



Lodz University of Technology



# Current methods of testing paper properties

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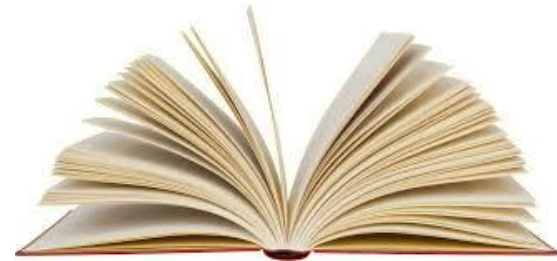
# Factors influencing the permanence of paper

## External

- Pollution and dust, excessive moisture content, air flow, temperature;
- Sunlight, artificial light;
- Chemical pollutants in the air;
- Migration of ink components, printing colours and ingredients of synthetic envelopes into paper;
- Natural disasters;
- Insects;
- Microorganisms growth.

## Internal

- Paper composition (type of pulp, sizing agent, filler e.g. rosin-based, and other additives used in papermaking);
- Technological conditions of paper production (primarily the paper sizing method and surface finishing method).



# Mechanism of paper deterioration

Acidic hydrolysis

Photolytic degradation

Oxidative degradation

Microbial metabolism

**Influence on:**

- physicochemical
  - mechanical
  - optical
- paper properties**

**and result as:**

- discoloration/reduced brightness and increased yellowness
- more brown and brittle edges
- cellulose depolymerization/ decomposition and reduction of strength
- specific musty smell
- petrification
- foxing

# Preservation and conservation of libraries collections

**Historical books collections**

**Evaluation of preservation state**

**Disinfection, deacidification and conservation**



**Methods of investigation**

# METHODS FOR THE EVALUATION OF PAPER PROPERTIES

	SUBJECTIVE	INSTRUMENTAL
NON-DESTRUCTIVE	Stanford method; visual assessment of optical properties	pH of paper surface; brightness; yellowness; CIE L*a*b*; air resistance; thickness; AAS; AFM; SEM; FTIR; XRD; SPME
DESTRUCTIVE	microscopic fibre composition analysis; filler/sizing agent content and type analysis	pH of extract; computer image analysis of fibres distribution; basis weight; bulk; Kappa number; intrinsic viscosity; Zero Span Tensile Strength; Zero Span Fibre Strength (ZSFS); stretch; tensile strength; burst; TEA index; tear resistance; folding endurance; determination of alkaline reserve; TG; DART-MS; SEC

FTIR-Fourier Transform Infrared Spectroscopy; SEM-Scanning Electron Microscopy; XRD-X-ray diffraction; AAS-Atomic Absorption Spectroscopy; TG-thermogravimetry; AFM-Atomic Force Microscopy; SPME-Solid Phase Microextraction; DART-MS- Direct Analysis in RT Mass Spectrometry; SEC-Size Exclusion Chromatography

# The aim of the study

- **Evaluation of preservation state of historical books**
- **Determination of disinfection influence on properties of paper from historical books**



# Materials-Books investigated for the assessment of historical books preservation state

Item	Title/Place of publishing	Year	Type of cover material	Size (cm) (L×W×H)	Macroscopic evaluation
3	Meyers Konversations Lexicon/ Germany	1896	Cardboard and paper	24.5×16.5×3.7	Fungal growth, discoloration, damp patches
7	Schmelzen des Glases/ Germany	1928	Cardboard and paper	22.7×15.6×1.0	Fungal growth, damp patches, permanent staining
9	Dziennik Ustaw/ Poland	1933	Cardboard, paper and fabric	31.2×23.2×5.2	Damp patches

# Materials-Books investigated for the effectiveness of disinfection of paper on its properties

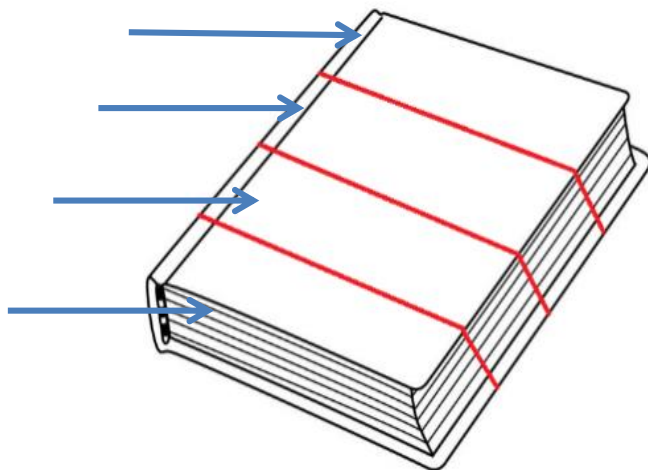
Item	Title	Year	Type of cover material	Size (cm) (L×W×H)	Macroscopic evaluation
1	Dziennik Ustaw	1924	Cardboard and fabric	30.0×23.5×3.0	Fungal growth, discoloration, permanent staining
4	Konsuelo	1865	Cardboard and paper	18.8×11.0×2.7	Fungal growth, discoloration, loss of structure, musty odour

control

TEO

LTP

AgNPs



TEO-thyme essential oil microatmosphere  
LTP-low temperature plasma  
AgNPs-silver nanoparticles misting



# Methods

## Instrumental analysis

Type of analysis	Analytical method	Type of analysis	Analytical method
Fibre composition	TAPPI T263 om-93, TAPPI T259 om-93	Tensile strength/ TEA	ISO 1924-2:2008
Kappa number	ISO 302:1981	Burst strength	ISO 2758:2008
Basis weight	ISO 536:2012	Tear strength	EN 21974:2002
Thickness/bulk	ISO 534:2011	Bending stiffness	ISO 5628:2012
Air resistance	ISO 5636-5:2003	Zero Span Fibre Strength index	ISO 15361:2000
pH of water extract	ISO 6588-1:2005	Folding endurance	ISO 5626:1993
Intrinsic viscosity	ISO 5351-1:1981	Brightness/ Yellowness	ISO 2471-1:2008

## Visual analysis

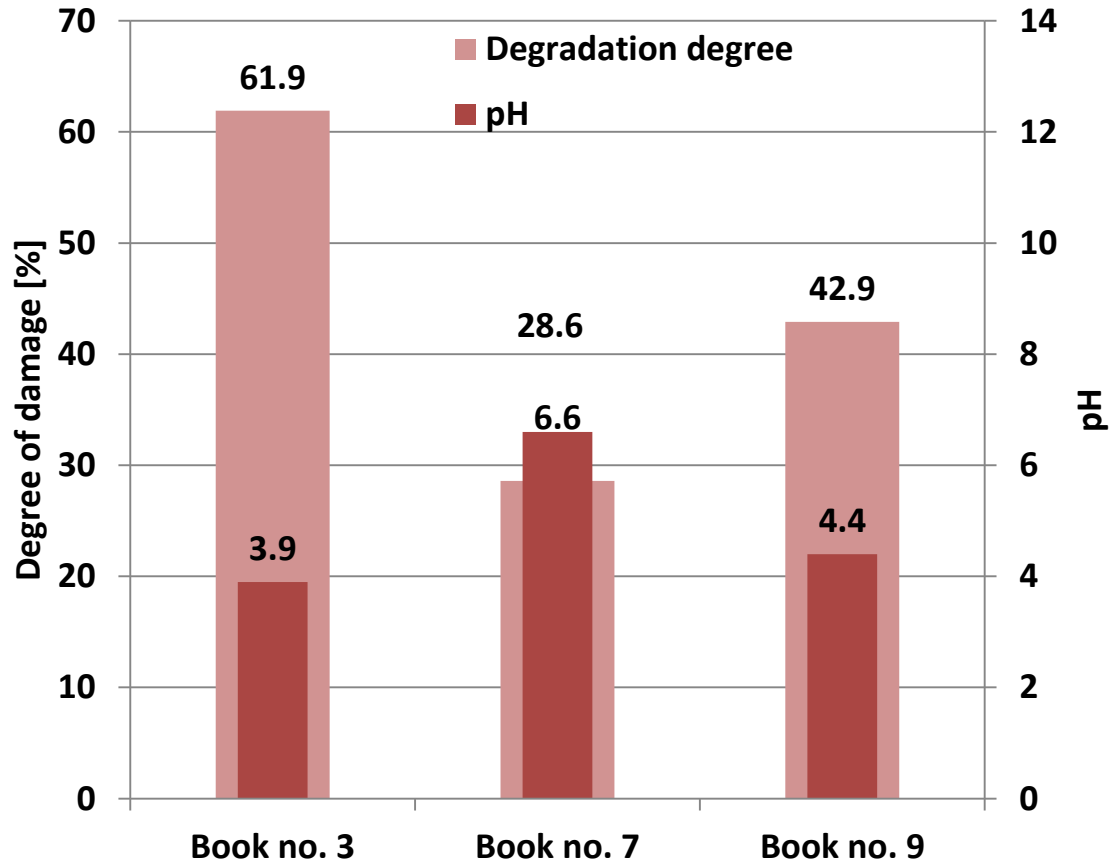
**0-1 system, where 0 means no damage and 1 means its occurrence**

**TAPPI- standards of Technical Association of the Pulp and Paper Industry; ISO- standards of International Organization for Standardization; EN-European standards**

# Comparison of historical books preservation state



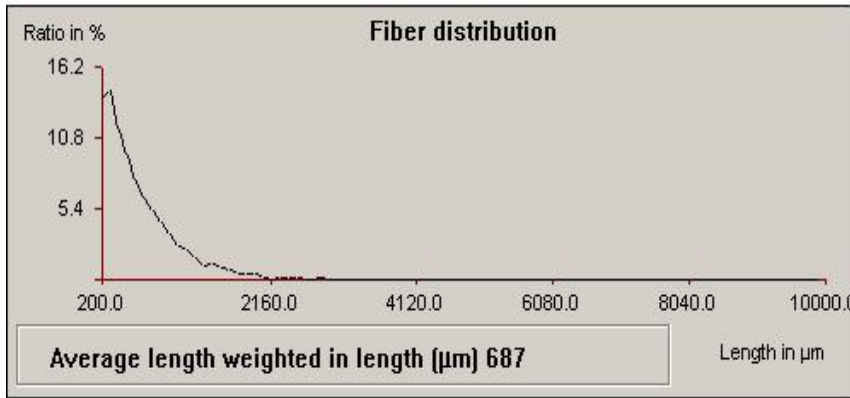
# The degree of damage



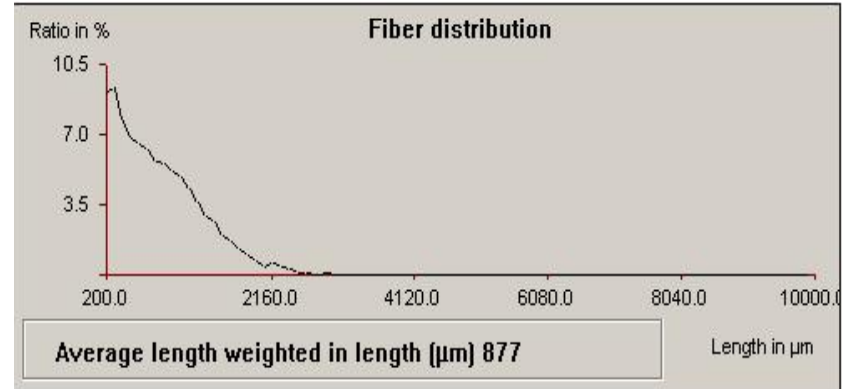
# Fibrous composition, fibres width and kappa number

Book number	3 (1896)	7 (1928)	9 (1933)
Source of fibres	<ul style="list-style-type: none"> <li>▪ Straw chemical pulp</li> <li>▪ Rags pulp</li> <li>▪ Spruce chemical</li> <li>▪ Groundwood</li> </ul>	<ul style="list-style-type: none"> <li>▪ Spruce chemical pulp</li> <li>▪ Rags pulp</li> </ul>	<ul style="list-style-type: none"> <li>▪ Groundwood</li> <li>▪ Spruce chemical pulp</li> </ul>
Fibres width (µm)	26.3	31.4	35.1
Kappa number	8.4	8.3	84.1

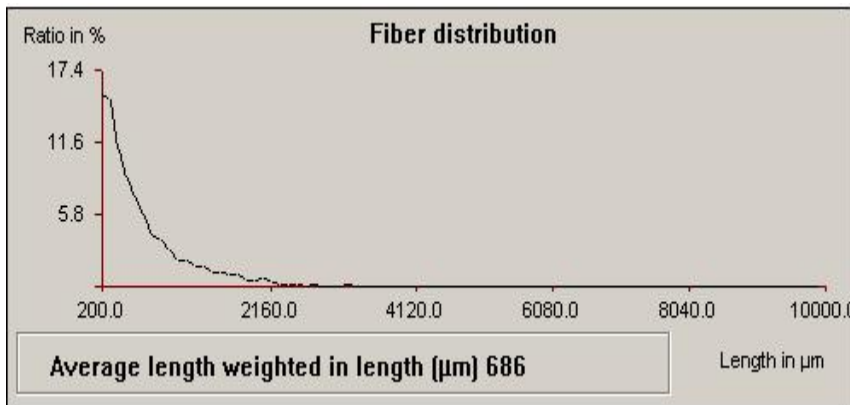
# Fibers distribution



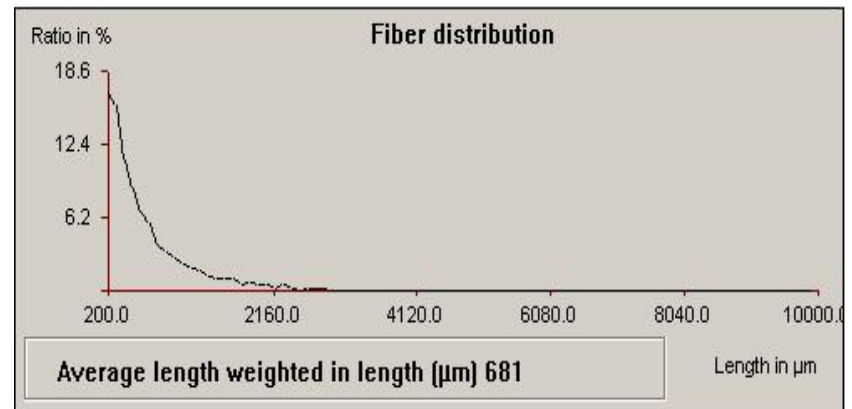
Book no. 3 (1896)



Wheat straw chemical pulp

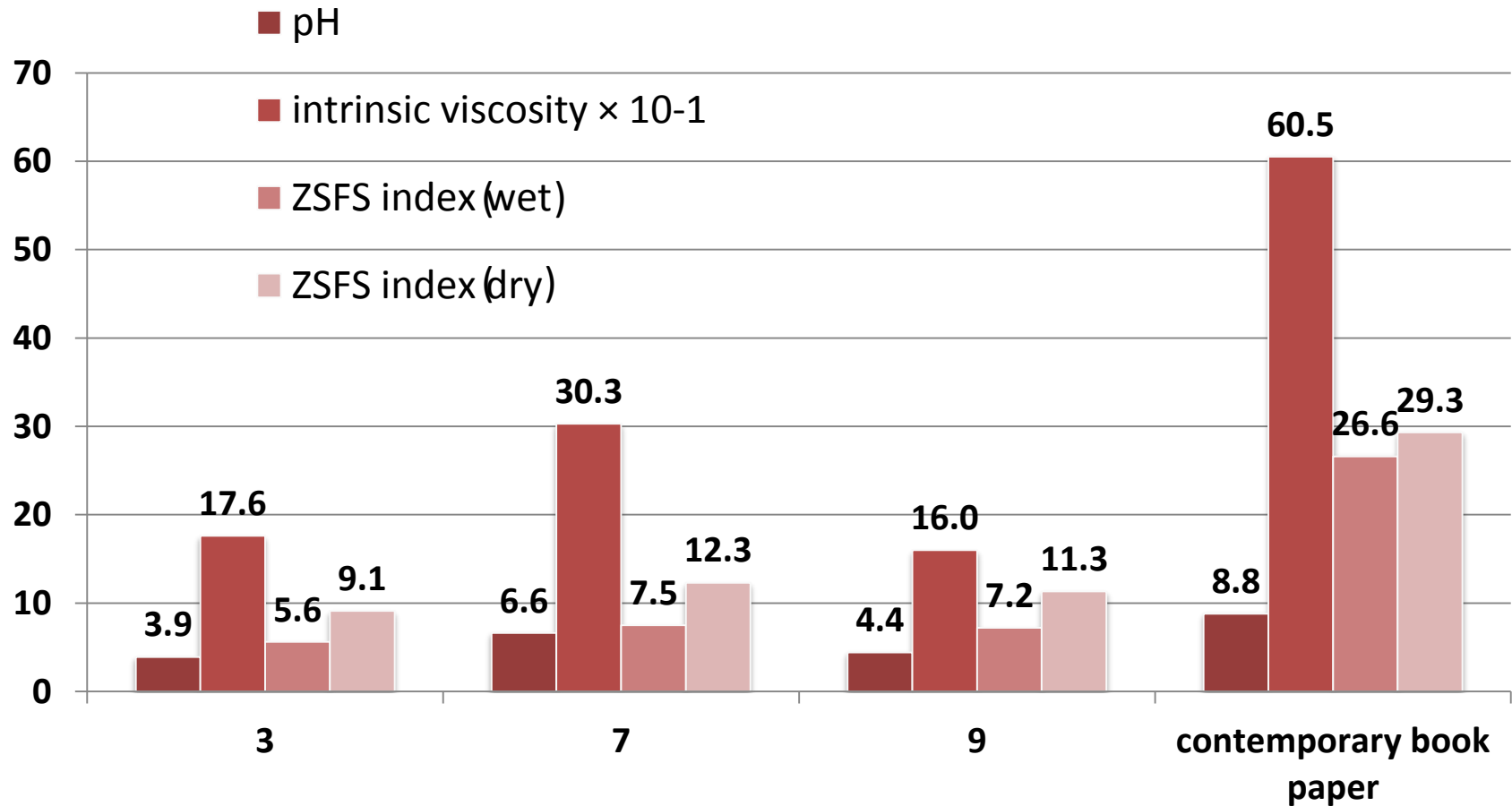


Book no. 9 (1933)



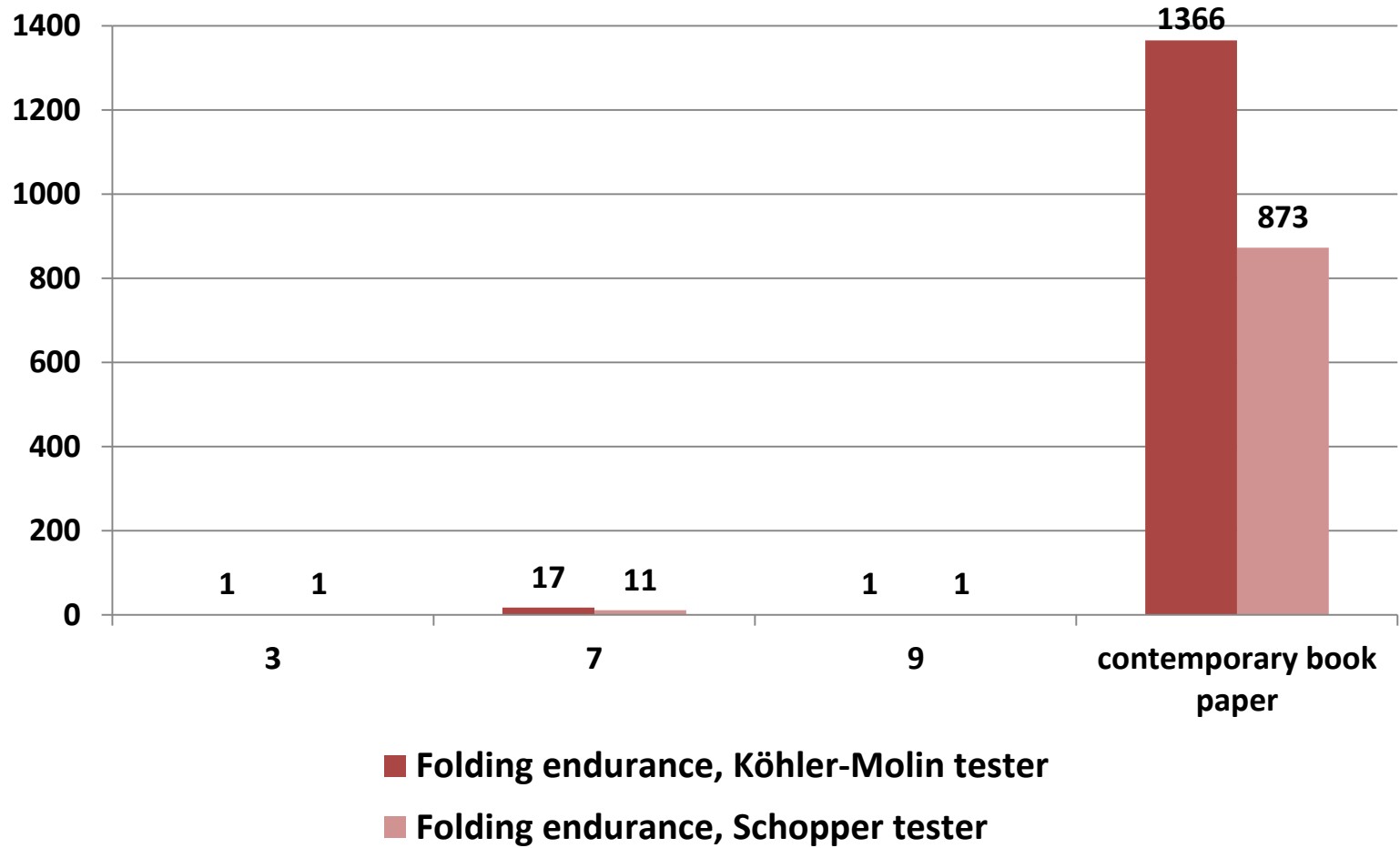
Spruce groundwood

# pH, intrinsic viscosity and ZSFS indices (wet and dry)

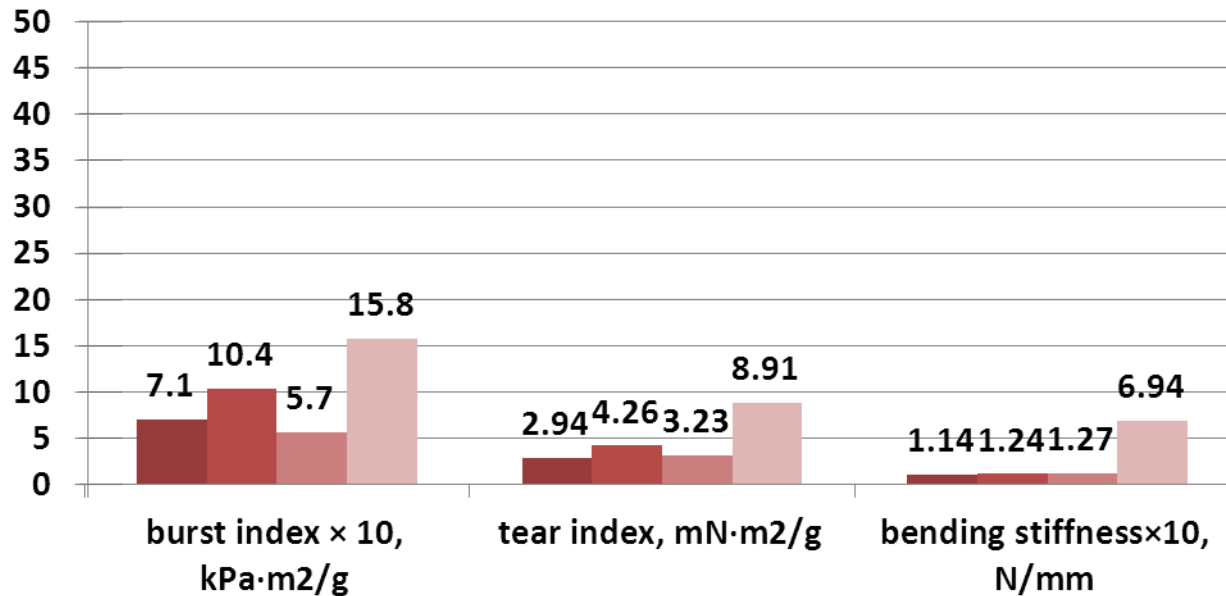
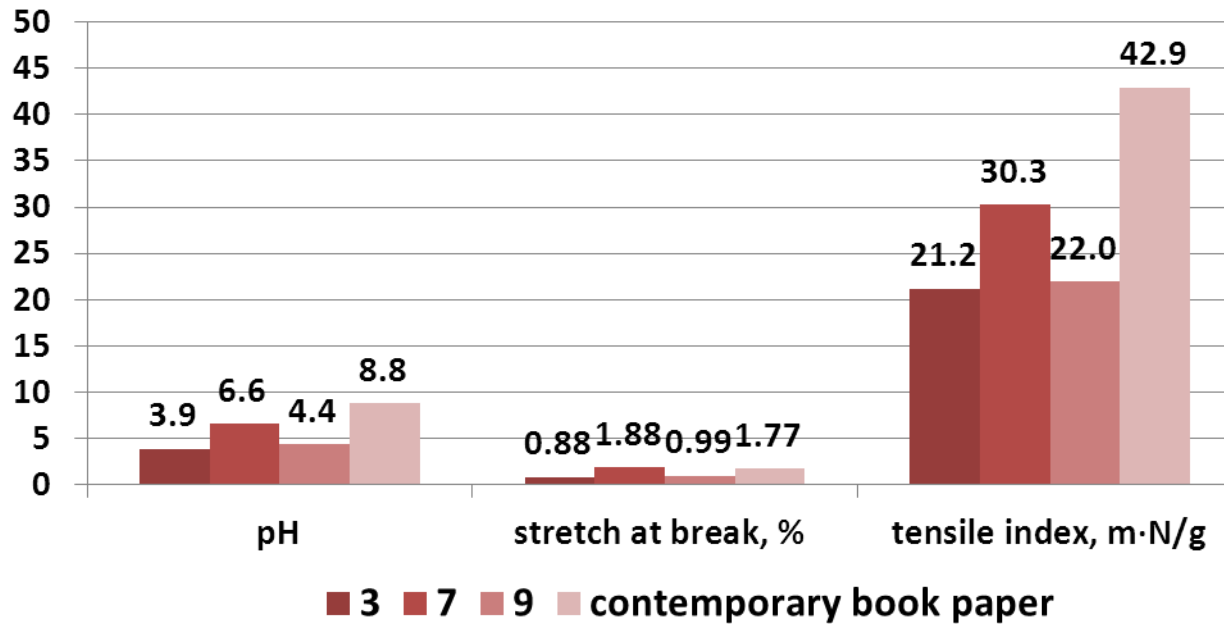


ZSFS - Zero Span Fibre Strength

# Folding endurance



# pH and mechanical properties of paper from historical books





# **Comparison of influence of disinfection method on properties of paper from historical books**



# Disinfection *versus* physicochemical properties of paper

Disinfection method	LTP		AgNPs		TEO	
Book number	1	4	1	4	1	4
Difference	rel. %					
Thickness	0.8	5.0	2.2	0.7	0.0	4.8
Bulk	1.2	1.2	2.5	2.5	0.1	0.7
pH	10.2	11.1	8.2	22.2	10.2	6.7

positive
  negative
  neutral

LTP - low temperature plasma; AgNPs - silver nanoparticles misting; TEO - thyme essential oil microatmosphere

# Disinfection *versus* intrinsic viscosity and ZSFS index

Disinfection method	LTP		AgNPs		TEO	
Book number	1	4	1	4	1	4
Difference	rel. %					
Intrinsic viscosity	2.6	1.3	7.6	2.1	1.8	1.5
ZSFS index (wet)	1.1	4.0	3.4	2.0	1.1	27.3
ZSFS index (dry)	1.6	1.2	4.0	1.9	4.0	0.6

 positive     negative

ZSFS-Zero Span Fibre Strength; LTP-low temperature plasma; AgNPs-silver nanoparticles misting; TEO-thyme essential oil microatmosphere

# Disinfection *versus* mechanical properties of paper from book no. 1

Paper direction	MD			CD		
Disinfection method	LTP	AgNPs	TEO	LTP	AgNPs	TEO
Difference	rel. %					
Stretch at break	26.3	8.8	7.0	3.2	12.9	17.2
Tensile index	31.2	7.4	6.3	19.2	4.3	30.8
TEA	20.0	10.0	20.0	28.6	42.3	28.6
Tear index	0.9	2.2	1.3	8.7	5.2	8.7
Folding endurance	nt	nt	nt	0.0	0.0	0.0
Bending stiffness	3.7	7.8	6.1	13.2	13.2	1.1

positive
  negative
  neutral

MD - machine direction; CD - cross to machine direction; LTP - low temperature plasma;  
 AgNPs - silver nanoparticles misting; TEO - thyme essential oil microatmosphere; nt - not tested

## Disinfection *versus* mechanical properties of paper from book no. 4

Paper direction	MD			CD		
Disinfection method	LTP	AgNPs	TEO	LTP	AgNPs	TEO
Difference	rel. %					
Stretch at break	147.8	8.7	137.0	2.9	4.4	16.2
Tensile index	184.6	165.9	163.7	0.4	9.3	10.6
TEA	661.0	518.7	587.0	12.8	12.2	6.2
Tear index	2.7	21.0	4.6	nt	nt	nt
Folding endurance	175.0	100.0	225.0	nt	nt	nt
Bending stiffness	0.9	5.6	1.9	14.3	19.0	9.5

 positive  negative

MD - machine direction; CD - cross to machine direction; LTP - low temperature plasma; AgNPs - silver nanoparticles misting; TEO - thyme essential oil microatmosphere; nt-not tested

# Disinfection *versus* optical properties of paper

Disinfection method	LTP		AgNPs		TEO	
	1	4	1	4	1	4
Difference	rel. %					
Brightness	5.0	12.6	3.8	30.8	2.8	20.3
Yellowness	0.4	13.9	2.2	18.0	4.2	17.5

 positive     negative

LTP - low temperature plasma; AgNPs - silver nanoparticles misting; TEO - thyme essential oil microatmosphere

# Summary and conclusion

- **Mechanical properties of paper from historical books were reduced and correlated with paper acidification, and fibrous characteristic as well as with overall visual assessment of preservation state.**
- **Disinfection of paper from historical books conducted with LTP, AgNPs and TEO preserved mechanical properties of paper.**
- **The applied disinfection methods did not affect or affected marginally negatively on optical properties of paper.**





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