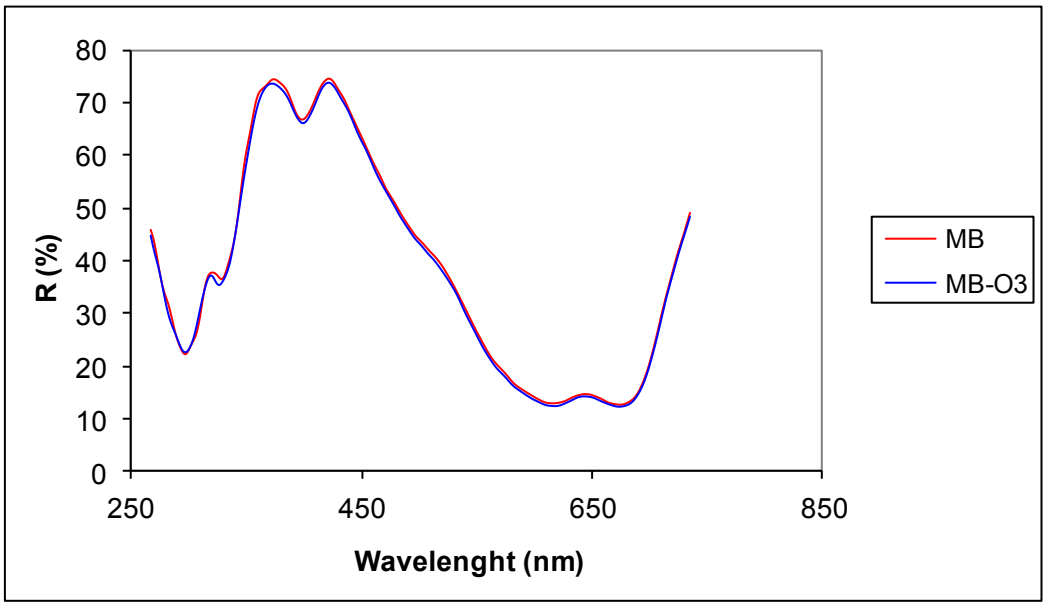


Fig. 42 **Effect of ozonization on the UV/VIS reflectance spectra of the dye Basic Blue 6**

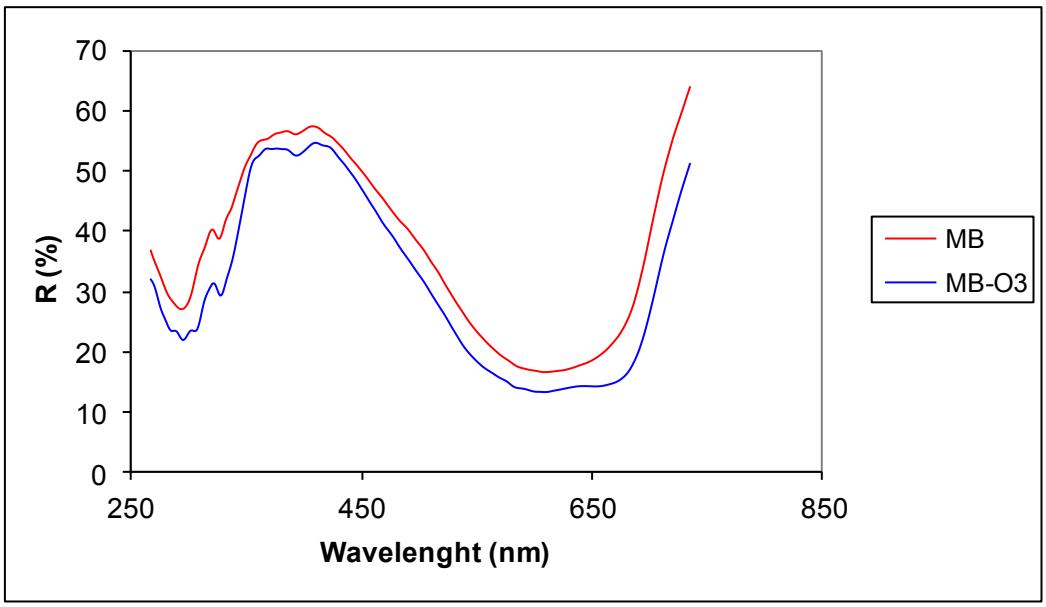


Fig. 43 **Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Blue 6**

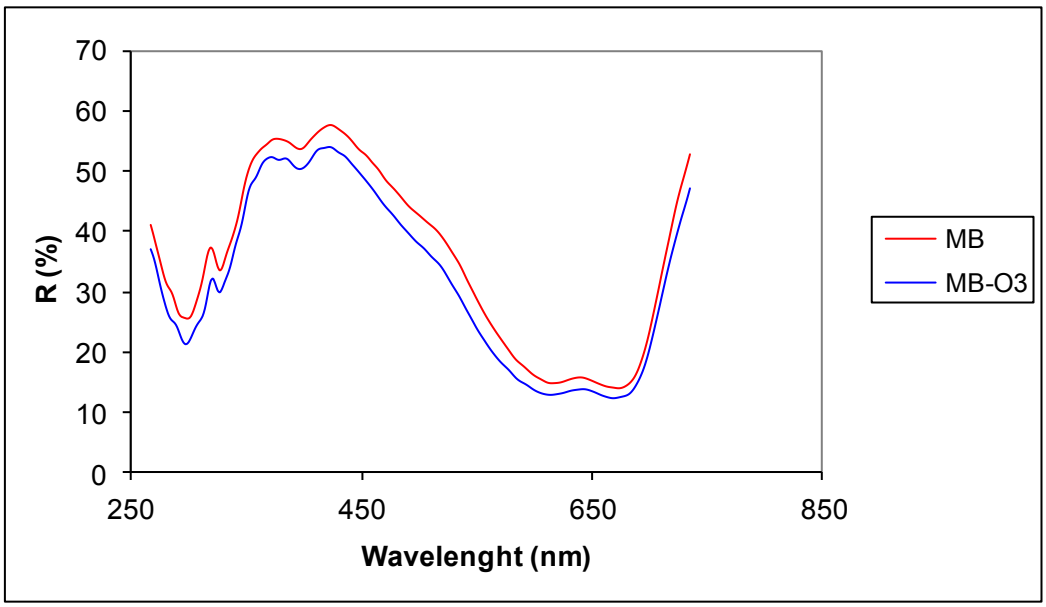


Fig. 44 **Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Blue 6**

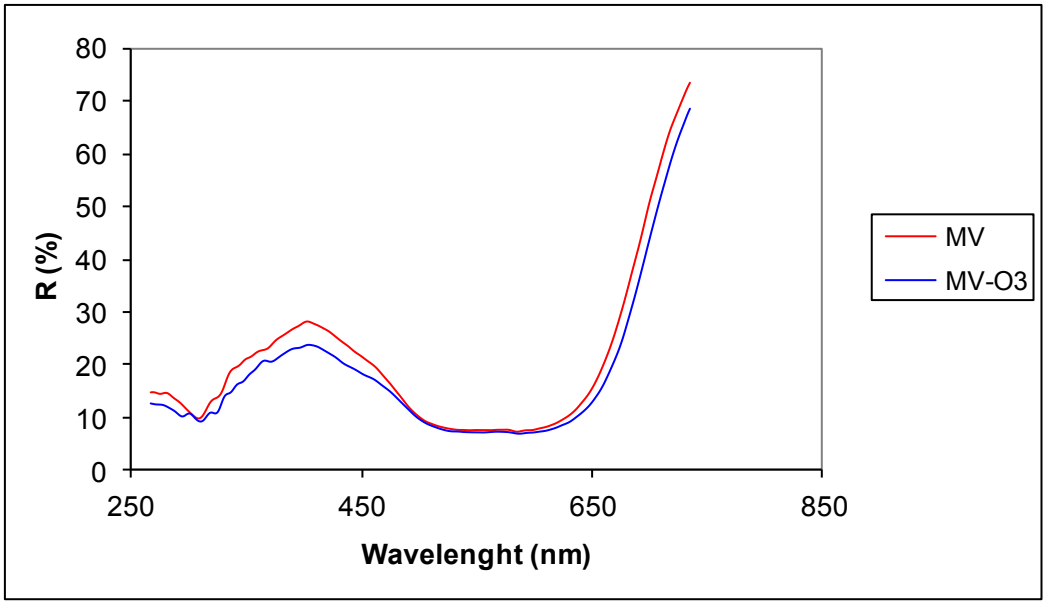


Fig. 45 **Effect of ozonization on the UV/VIS reflectance spectra of the dye Basic Violet 1**

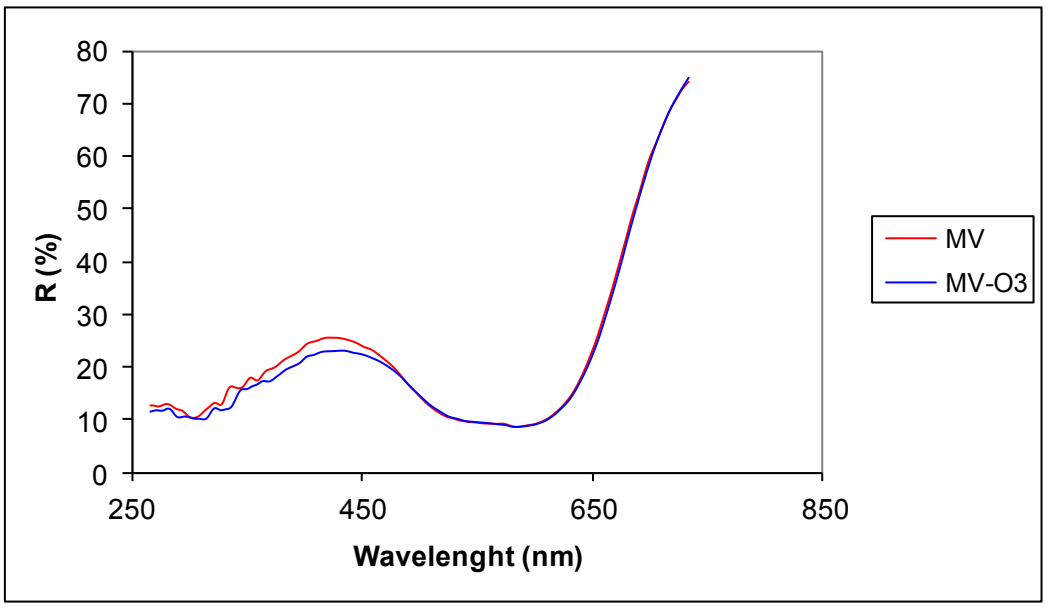


Fig. 46 **Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Violet 1**

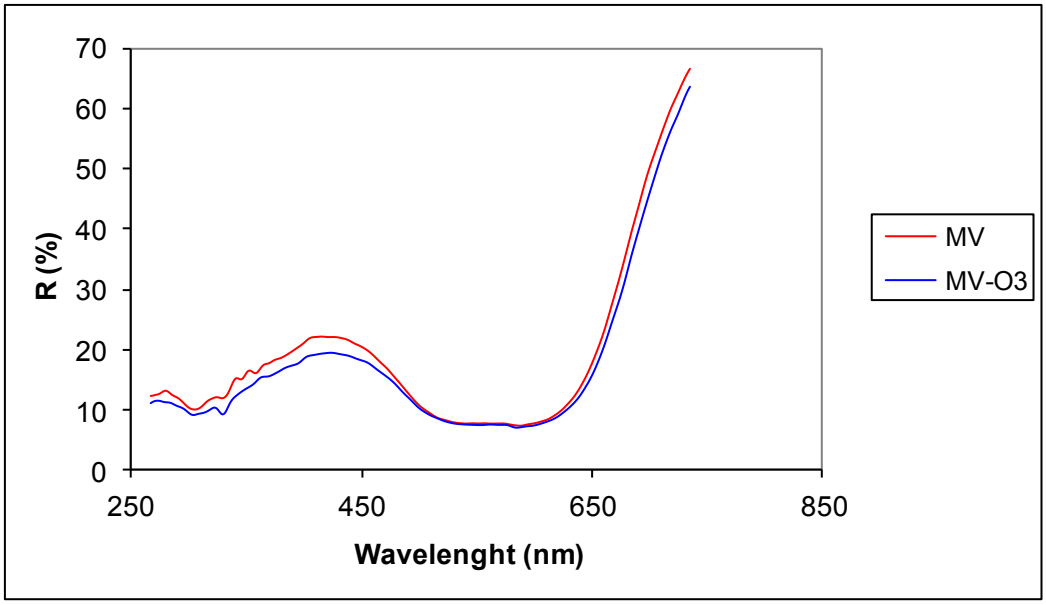


Fig. 47 **Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Basic Violet 1**

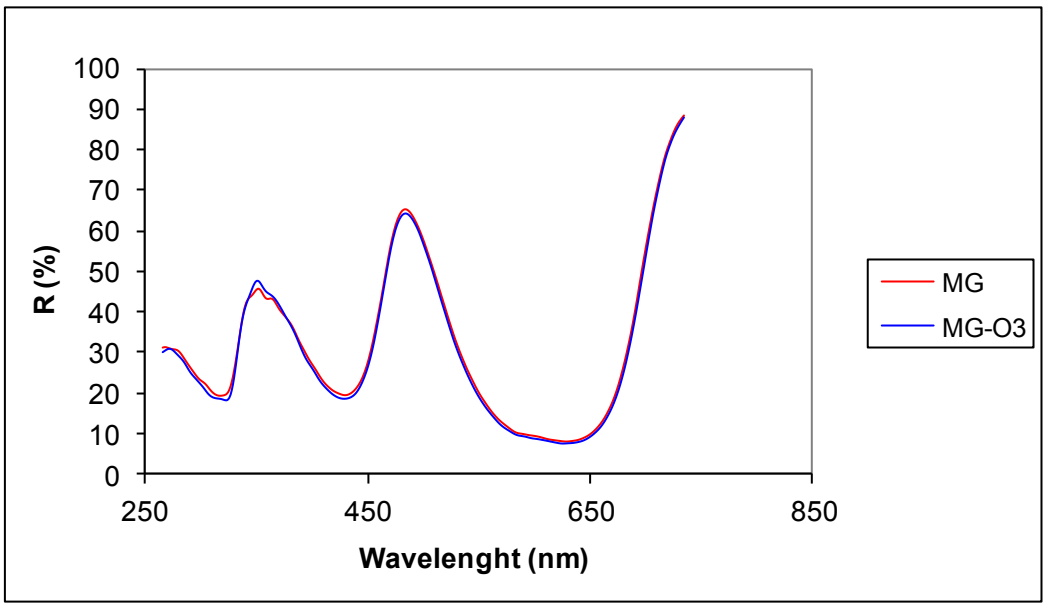


Fig. 48 **Effect of ozonization on the UV/VIS reflectance spectra of the dye Malachite Green**

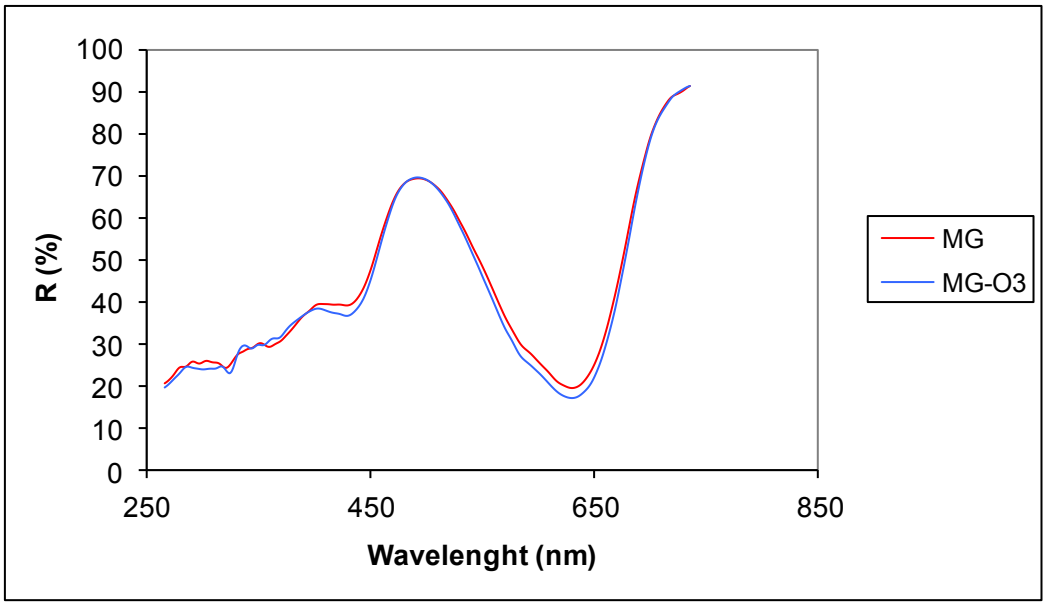


Fig. 49 **Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Malachite Green**

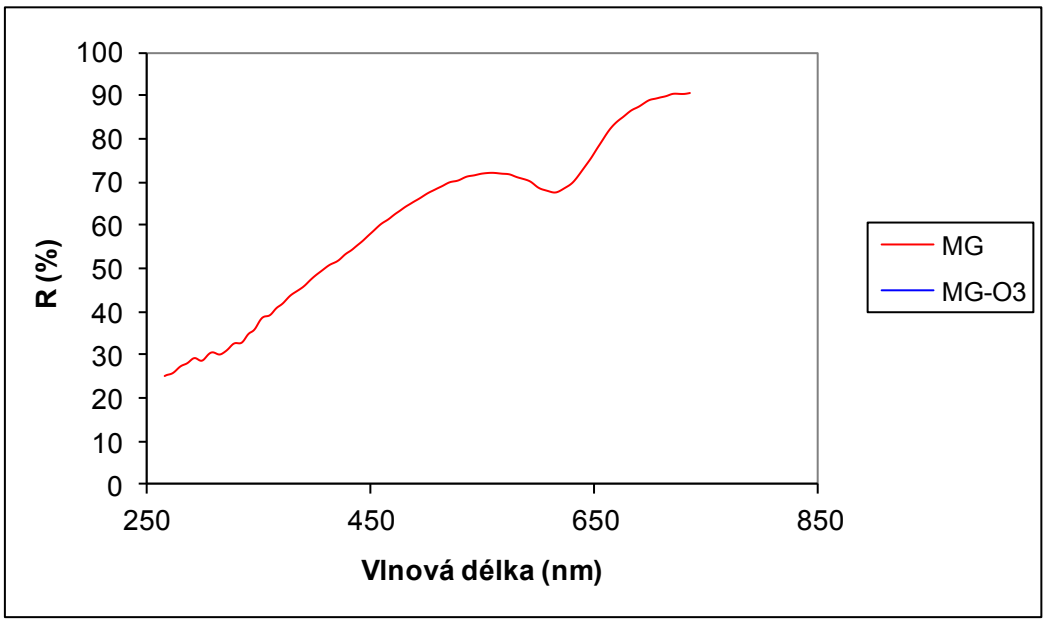


Fig. 50 **Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Malachite Green**

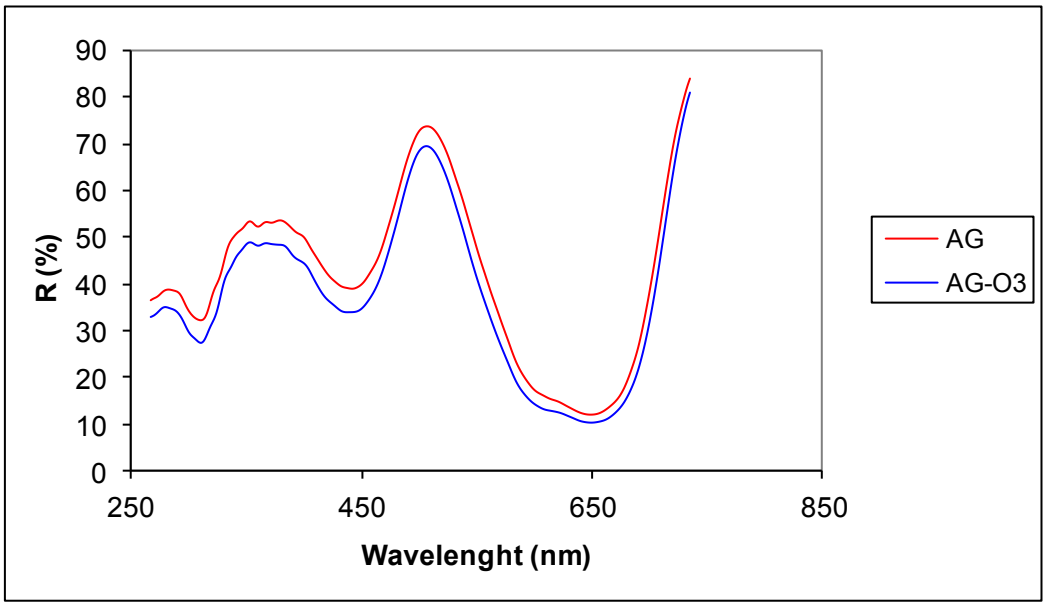


Fig. 51 **Effect of ozonization on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16**

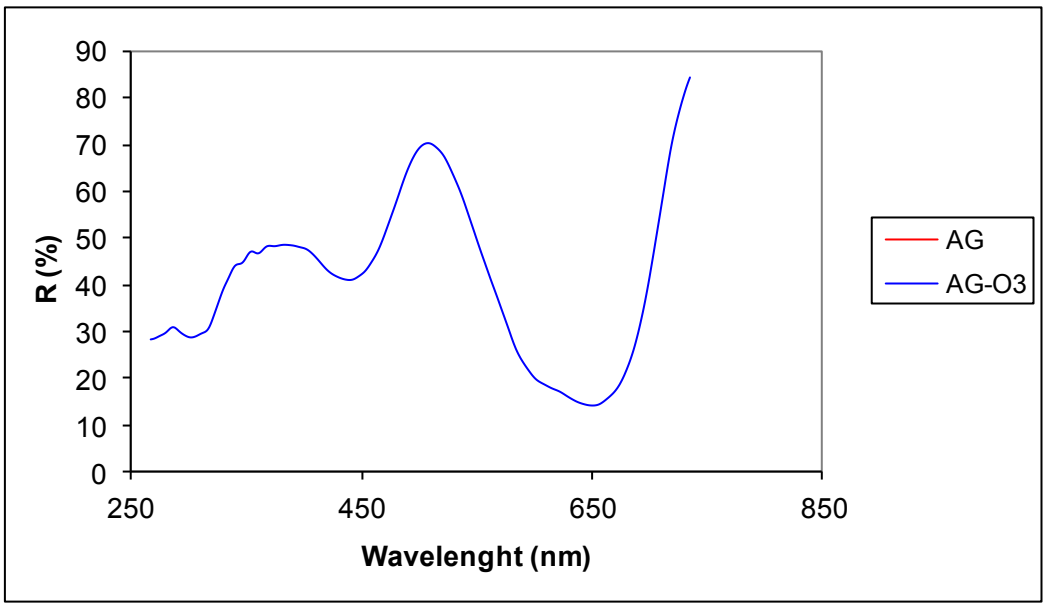


Fig. 52 **Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16**

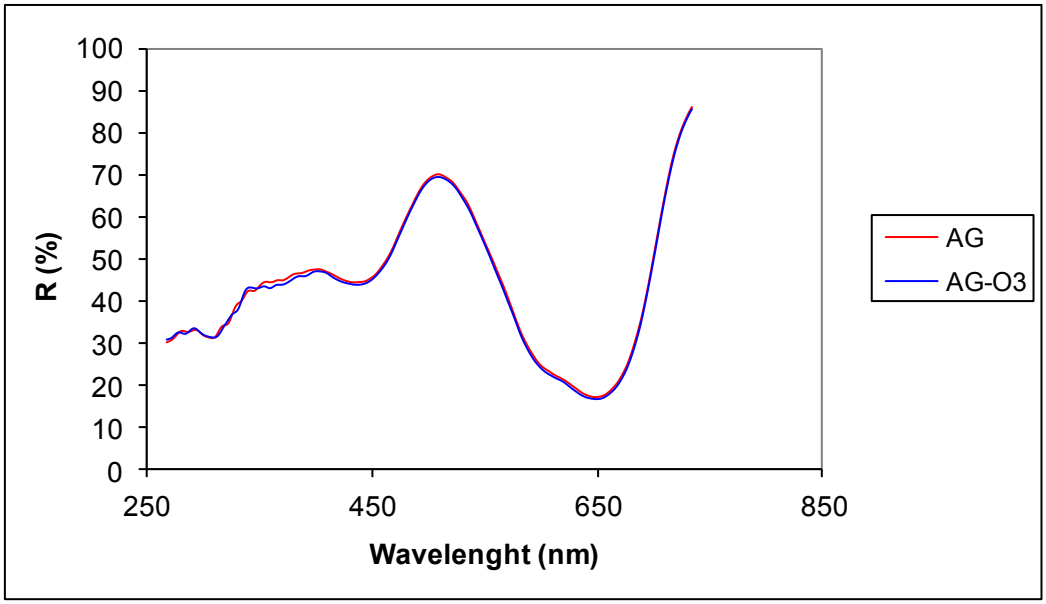


Fig. 53 **Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Green 16**

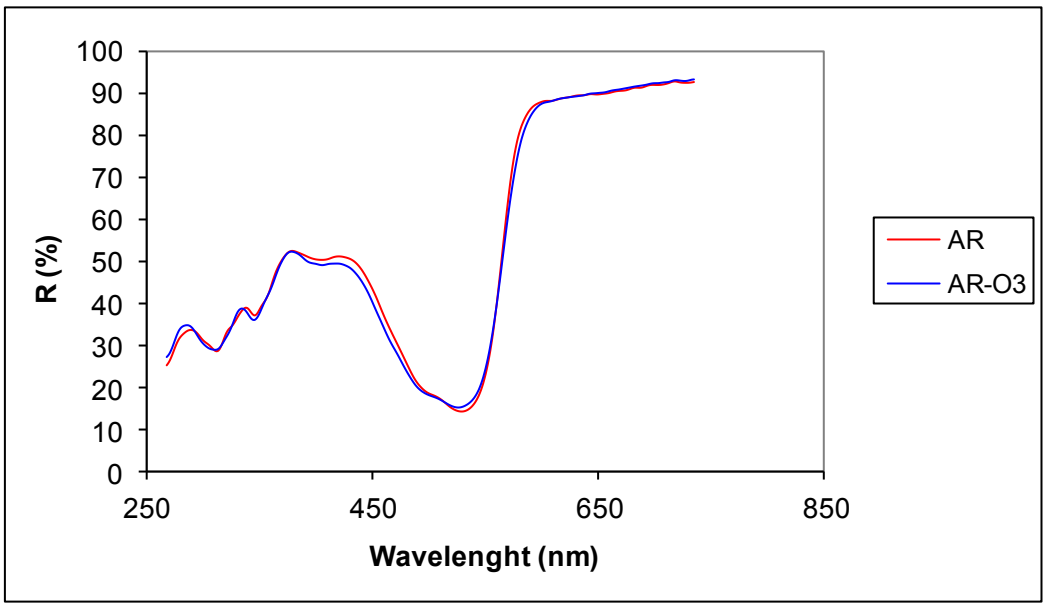


Fig. 54 **Effect of ozonization on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87**

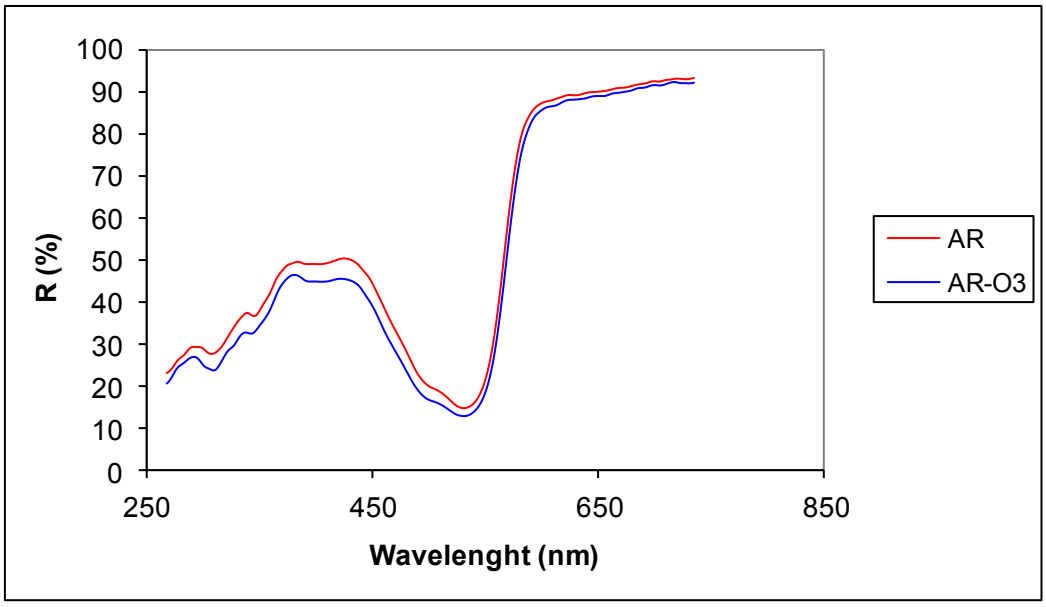


Fig. 55 **Effect of ozonization and artificial ageing by dry heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87**

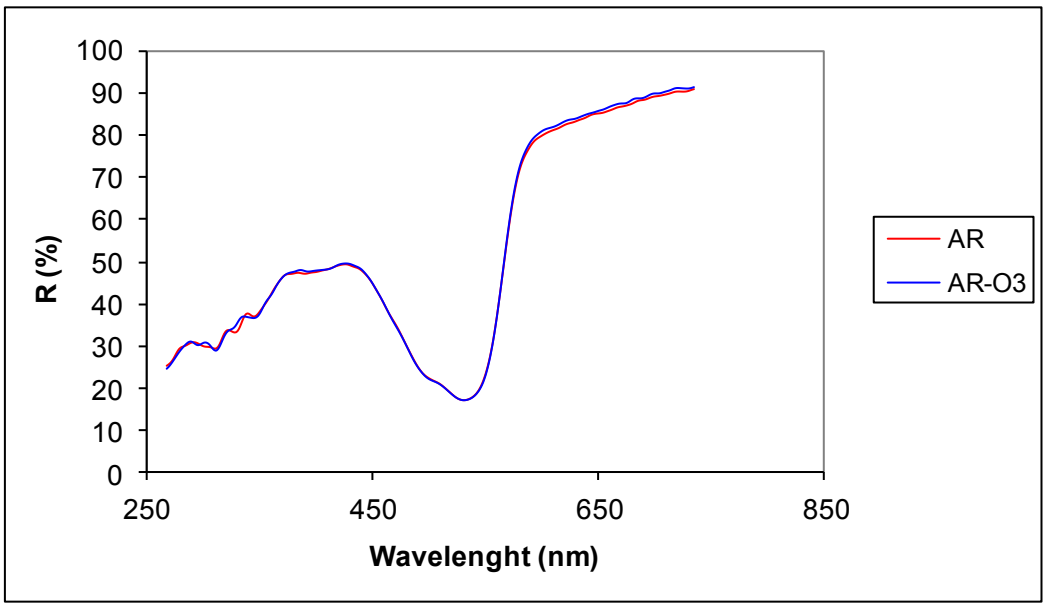


Fig. 56 **Effect of ozonization and artificial ageing by moist heat on the UV/VIS reflectance spectra of the aryl methane dye Acid Red 87**

*3.6.2 Total colour difference ΔE**

It follows from the data on the total colour difference ΔE* of aryl 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 ΔE* of the individual kinds of aryl methane dyes.**

Paper sample	ΔE*
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

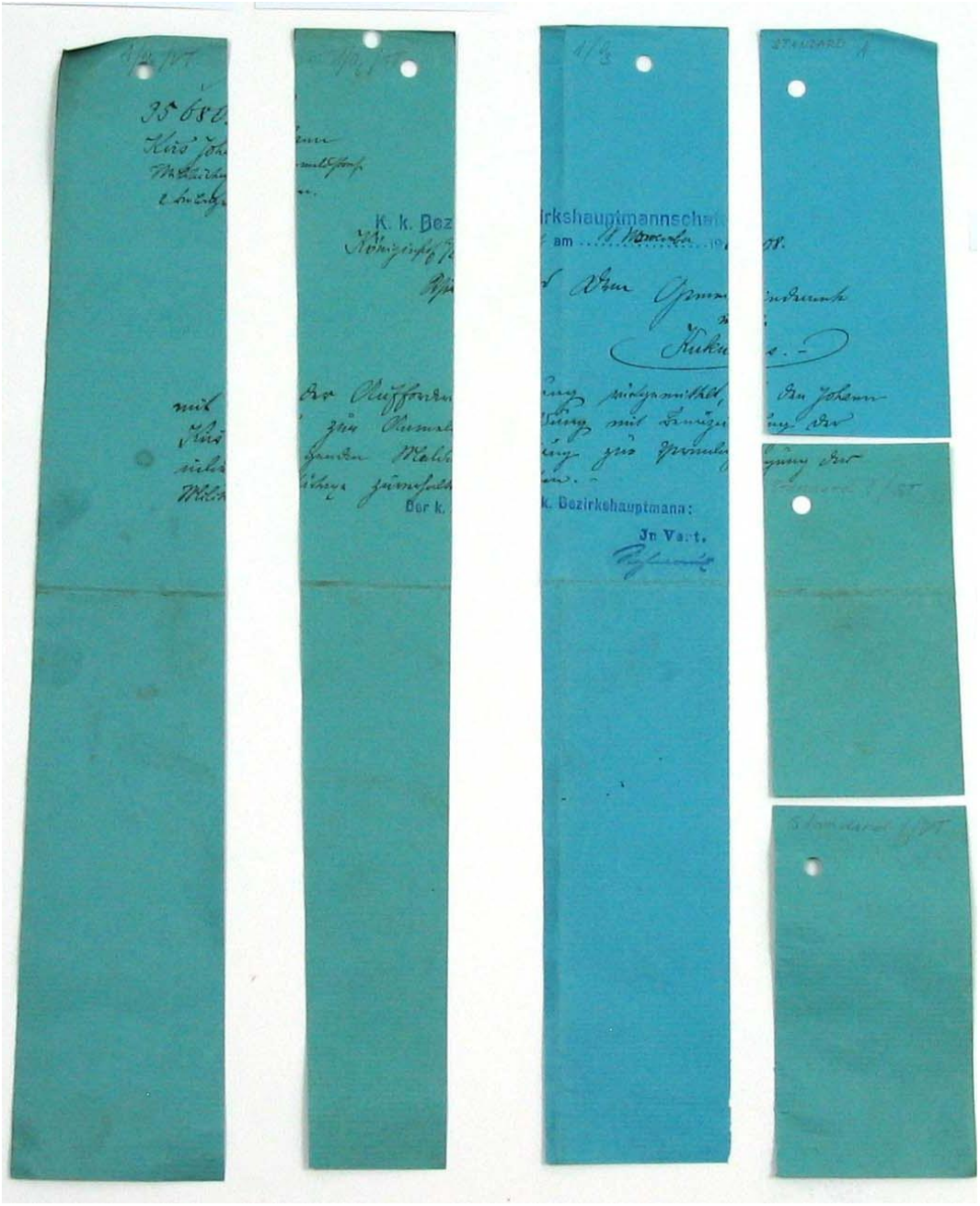
3.7 Visual evaluation of changes in the colours of archive documents

3.7.1 Visual evaluation of changes in the colours of archive documents

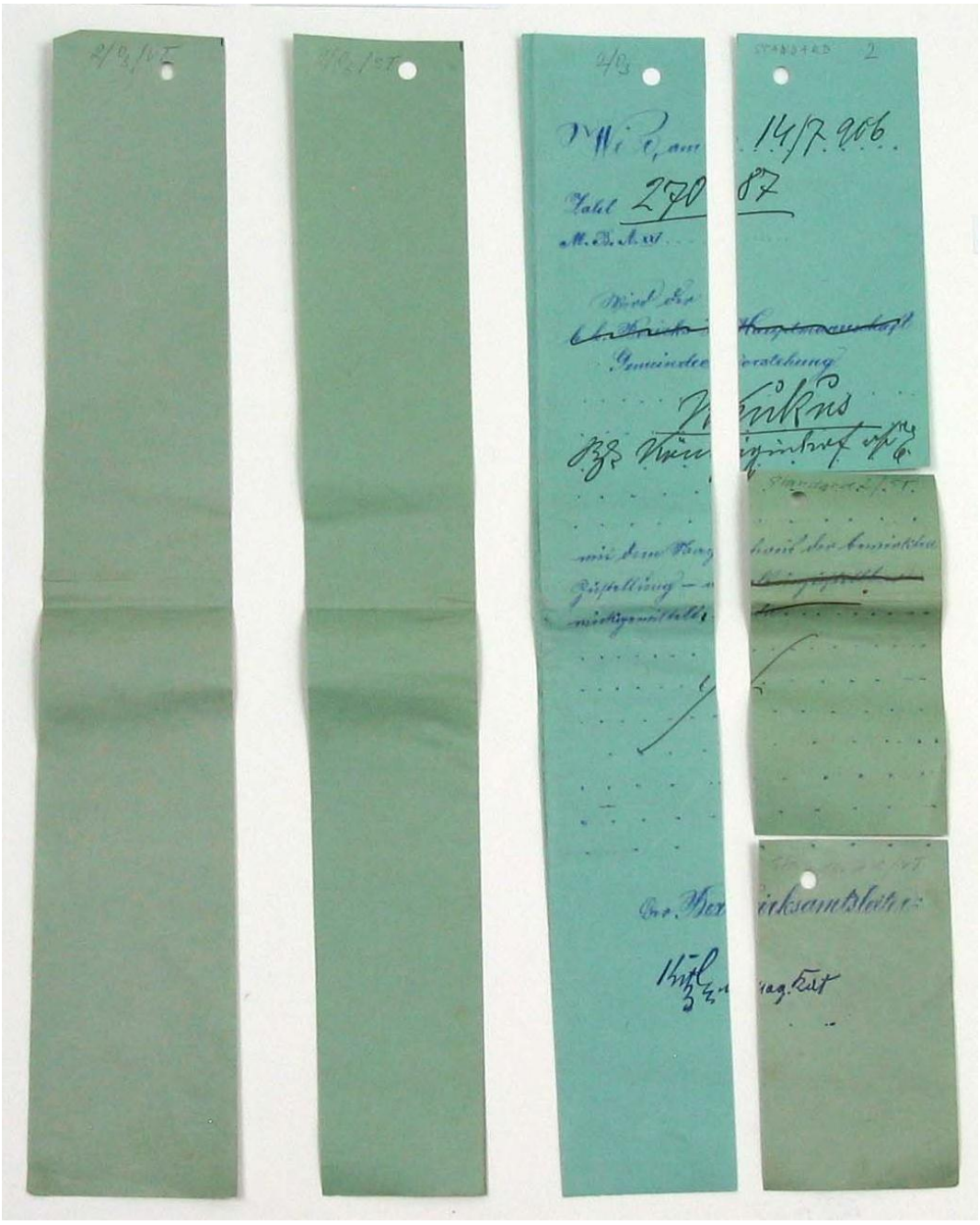
Visual comparison of the effect of ozonization and artificial ageing on archive documents from the 19th and 20th centuries was performed by ordering these documents according to the following scheme and were then photographed (*samples No. 1 to 14)*:

<table>
<tr><td rowspan="3">1
ozonization, moist heat ageing</td><td rowspan="3">2
ozonization, dryheat ageing</td><td rowspan="3">3
ozonization, unaged</td><td>4
standard, unaged</td></tr>
<tr><td>5
standard, dry heat ageing</td></tr>
<tr><td>6
standard, moist heat ageing</td></tr>
</table>

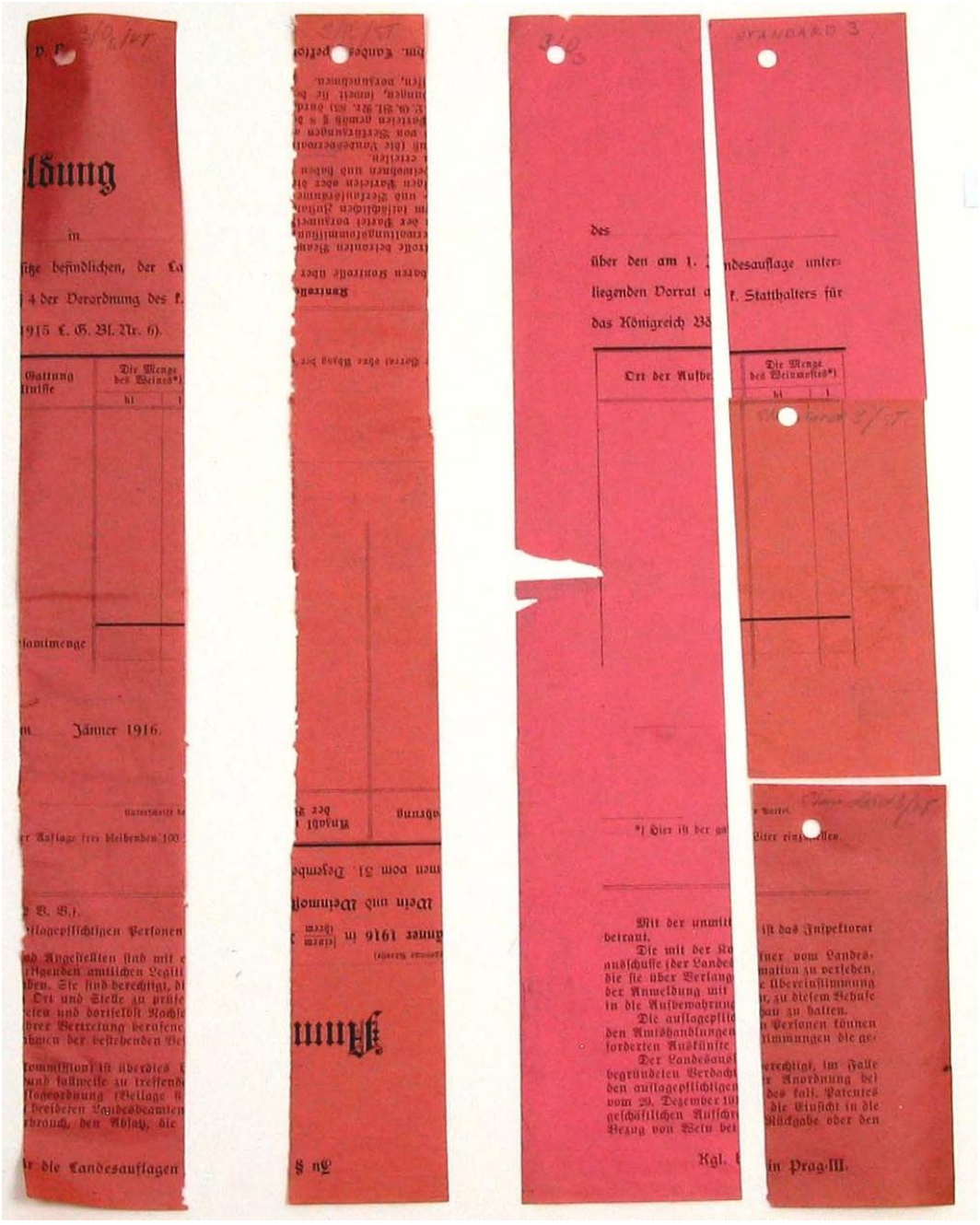
Sample No. 1



Sample No. 2



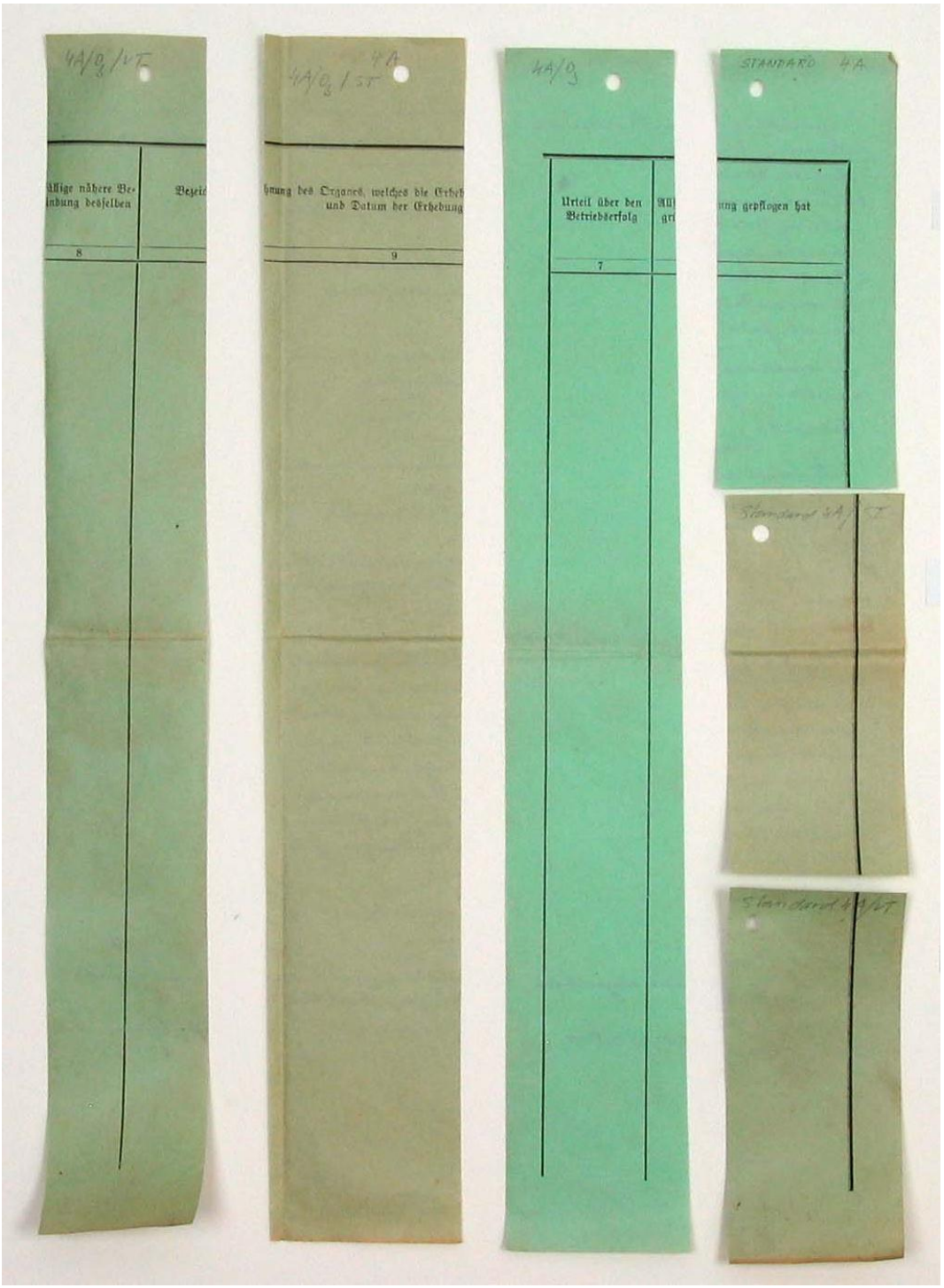
Sample No. 3


STANDARD 3
Jänner 1916.
Ort der Aufbe
Die Menge des Weinmostes*)
*) Hier ist der ga
Mit der unmitt
betraut.
Die mit der Ko
ausschusse (der Landes
die sie über Verlang
der Anmeldung mit
in die Aufbewahrun
Die auflagepflic
den Amtshandlungen
forderten Auskünfte
Der Landesaus
begründeten Verdach
den auflagepflichtigen
vom 29. Dezember 19
geschäftlichen Aufschr
Bezug von Wein bei
Kgl.
in Prag-III.

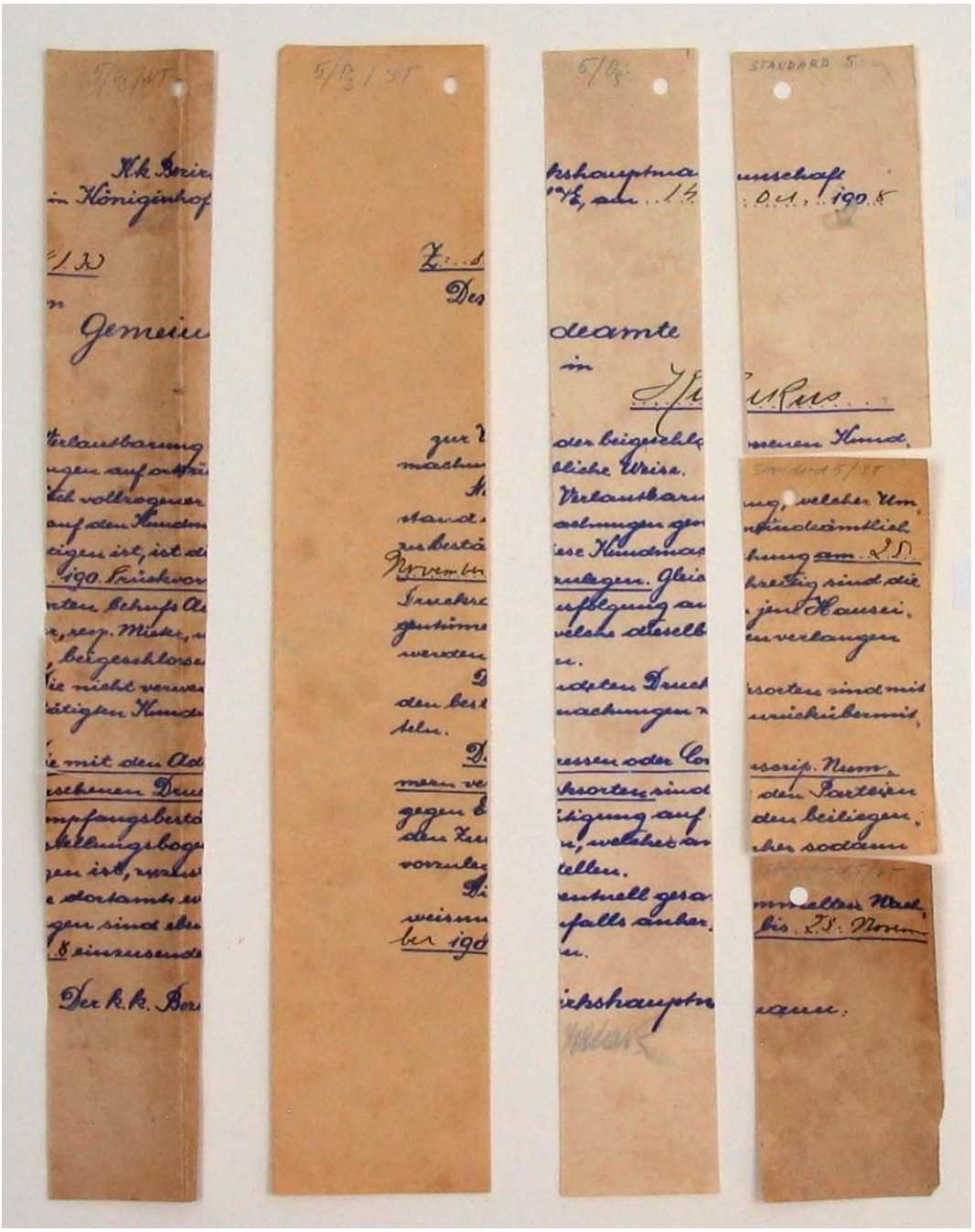
Sample No. 4


Königreich Böhmen.
Steuerbehörde:
Steueramtsbezirk:
Steuergemeinde:
Kleinkorn pt

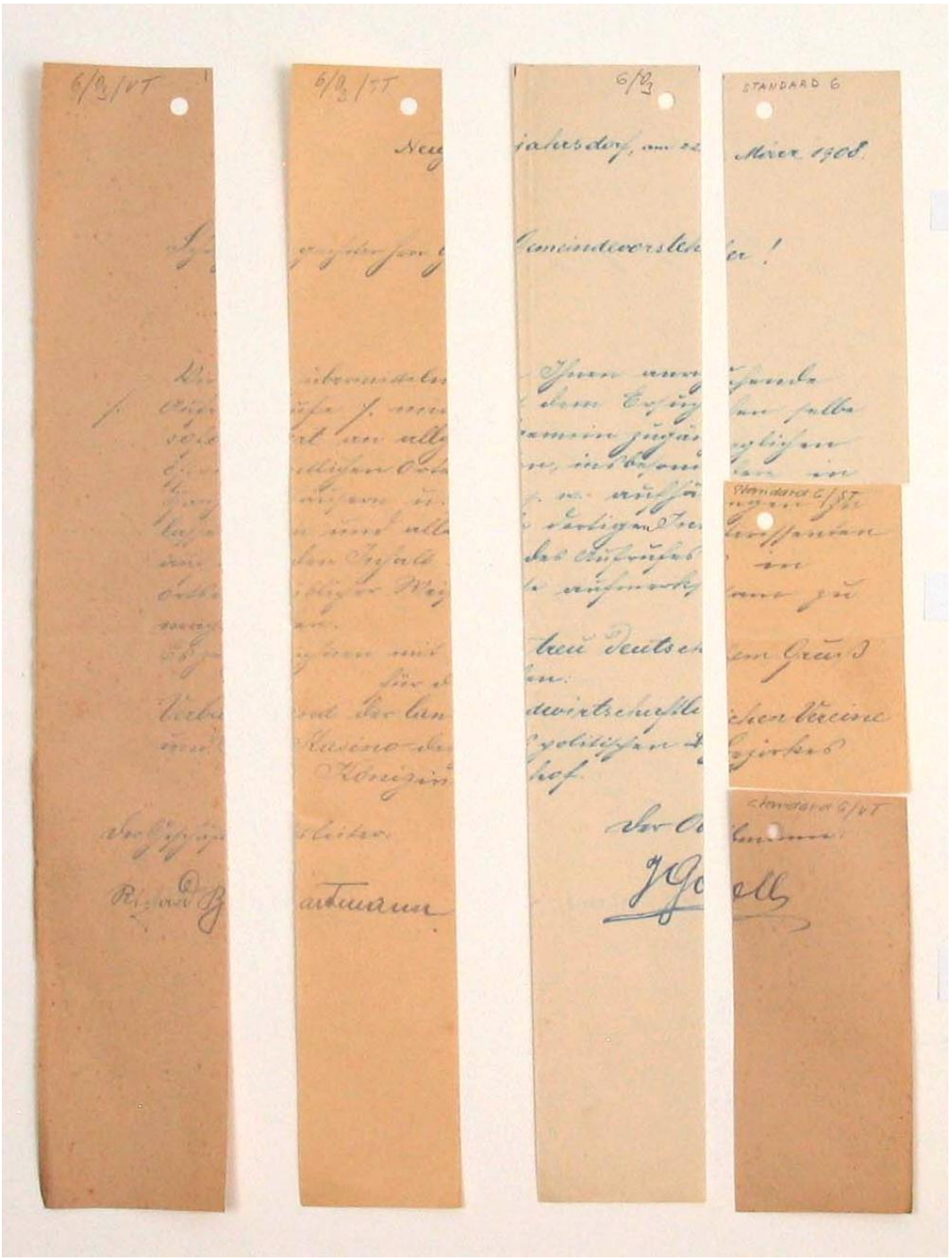
Sample No. 4a


4A/S/VT
4A/S/ST
4A
4A/S
Urteil über den Betriebserfolg
7
8
9
STANDARD 4A
Standard 4A/VT
Standard 4A/ST

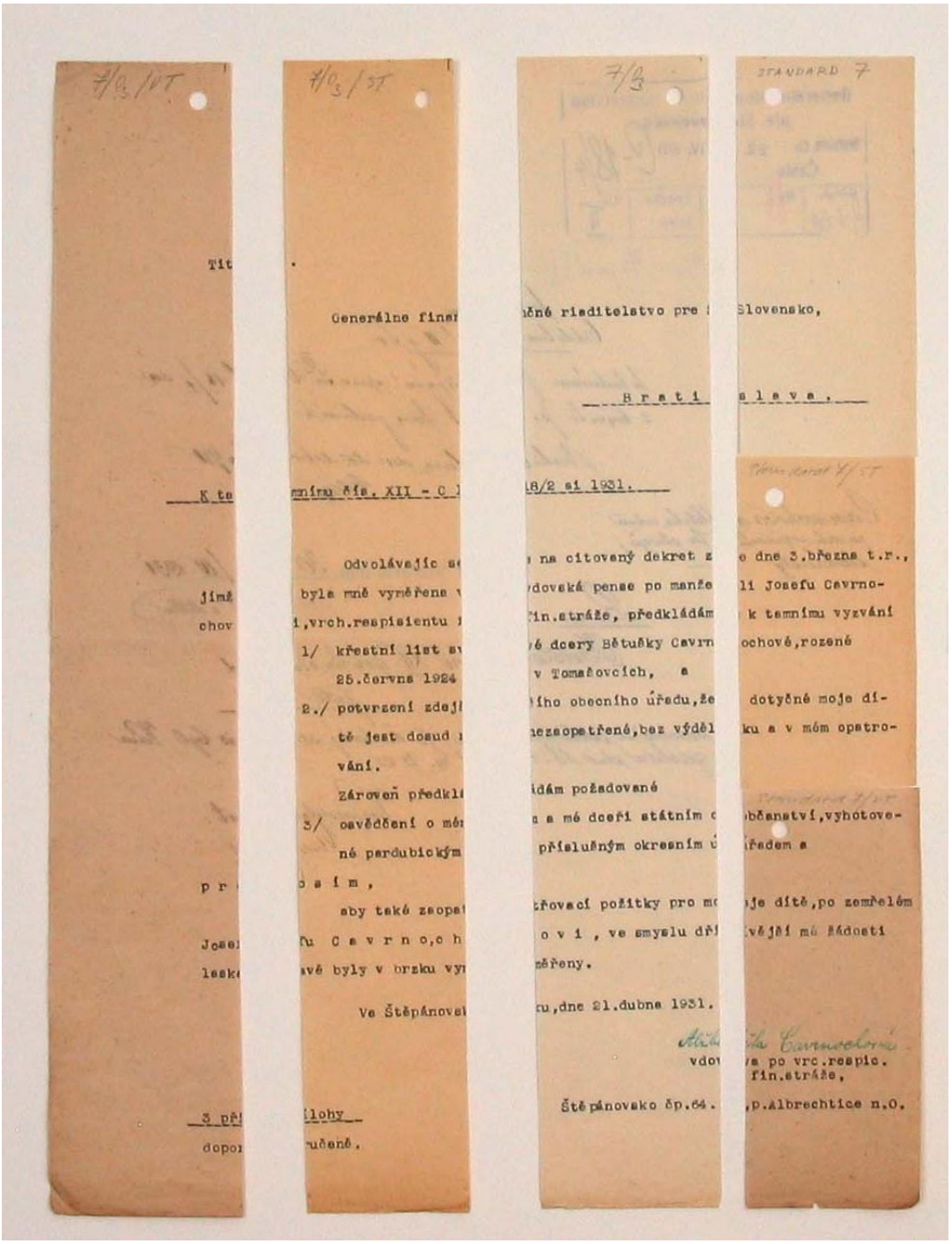
Sample No. 5



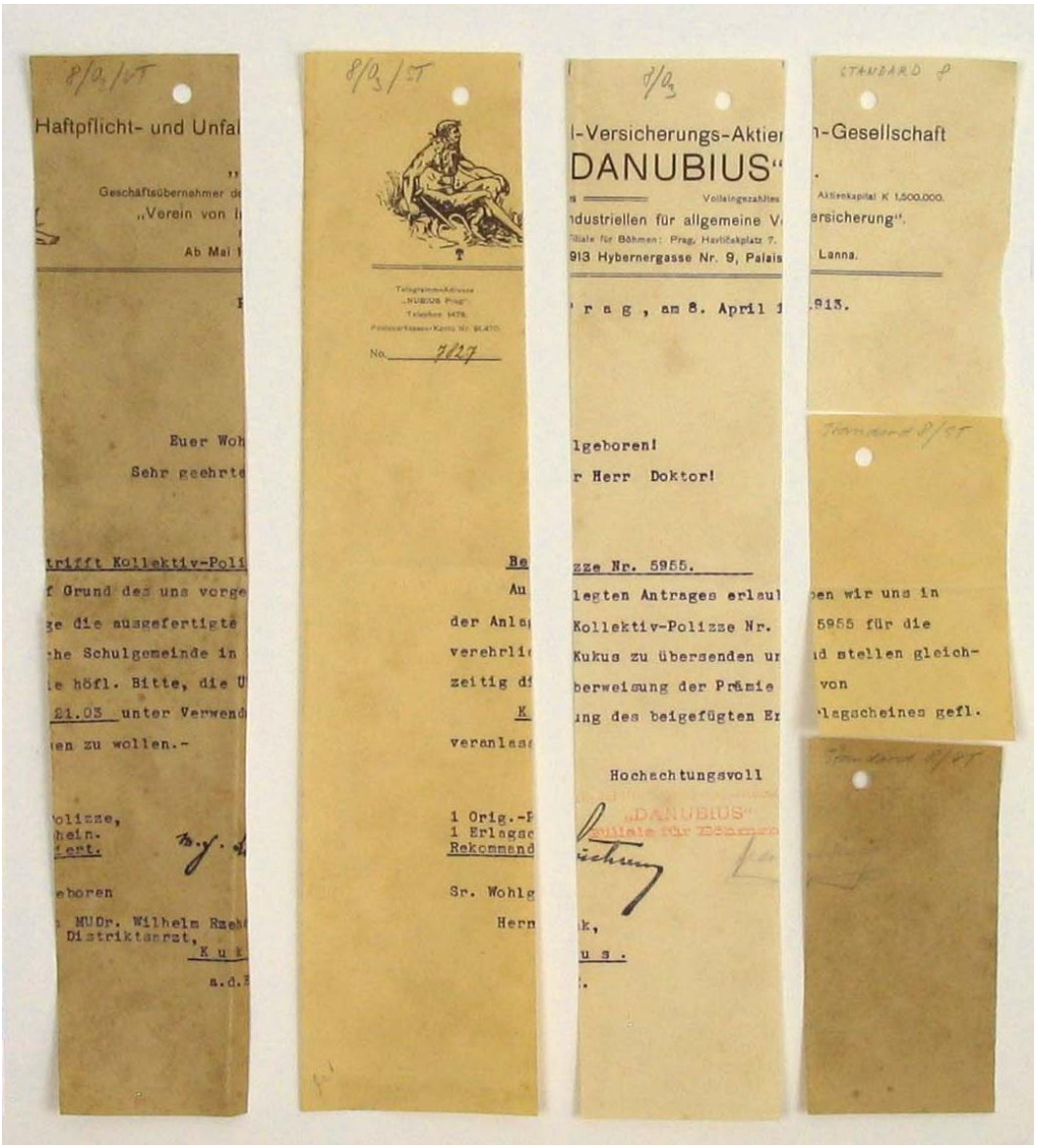
Sample No. 6



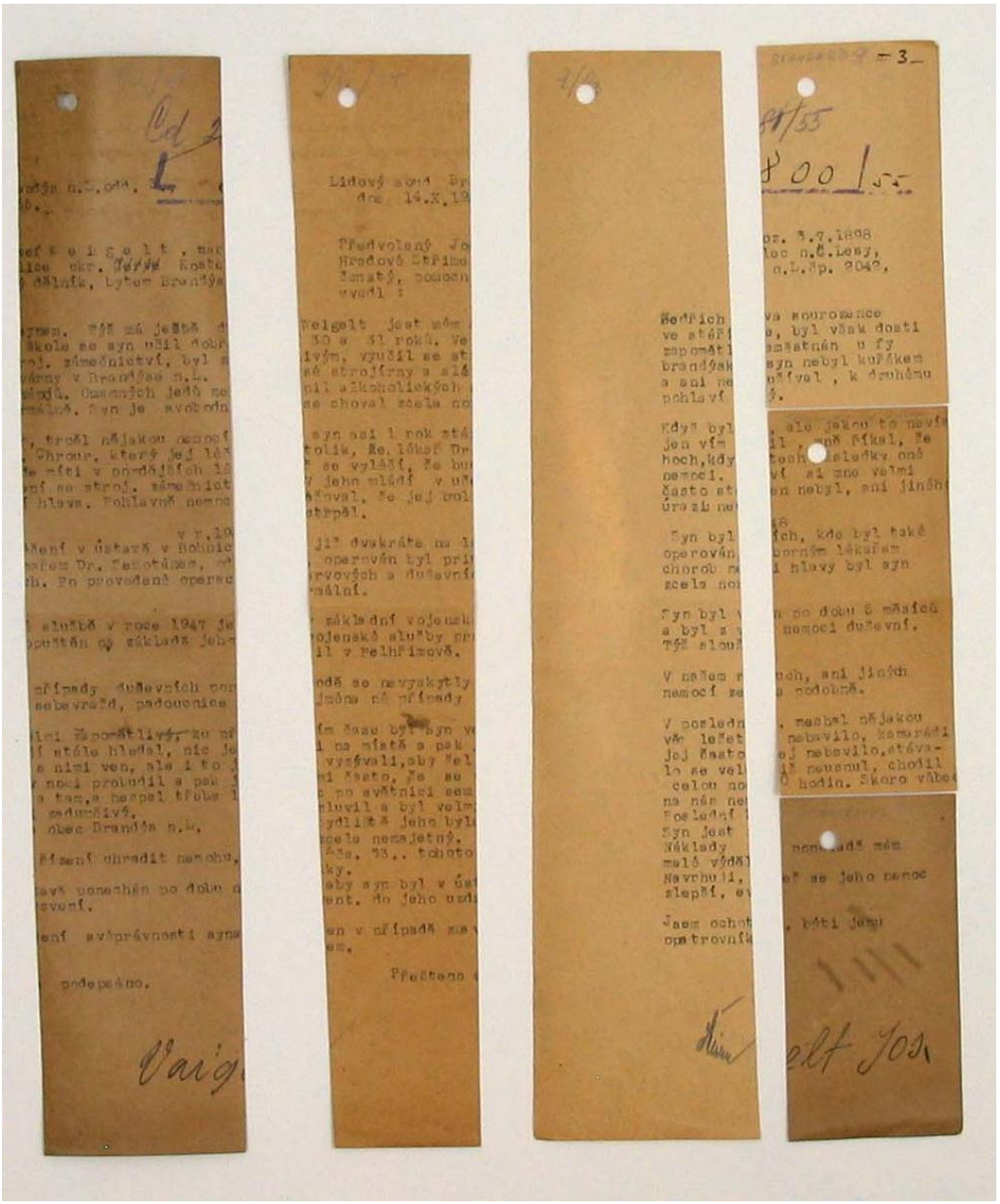
Sample No. 7



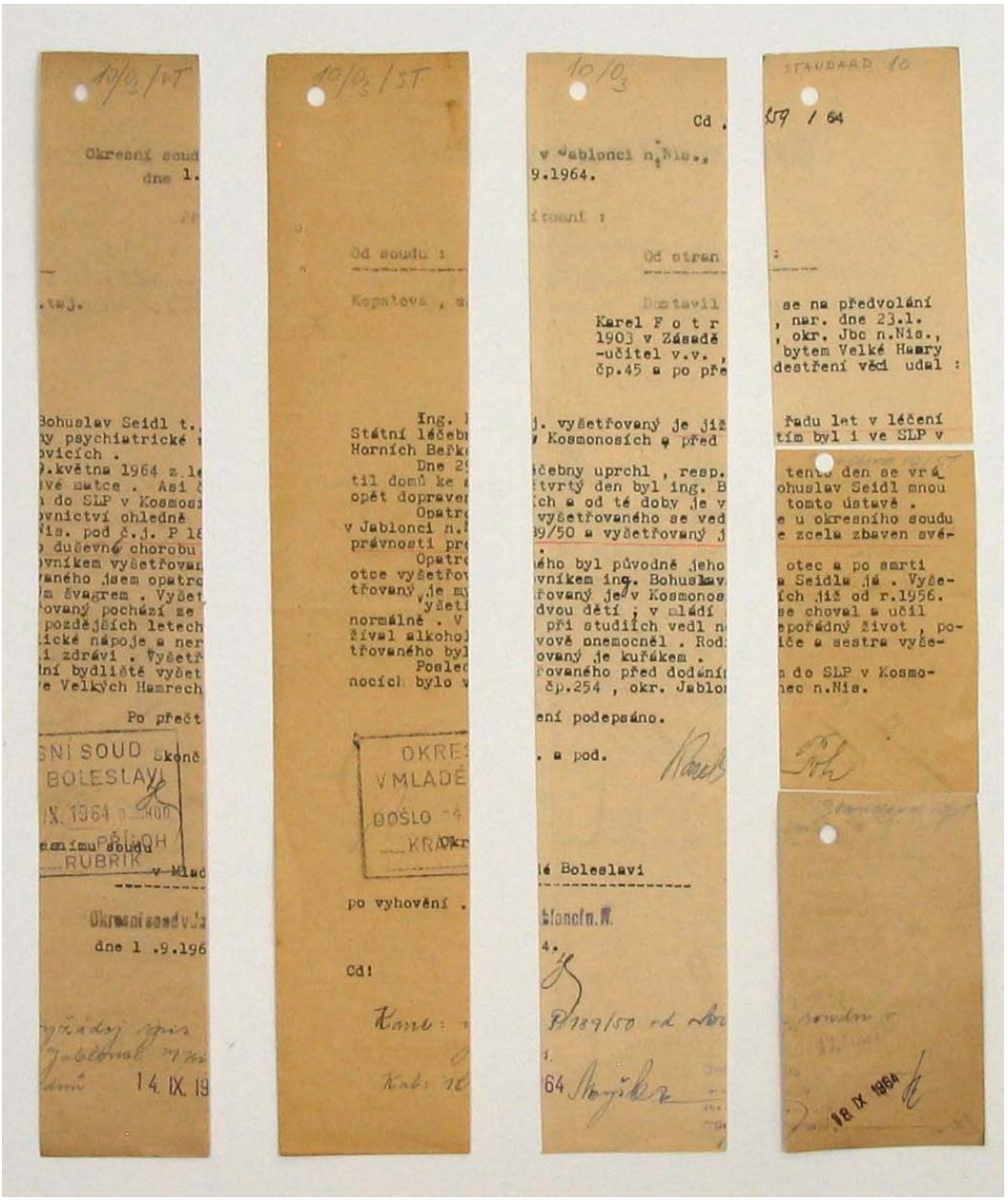
Sample No. 8


Haftpflicht- und Unfal
„Verein von
Ab Mai
Euer Woh
Sehr geehrte
trifft Kollektiv-Poli
f Grund des uns vorge
ge die ausgefertigte
he Schulgemeinde in
e höfl. Bitte, die U
21.03 unter Verwend
en zu wollen.-
olizze,
hein.
ert.
eboren
MUDr. Wilhelm Rzeh
Distriktsarzt,
K u k
a.d.
No. 7627
Be
Au
der Anla
verehrli
zeitig di
K
veranlas
1 Orig.-P
1 Erlagsc
Rekommend
Sr. Wohlg
Herr
-Versicherungs-Aktie
DANUBIUS"
ndustriellen für allgemeine V
913 Hybernergasse Nr. 9, Palais
r a g , am 8. April
lgeboren!
r Herr Doktor!
zze Nr. 5955.
legten Antrages erlaub
Kollektiv-Polizze Nr.
Kukus zu übersenden ur
berweisung der Prämie
ing des beigefügten Er
Hochachtungsvoll
„DANUBIUS"
k,
u s .
n-Gesellschaft
ersicherung".
Lanna.
913.
ben wir uns in
5955 für die
id stellen gleich-
von
lagscheines gefl.

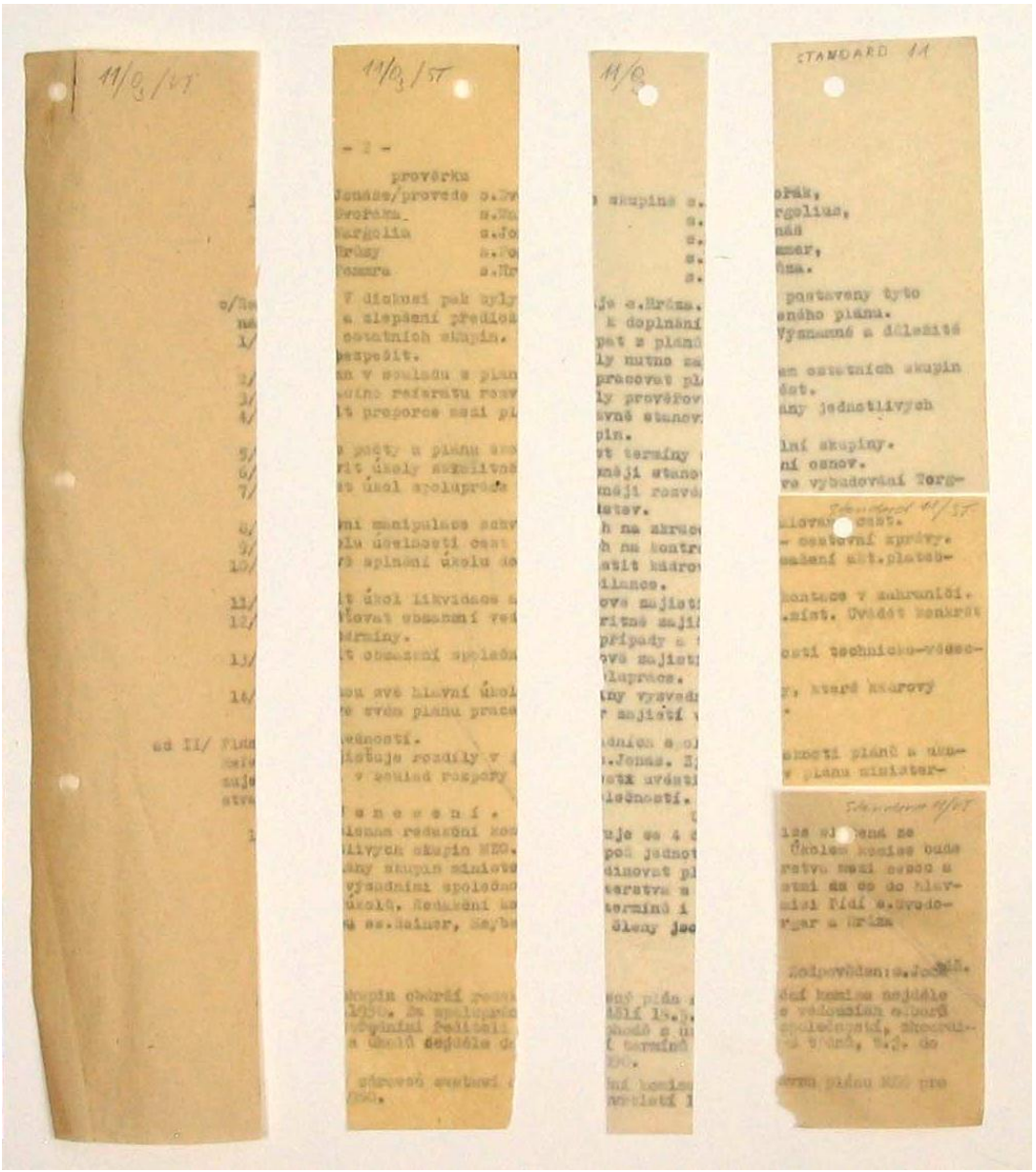
Sample No. 9



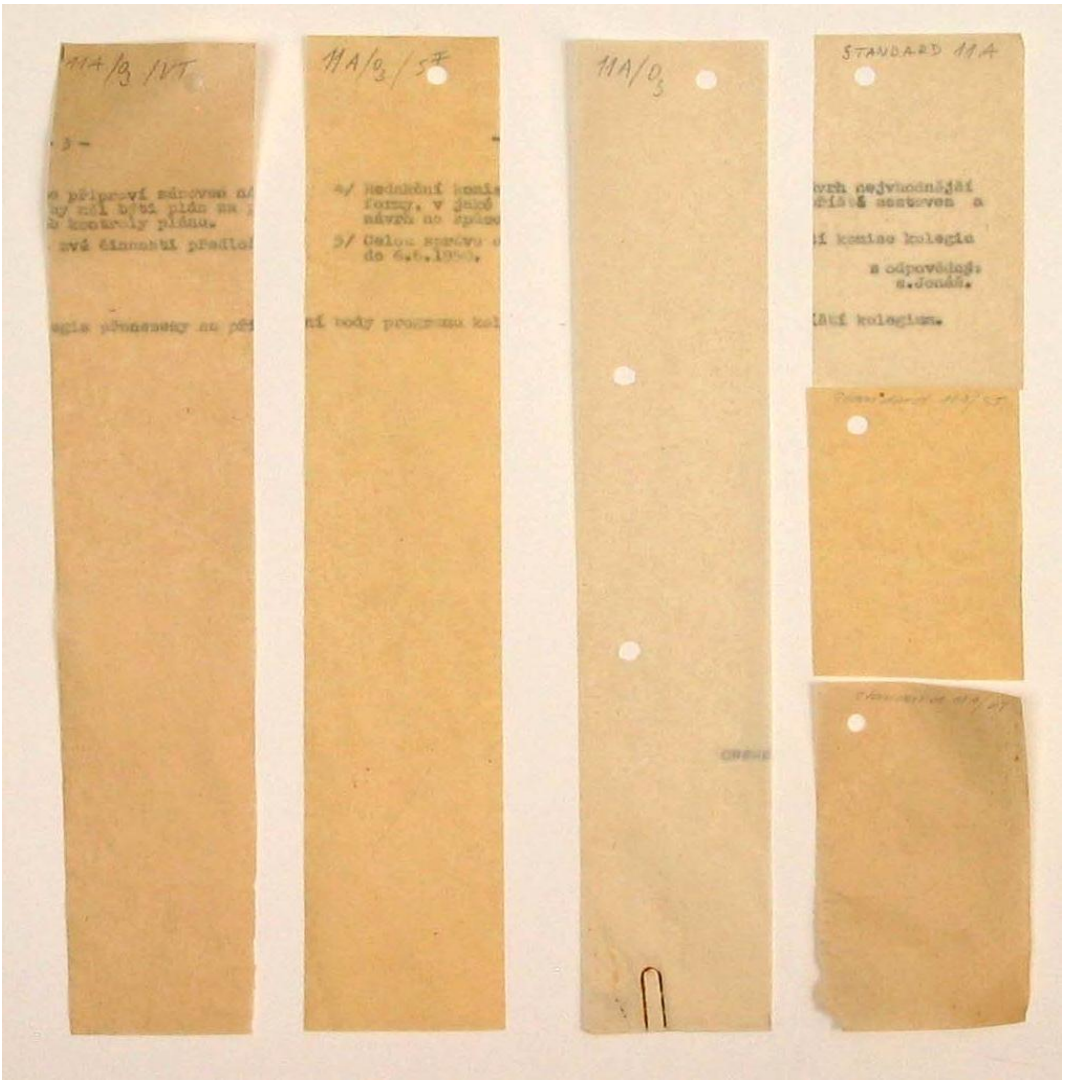
Sample No. 10



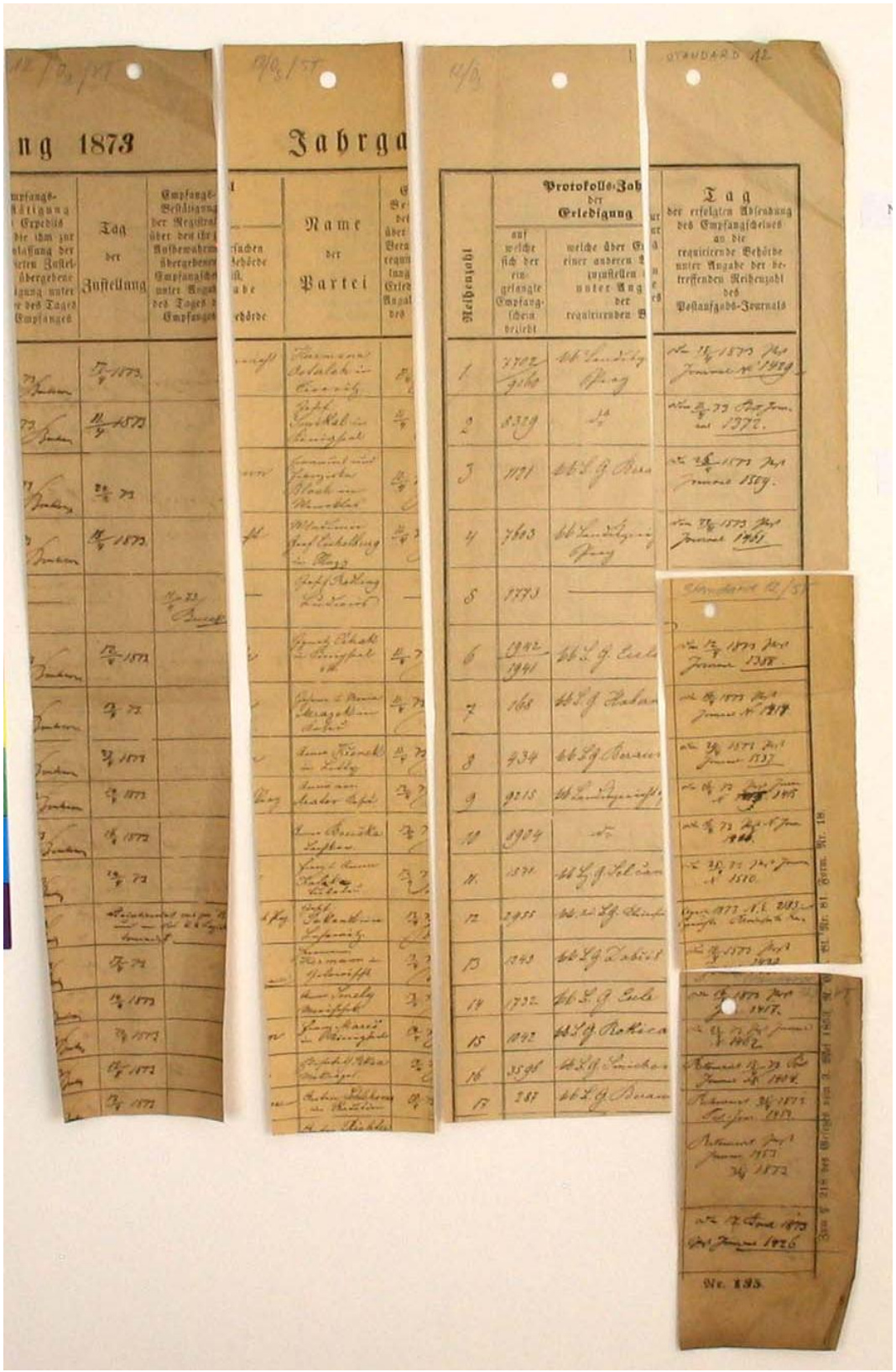
Sample No. 11



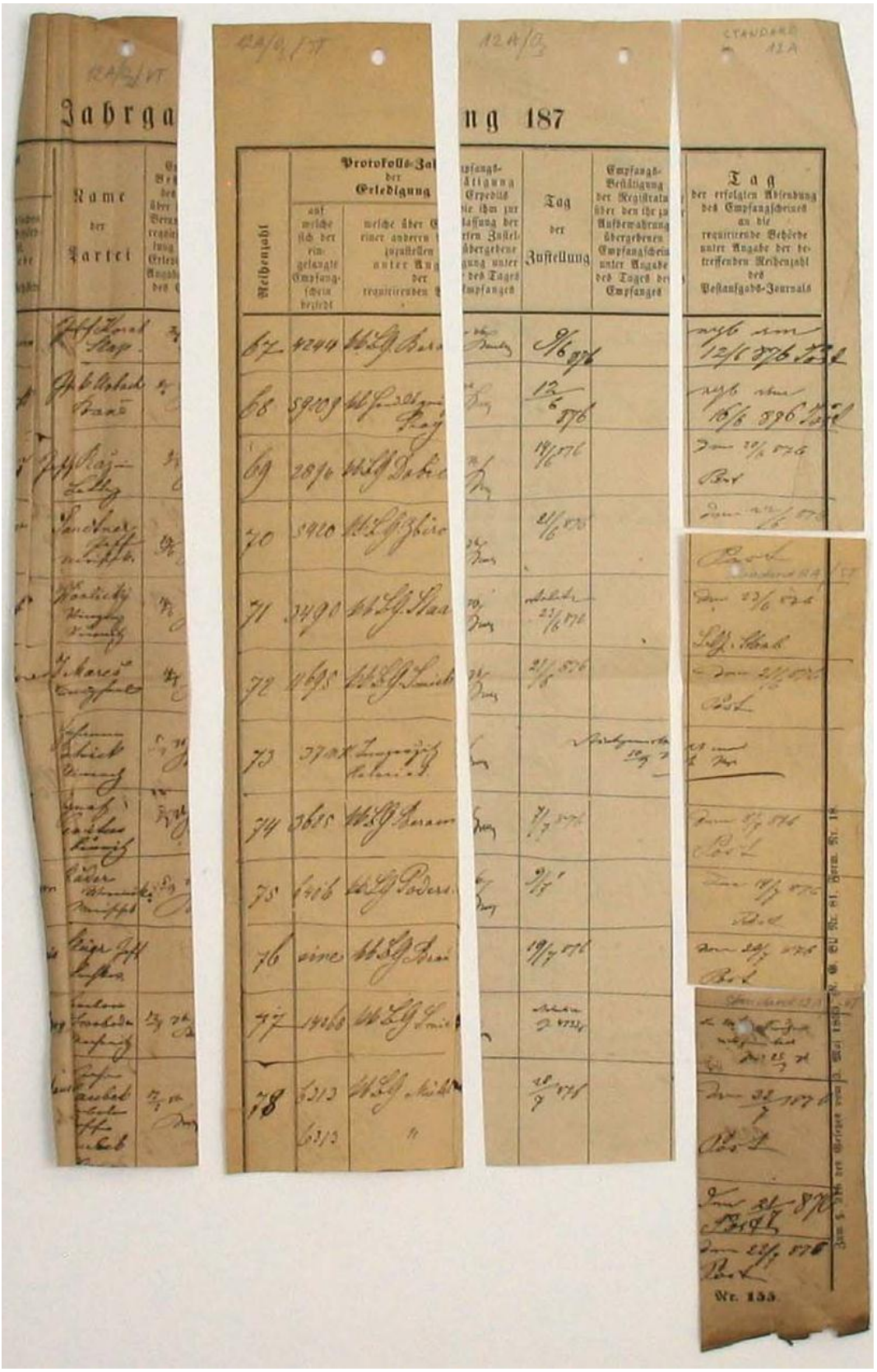
Sample No. 11



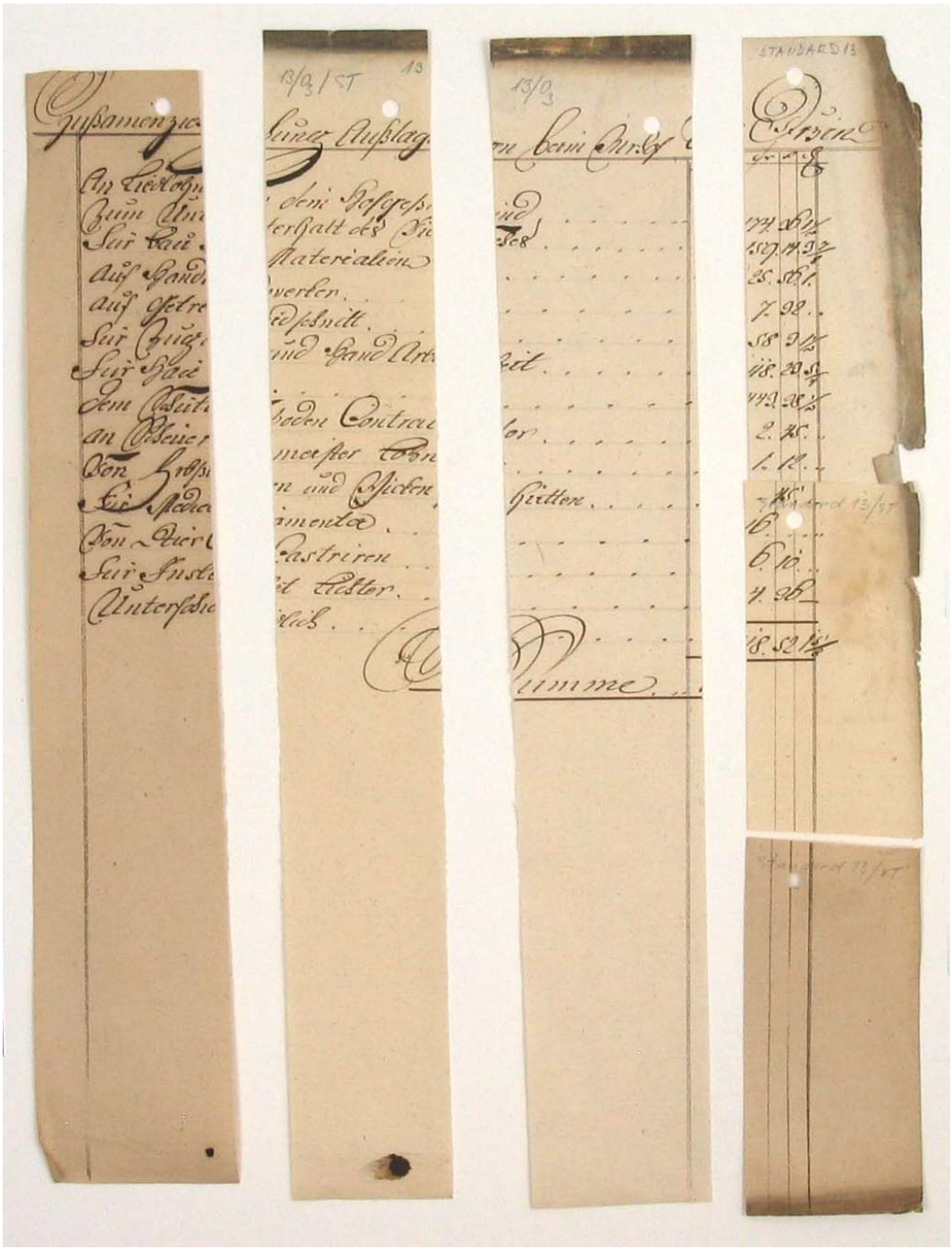
Sample No. 12


ung 1873
Jahrga
Name der Partei
Tag der Zustellung
Reihenzahl
Protokolle-Zah der Erledigung
Tag der erfolgten Absendung des Empfangscheines an die requirierende Behörde unter Angabe der betreffenden Reihenzahl des Postaufgabs-Journals
STANDARD 12

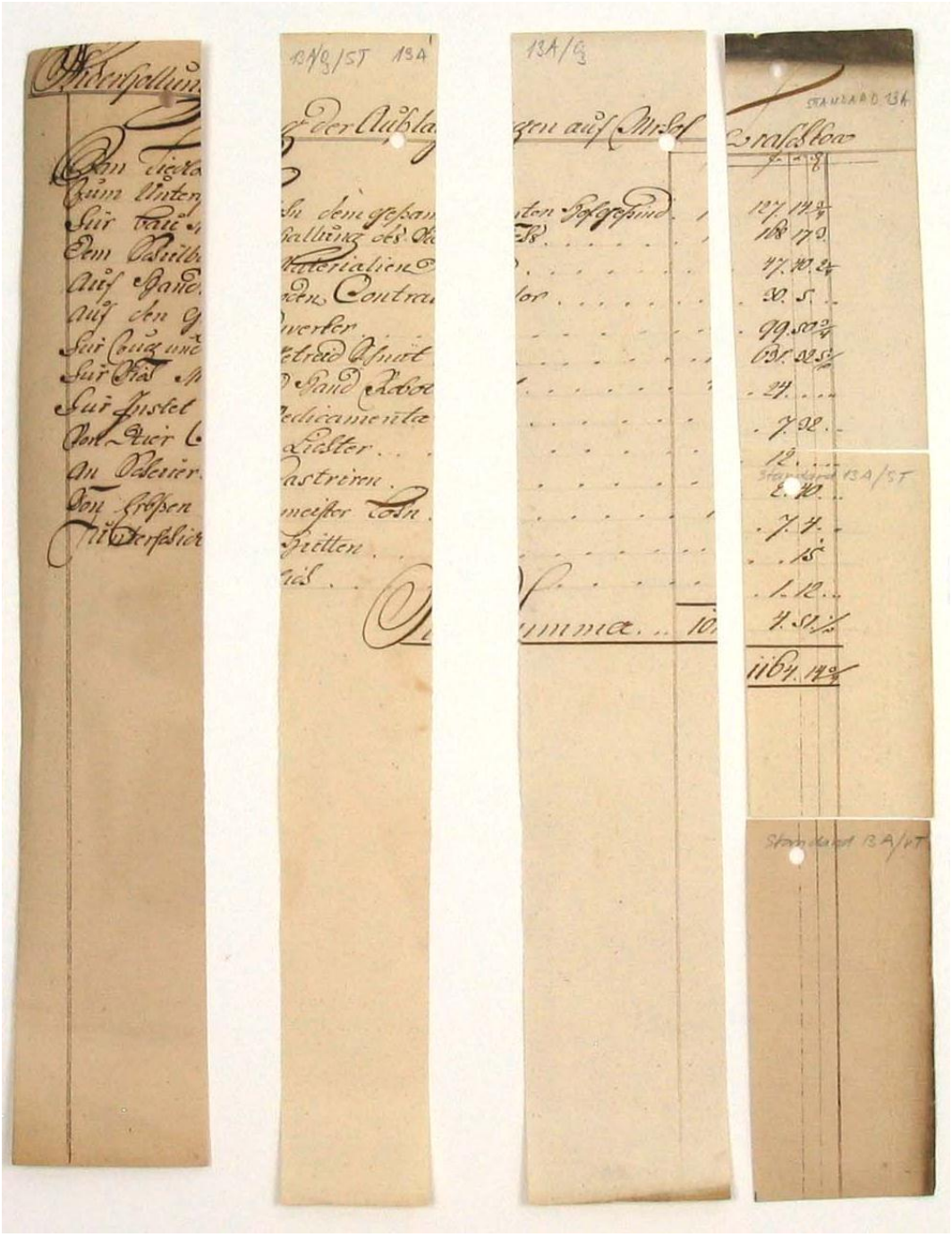
Sample No. 12a



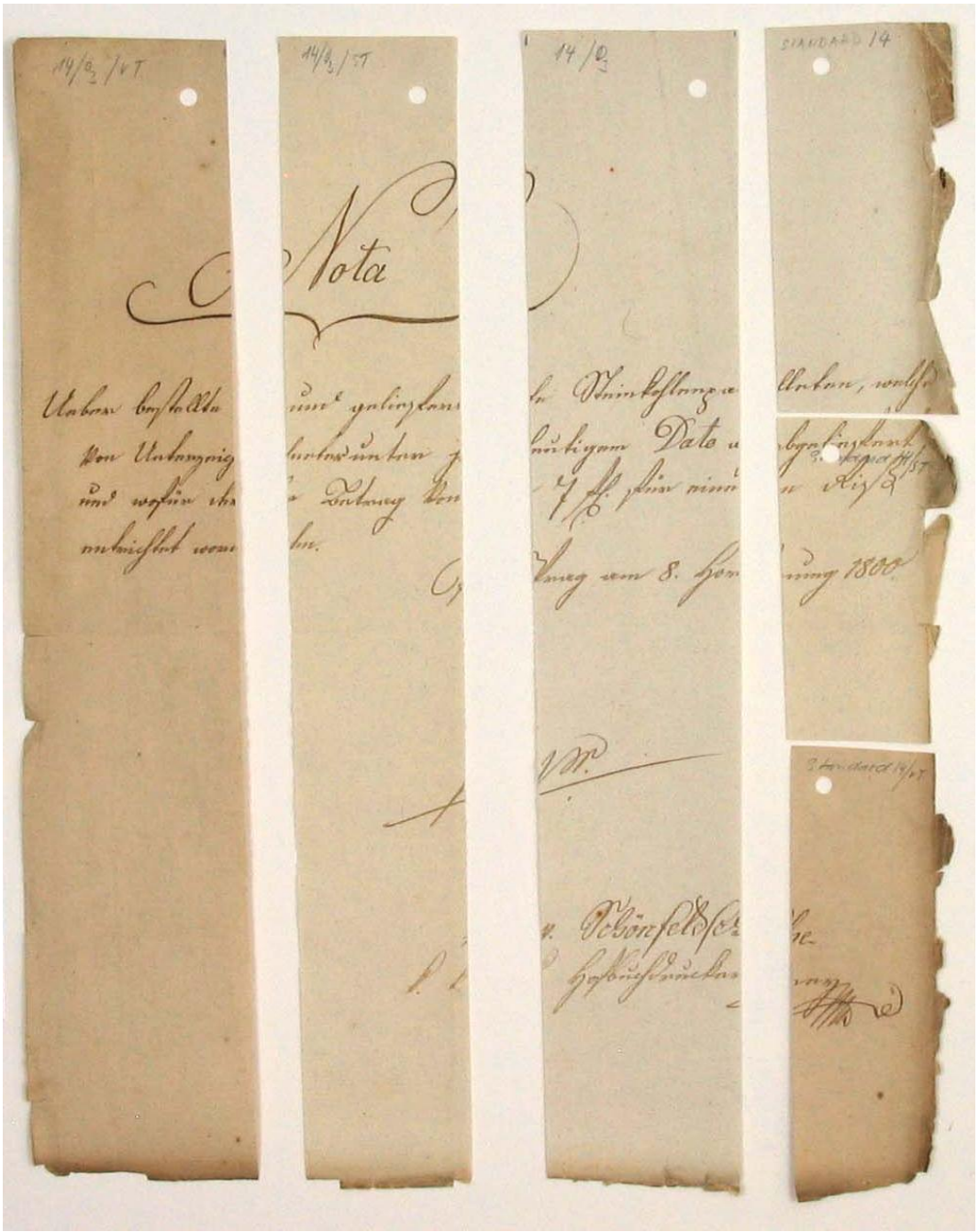
Sample No. 13



Sample No. 13a



Sample No. 14



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 ΔE 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*).

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

Paper sample	L*	a*	b*	ΔL*	Δa*	Δb*	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 continued

Paper sample	L*	a*	b*	ΔL*	Δa*	Δb*	ΔE*
7 – unaged	88.47	−0.17	14.56				
7 – moist heat	79.85	3.56	19.85	−8.62	3.73	5.29	**10.8**
7 – dry heat	83.83	1.60	22.71	−4.64	1.77	8.15	**9.54**
7 – ozonization – unaged	88.96	−0.56	13.50	0.49	−0.38	−1.06	**1.23**
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	84.05	2.82	18.29				
8 – moist heat	66.06	6.43	20.78	−18.0	3.61	2.48	**18.5**
8 – dry 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 – 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 – unaged	72.91	7.01	26.36				
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				
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 – 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				
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				
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 – 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 – 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.

Tab. 6. **Effect of ozonization on selected archive microorganisms.**

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

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)
\+ 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.