Lappeenranta University of Technology
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PAPER DEACIDIFICATION AND PRESERVATION USING ZINC, ALUMINIUM AND TITANIUM OXIDES ATOMIC LAYER DEPOSITION

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ABSTRACT

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Paper Deacidification and Preservation Using Zinc Aluminium and Titanium Oxides Atomic Layer Deposition

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Preservation of historical heritage for future generation is an important part of the modern world. Most the centuries, knowledges of humanity were recorded on the papers, and cellulose paper being an organic material has its durability limits. In this thesis research work, paper deacidification with the use of zinc, aluminium, and titanium oxides was studied, where the coating was performed by atomic layer deposition (ALD). Major analytical efforts were directed on the observation of zinc oxide due to its positive dynamics in paper deacidification, which was reviewed in previous studies and proved practically in Laboratory of Green Chemistry, Lappenranta University of Technology. Samples were received from National Library of Finland, which had an evident acidic degradation. Methods to analyse the condition of the samples before and after the treatment were performed by determination of pH value by contact and TAPPI standard T-509 methods, examination of hydrophobic properties measured by contact angle (CA), elasticity of the paper by folding test, and observation of the paper fibre structure by SEM. Ecotoxicological profile of diethyl zinc and zinc oxide was studied. According to received results, deposition of zinc oxide by ALD has positive effects for paper deacidification.

PREFACE

Research work for this master thesis was conducted at the Lappeenranta University of Technology Laboratory of Green Chemistry. Studies were financially supported by Memory Park Project, which was arranged by Mikkelin Kehitysyhtiö Miksei Oy and National Library of Finland.

I express my gratitude for my friend, supervisor and guru of ALD technologies Philipp Maydannik for his competent guidance in my scientific research. I am grateful to Mika Sillapää and Vesa Sorasahi for providing me the opportunity to perform this study in the brilliant working environment, any researcher can only imagine.

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LIST OF PUBLICATIONS

Attachment of Poly(L-lactide) Nanoparticles to Plasma-Treated Non-Woven Polymer Fabrics Using Inkjet Printing

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NOMENCLATURE

n	Quantity of material/Number of data points	mol / -
m	Weight of sample	g
T	Temperature	K or ^{0}C
V	Volume of solution	L or cm^3
P	Pressure	mbar

Abbreviations

ALD	Atomic layer deposition
DEZ	Diethyl zinc
TMA	Trimethylaluminium
$CaCO_3$	Calcium carbonate
SEM	Scanning electron microscope
UV	Ultra violet
CA	Contact angle
calc	Calculated
exp	Experimental
rpm	Rotation per minute
sccm	Standard cubic centimetres
h	Hour
TFS	Thin film system
MgO	Magnesium oxide
SOx	Sulphur dioxide
NOx	Nitrogen oxides
COx	Carbon oxides
TFS	Thin Film System (Beneq)
CVD	Chemical vapour deposition
STP	Standard temperature (0^0 C/273 K) and pressure (1 bar/0.987 atm)
NTP	Normal temperature (20^0 C/293 K) and pressure (1 atm)
LC_{50}	Lethal concentration of toxin/pathogen required to kill 50% of studied species

1 INTRODUCTION

Durability of cellulose materials depends on various factors that include material selection and processing, manufacturing and storage conditions. Paper decay is a common problem of libraries all over the world, where the importance to save historical heritage or strategically valuable paper documentation and to deliver a knowledge to future generations is a main agenda [1]. Paper related problems were brighter marked in the early 18^{th} and 19^{th} centuries, which were described as an increase of acidity leading to paper acidification with a further depolymerisation [2, 3]. Nowadays, paper and pulp industries are able eliminate paper's degradation related contend, such as lignin, aluminium sulphate and iron gall ink, by producing acid-free papers with alkali buffering compounds [4].

Degradation of cellulose paper is based on the decrease of pH value, which results in loss of mechanical endurance represented as a high embrittlement and yellowing. Associated paper problems include presence of air pollutants, acidic reaction catalysts, and natural aging process due to appearance of the carboxyl group. Methods to neutralize acidity and to retain base balance have been developed during the last century and named as mass deaciditication. The concept is based on two common methods, which are liquid-based and vapour-phase processes of paper impregnation with the alkaline agents (MgO, $MgTiO_3$, ZnO) onto cellulose fibre structure. [1, 3] Both methods are in active use and have a strong position in market. Nevertheless, development in area of paper preservation is not standing still. North Carolina State University has published an article called "Paper deacidification and UV protection using ZnO ALD" [5], where the applied method has shown some positive dynamics in neutralization of acidity in old books.

Atomic layer deposition (ALD) has a great potential to deliver an exact amount of the target reagents onto multistructural material surfaces, such as cellulose paper. Appling ALD process can provide an atomic preciseness in reagent deposition due to high penetrative ability of DEZ. Reagent diffusion can reach active zone even in material with porous structure (e.g. to distribute alkaline agent and neutralize acid content in paper). [6] Coating performs under vacuum, which makes pyrophoric compounds, such as DEZ, safer to use. Previously, just few studies been tested in area of paper preservation using ZnO deposited by ALD [5]. These results had positive dynamics in neutralization and buffering the acid content in the paper structure. In this studies, ALD methods to neutralize acidity has been tested.

1.1 Objectives and contents

This thesis work is aimed to study ALD technology applied for paper preservation to tackle paper associated problems, such as acidic degradation, which leads to embrittlement and yellowing. Main target is to prove reliability of the ALD method for neutralization of acidity in the paper with a use of ZnO. The resources of previous studies are limited in area of applying ALD of ZnO for paper deacidification. Publication from North Carolina State University has a research in this field. The study will be repeated for further improvement and optimization. The purpose of the thesis is to advance paper deacidification techniques development with a use of ALD. Additionally, TMA and TTIP will be tested to identify a possible acid neutralization effect.

Firstly, paper analysis will be performed to evaluate damage caused by acidification to plan a treatment programme according to individual properties and conditions of each sample. Samples were stored at least for several decays, where with a naked eye mechanical and cosmetic problems can be detected. Initial analysis starts from determination of pH value by contact and TAPPI standard T-509 methods [5, 7, 8]. Further paper analysis includes examination of hydrophobic properties measured by CA [9], elasticity of the paper by folding test [10] and observation paper fibre structure by SEM [11]. Second step is an actual paper treatment, which is aimed to neutralize acid content of the studied papers by depositing DEZ, TMA, and TTIP. Studied precursors are delivered onto the papers by ALD systems (TFS 200 and TFS 500 Beneq) [12, 13]. Where the introduced alkaline agent will neutralize acidity in cellulose papers. Applying ALD process can provide atomic preciseness in where reagents are controllably deposited on material's surface. Coating performs under vacuum, which makes highly reactive with air and humidity DEZ [1, 5] and TMA safer to use. Paper deacidification process should fulfil certain treatment criteria:

- Complete neutralization of acidity has to produce pH value not less than 7
- Deposited compounds should keep base balance as a buffer to retain further acidic degradation
- Deposition has to be homogeneous over sample's surface area to ensure high effectiveness of deacidification

- Paper's fibre matrix has to be undamaged, without significant decrease of elasticity and mechanical strength, which could lead to swelling or warping of the paper
- ALD treatment should not have decolourisation and tinting effects to inks, dyes and adhesives
- Treated samples should be environmentally friendly

1.2 Paper

Paper is a complex multicomponent polymer where the composition depends on manufacturing type of cellulose purification and treatment methods, and chemical additives. Organic polymer cellulose with a formula $(C_6H_{10}O_5)_n$ (*n* is repeating units; Figure 1) is the most abundant polysaccharide in the world. Cellulose is a major element of the embryophyte and represented in their cell walls. The polysaccharide's molecule has a liner macromolecular structure. The chemical properties of cellulose are determined by the presence of long chain glycosidic linkages between elementary monosaccharide (or beta glucose) moiety and hydroxyl groups (-OH). [14, 15] It gives a great mechanical strength with a retained elasticity. Cellulose is a biodegradable, white, solid and odourless matter. It is insoluble in water and soluble in ionic liquids or organic solvents [16]. Concentrated acids and high temperature (over 200º C) can break down cellulose structure on monosaccharides [14, 17].

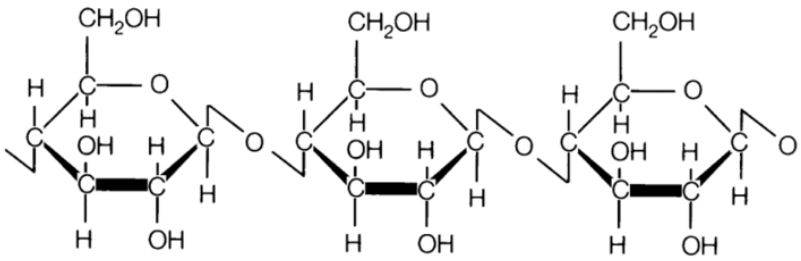


Figure 1. Cellulose chemical formula, chain of glycosidic linkages [15]

Source material for paper manufacturing is cellulose fibers extracted from wood, fiber crops or recovered from paper wastes. These raw materials of cellulose fibers are converted into lignocellulosic fibrous pulp separated by chemical and mechanical methods. Both pulp types could be manufactured separately or combined. Another raw material source is a cotton used to produce high-quality papers. [18, 19]

Chemical pulp

Chemical pulp is divided on alkaline and acidic thermochemical methods of pulping. Sulphate or Kraft process is a major industrial method to produce cellulose. The technique is based on alkaline delignification to pulp of the wood chips in aqueous solution containing sodium hydroxide (NaOH) and sodium sulphide (Na_2S). Technically process occurs in digesters where NaOH and Na_2S are mixed with wood chips at 170-175^0 C to break down lignin. Kraft process is a most widespread method to produce cellulose. [20, 21]

Sulphite process is an acid based thermochemical process of delignification of wood to produce pulp. Pulping wood is treated with a solution containing sulphur dioxide (SO_2) and salts of sulphurous acid (sulphite and sodium bisulphite, calcium, ammonium, potassium, or magnesium) at elevated temperature and pressure. [15, 20, 21]

Chemical pulps represent high quality paper product, which are durable, flexible and dense. Commonly used for archival and high quality publications. [20, 21]

Mechanical pulping

Mechanical pulping is a process based on dominantly physical impact onto wood chip through high temperature, high pressure, steam and milling by refiner plates. Quality of end product is low with a significant presence of lignin. Thus, it accelerates yellowing and embrittlement. Mechanical pulping is a cost effective process in terms of producing paper with large circulation, such as newsprint and paperboards. [20, 21]

1.3 Durability challenges

Nevertheless, all organic materials have its life duration limits as it has a cellulose paper. Aging of the paper is a long-term process if favourable conditions are adjusted. Composition of the ready-made paper products plays a crucial role and depends on quality related factors, such as the source of raw materials, type of pulping process, and a purpose of use. Additionally, additives as dyes, paper sizing adhesives (aluminium sulphate) and printing inks can impact on the paper's lifetime. Next significant moment is quality of paper with such preserving variables as relative humidity, temperature, air quality and UV exposures controls.

Lignin and aluminium sulphate contents in the paper are the key factor of quality deterioration with a further degradation. These compounds are lead to acidification with a presence of moisture. Result of paper acidification increases rate of embrittlement and continued with total loss of mechanical strength. Yellowing of the papers usually linked with availability of lignin, which in turn decreases pH value. Acid depolymerisation of the cellulose paper is an autocatalytic process, which indicates acceleration of the reaction rate of degradation over time. Additionally, a poor maintenance can have a catalytic dynamic in paper depolymerisation.

Lignin

Lignin is an organic polymer included in the composition of majority of green plants. It impacts on acidity, surface roughness, brittleness and yellowing factors. Paper industry uses chlorine treatment to completely remove it or alkali treatment (Kraft pulping) where lignin is extracted or dissolved as a by-product during a cellulose cooking. High concentrations of lignin are present in low cost books and newspapers. [15]

Aluminium sulphate

Aluminium sulphate ($Al_2(SO_4)_3$) is another durability influencing reagent used as a fixative to form rosin glue particles (aluminium resinate) and used almost in all types of paper. Aluminium sulphate is used in papermaking to strengthen fibre adhesion by fixing anionic compounds, and it increases hydrophobicity of paper. Currently, it is replaced by synthetic cationic rosins (e.g. polyethyleneimine or polyacrylamide resins) due to strong impact on paper's degradation. [4]

Iron gall ink

Iron gall ink is a ferrous based printing inks commonly applied in 19^{th} and 20^{th} centuries. The principle of the ink darkening is based on oxidation reaction of iron with oxidation number 2 to iron(III) under the presence of oxygen in ambient air. Acidification factor is represented in high concentration of ferrous sulphate which decays printed rows. [20]

Environmental issue

Air pollution accelerates a depolymerisation reaction rate of paper material especially in the air of industrial cities, which contains significant amount of SOx, NOx and COx. Those contaminants are adsorbed through the ambient air particularly on the edges of the sheet and on the spine of the books. Sulphur dioxide absorbed by paper is oxidized by atmospheric oxygen to sulphur trioxide and in the presence of atmospheric moisture turns into sulphuric acid. NOx

have photo-oxidation nature of the reaction and with the presence of UV irradiation and humidity increases acidity of the material's surfaces. Accumulation of carbon dioxide influencing on the pH value and appearance of carboxyl group. [2, 15, 18]

Paper preservation technologies

Cellulose paper problems are originated from 17-20th and earlier centuries. Some chronicles state that books were losing mechanical strength (fragile and powdering effect) and colour brightness overtime. Whereupon, a necessity to preserve historically and strategically valuable books became a main agenda of the national libraries all over the world. Methods to neutralize acidity and to extend life of books have started to develop in 20th century and named as mass deaciditication. The word "mass" represents a scale of treatment which requires huge quantities of the target reagents to tackle at least few stacks of books. The concept is based on two common methods, which are liquid-based and vapour-phase processes of impregnation of the alkaline agents (MgO, DEZ and $CaCO_3$) to acidic paper [1, 3]. Since, these methods were developing and applying all over the world but homogeneity of treatment was not fully reached. Problems related to mechanical damage, decolourisation and volume growth were taking place [1, 2]. Currently, mass deacidification is significantly improved. [22]

Usually handling huge quantity of reagents is not a problem but compounds such as DEZ are required specific conditions to control its transportation, storage and usage due to its flammability. Diethyl zinc and trimethylaluminum are known as flammable substances, which are aggressively react with oxygen and humidity presented in air. Pyrophoric nature of these reagents requires proper precautionary measures in handling and storing them including systematic maintenance. Due to previous accidents in book deacidification facilities, DEZ has to be stored and used far from the treatment plans, which requires an additional transportation costs to deliver books in treatment facility and back to library. [5]

ALD method applied in this study has several advantages over mass deacidification techniques. Initially it has to be pointed out that deacidification by ALD based on atomic preciseness of reagent distribution. Where the demand in target chemicals can be minimised and optimised regarding to paper damage, which makes a use of DEZ more controllable. According to the results from the previous study, zinc oxide adsorbed on paper's fibres makes alkaline condition and stands as a buffer to retain further acidic development.

1.4 ALD

Atomic layer deposition (ALD) is a gaseous phase technique to deposit atomic scale layers on a substrate of choice. The atomic accuracy of the thin film deposition process is supported by the sequential use of chemical compounds, which are reacting with active sides of substrate. [7] Accordingly, it maintains a high homogeneity achieved through completely chemisorbed compounds. Most of the ALD-reactions are using two chemical compounds, ordinary called precursors. Such precursors alternately react with the surface or already formed solid compounds on it. As a result, a controlled growth of a thin film thickness is occurred due to the sequential influence of multiple precursors. [23]

Principles of ALD

ALD process is initiated under vacuum (<1 mbar). Temperature is adjusted in accordance to material's individual characteristics or in a frames required by research study. ALD process is based on gas phase chemisorption between successively and alternately pulsed precursors on the substrate's surface. The reaction starts with a termination of –OH groups on the substrate's surface by organometallic compound (e.g. DEZ) where the formed compounds take only a part from the whole reaction and called half-reactions. Theoretically, the reaction occurs on the active sides of the surface and stops when it is saturated. Once the surface is saturated, water (or other oxidants e.g. ozone, plasma or hydrogen peroxide) is introduced to oxidize precursor. Between each cycle, a purging with inert gas (typically N_2 or Ar) is required to pump away chemically formed by-products and surplus of unreacted precursor. [6, 24] The chemical reaction could be described as follows in Figure 2 [13, 24]:

1) Substrate is placed in vacuumed reaction chamber. Homogeneity of ALD coating is significantly depending on substrate's surface chemistry, which has to be rich by equally distributed hydrogen groups. For better chemisorption between substrate and precursor, surface has to be decontaminated against oils, dust and etc.
2) The process starts with an introducing DEZ. Pulse of DEZ ($Zn(C_2H_5)_2$) is reacting with –OH groups on the substrate's surface and forming - O - $Zn(C_2H_5)$. Formed compound is a part of half reaction. Besides, the hydrogen from the surface –OH group is taken to form ethane (C_2H_6), which is a by-product. Then ethane and surplus of unreacted DEZ have to be purged away by inert gas (e.g. N_2).

3) On the next stage, water is pulsed to oxidize the - O - $Zn(C_2H_5)$ and form zinc oxide. Ethane is produced as a by-product. This half reaction is finalized by a pulse of N_2 to pump away unreacted compounds.
4) Finally, zinc oxide is forming monolayer.

This cycle can be repeated to controllably to deposit desired film thickness.

$$Zn(C_2H_5)_2 + -O - H \rightarrow -O - Zn(C_2H_5) + C_2H_6$$
$$H_2O + -O - 2Zn(C_2H_5) \rightarrow -O - ZnO + 2C_2H_6$$

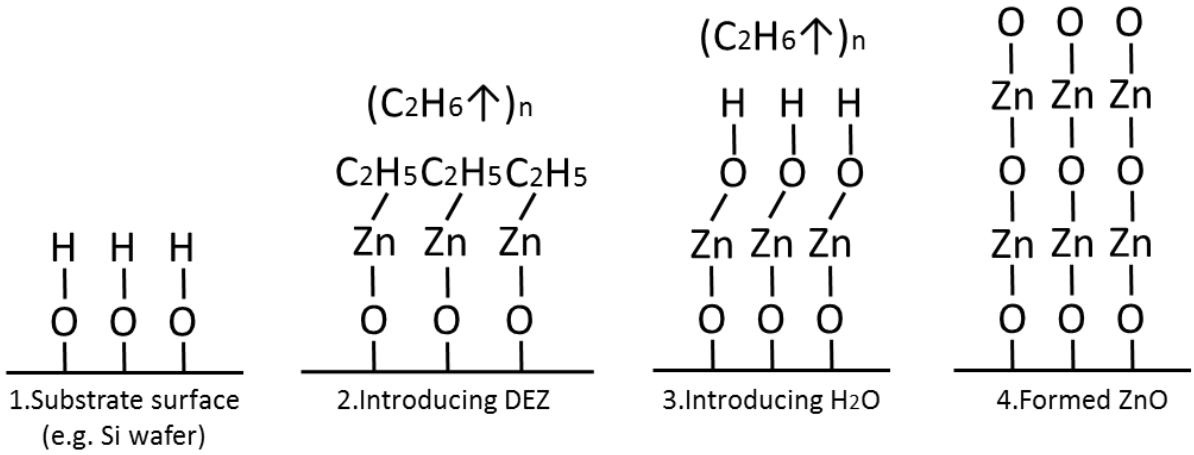


Figure 2. Schematic ALD cycle with DEZ

Area of use and advantages

ALD technology is widely applied in several areas as microelectronics (e.g. transistors, conductors and semi-conductors), biomedical applications to increase organic adsorption of inert implants, and in catalyst industry. Gaseous phase process provides uniform material distribution on any topology or 3D structure surfaces, which makes ALD highly precise technique in area of thin film technologies. [6, 24]

Materials as a cellulose paper treated by ALD has some restrictions. Cellulose paper is an organic material which is sensitive to high temperatures where the thermal degradation may occur already from 150° C. [21]. Paper has a huge surface area due to its porous structure with a high density of -OH groups, therefore it makes paper's surface extremely reactive in deposit organometallic compounds by ALD [20].

1.5 Ecotoxicology

Ecotoxicology is an interdisciplinary scientific and practical direction of toxicology associated with the toxic effects of chemicals on living organisms in certain ecosystem. This discipline studies a source of harmful substances, its distribution and transformation in the environment. Major biocoenosis (biological community) role in ecotoxicology plays humans health protection. Where the environment is considered as an active component, which studies a manifestation of toxicity in all living organisms. In the frames of this research study, ecotoxocological analysis has to be applied to define possible environmental and health impacts from infiltration of diethylzinc and zinc oxide. [24]

Both chemicals have different nature of their reactivity when they are released into the environment. Diethylzinc is the main precursor for deacidification reaction applied with ALD to form zinc oxide on the papers surface. Chemical family of DEZ comes from the metal alkyls, which are known for their pyrophoric nature. That results an unprompted ignition with air and moisture presented in it (see Figure 3). [25, 26]. High pyrophoric activity makes DEZ extremely hazardous. Therefore DEZ at atmospheric conditions and the presence of water molecules can burn an organic tissue when contacts, which is causing severe thermochemical burns. First aid measures after the removing victim from DEZ exposure area is an immediate flush with water of damaged skin or eye. Removal of the safety clothing is important if it is not stuck to the body. Prolonged inhalation of combustion products containing zinc may cause weakness, headache, nausea, vomiting, lungs and throat disorders, which is called as “metal fume fiver”. Fumes from ignition and further complete decomposition produce water, carbon dioxide and zinc oxide, additionally products like CO and hydrocarbons could be formed due to the incomplete combustion. Carcinogenicity of DEZ is not detected. Fire extinguishing measures are based on the appliance of the dry chemical agents. [27, 28]. NFPA 704 (Standard System for the Identification of the Hazards of Materials for Emergency Response) classifies DEZ via its “fire diamond” (see Figure X) as [29]:

- Flammability (red) index has number 4, which stands for the substances with a prompt and complete vaporization under STP.
- Health (blue) has number 3 that describes substances that could cause significant temporary or permanent injury.
- Instability/reactivity (yellow) index is 3, which includes substances with explosive nature due to initiating source as water, heat or shock.
- Special mark (white) where symbol ~~W~~ represents substances with an explosive or violent reaction behavior with water.

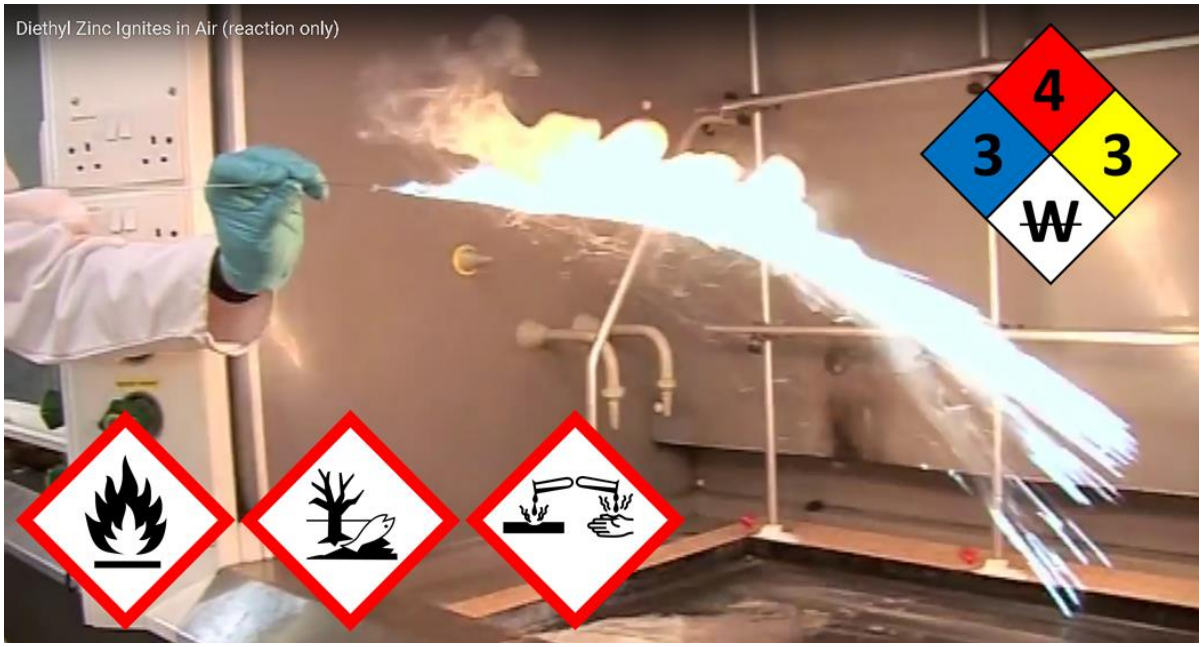


Figure 3. DEZ released from the syringe, which is followed with pyrophoric reaction of DEZ with air (picture captured from YouTube.com video); added NFPA 704 “fire diamond” and Globally Harmonized System of Classification and Labelling of Chemical (GHS) hazard pictograms [28, 29].

Oxidation of DEZ is followed by formation of zinc oxide, which is white or white-yellowish, odourless, solid, and water insoluble powder (Figure 4). The chemical is stable under NTP. Melting point is 1975º C. Zinc oxide is widely used in many industries, for example in pharmacological industries as a sun screening agent due to its ability to absorb solar spectrum wavelengths as UVA (320-400 nm) and UVB (290-320 nm) or in a role of antiseptic agent in assisting wound healing. [25, 26]

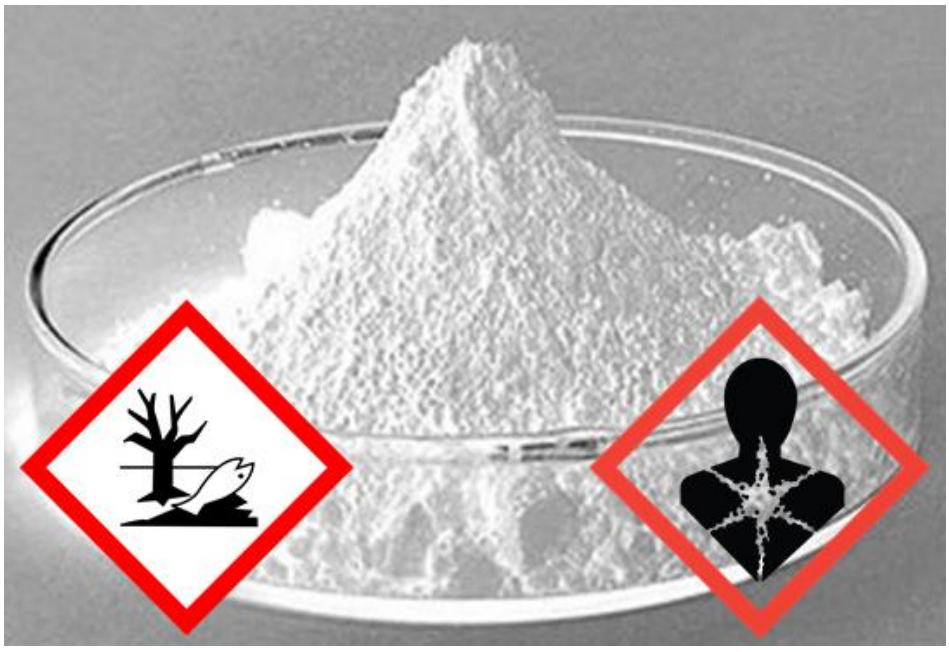


Figure 4. Zinc oxide powder; added GHS hazard pictogram.

Typical migration of zinc oxide into the environment from certain source falls on mining and chemical industry's wastewaters or exhaust gases, which could contain high concentration of zinc oxide. Released zinc containing compounds have significant hazardous effects for the environment and human health. ZnO may accumulate in surface waters, sediments and soils due to precipitation from fumes or release of wastewaters containing zinc. [29, 30]

Aquatic

According to GHS, hazard statement of ZnO towards aquatic life defined as a substance with high toxicity with long-lasting adverse effects. Where the effects may influence on a central nervous, respiratory or/and reproductive systems. [28, 29]. Therefore, any release of zinc oxide into the environment has to be avoided, or the spillage should be collected. Sources of zinc enriched wastewaters are typically discharged from chemical, mining, woodworking, metallurgical industries. High concentrations of zinc in the environment can be naturally present due to erosion and oxidation of zinc-containing ores. [31]

Occupation exposure limits for Zn^{2+} in drinking water is 5 µg/L, but galvanized water pipes may keep this limit temporary or constantly high. Discharges of wastewaters containing zinc into the environment should not exceed 0.5-7 mg/L acceding to EU regulations. Concentration of zinc in surface water may have a range from 0.002 to 50 mg/L. Averaged subthreshold concentration of zinc oxide in water which does not influence on the biochemical processes of the marine biota is 5 mg/L. [32, 33, 34, 35]

Lethal scenario for hydrobionts from zinc compounds is typically based on the damage of respiratory epithelium of gills, which leads to tachypnoea, later to asphyxia and death. Table 1 represents LC_{50} for few marine species analysed as biomarkers for exposure of zinc oxide. According to the result, the concentration of ZnO over 1 mg/L increases rate of mortality of the studied marine species within the limits of 48-96 hours. [24, 36, 37, 38]

Common name	Effect/measurement	Life stage [g]	Study time [h]	Mean ug/L
Rainbow trout	Mortality	0.78	96	1,100
Common carp (C.caprio)	Mortality	0.22	96	4,897
Striped bass	Mortality	Fertilized egg	48	1,770
Daphnia magna	Mortality	Neonates	2	70 (98)
Zebrafish	Mortality	Embryos	96	1,793
Zebrafish	Mortality	Larvae	96	1,550

Table 1. LC_{50} toxicity endpoint for marine species from ZnO.

Air

Zinc is naturally presented in the air where the concentration may vary between 10 to 100 ng/m^3. Atmospheric zinc concentration in urban areas can reach 100 to 500 ng/m3 [39]. Zinc oxide fume or dust have a significant poisoning effect, which leads to "metal fume fiver" [40]. Table 2 represents exposure limits for airborne ZnO dispersed as fume and dust. According to combined threshold limit values from Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) for airborne ZnO, concentration in 5 mg/m^3 requires minimum respiratory protection for exposure time in 8-10 hours. Higher concentrations of zinc oxide forces to use more efficient fume respirators for the concentration, which could reach a value in 250 mg/m^3. Self-contained breathing apparatuses are compulsory to be applied where the concentrations of ZnO are exceeding values over 1000 mg/m^3. LC_{50} for inhalation airborne zinc oxide dust and mist (particle size unknown) by rat and mouse during 4 hours is >5.7 g ZnO/m^3 and 2.5 g ZnO/m^3. [41, 42]

Airborne exposure limit for total ZnO fume and dust	**[mg/m^3]**	**Duration [hours]**	**Required respiratory protection**
Permissible exposure limit (PEL)	5	~8-10	Minimum respiratory protection
Short-term exposure limit	10	<1	Minimum respiratory protection
Not to be exceeded without respiratory protection	15	0	Fume respirator
Not to be exceeded without respiratory protection	50	0	Fume respirator
Not to be exceeded without respiratory protection	250	0	High efficiency particulate filter respirator
Not to be exceeded without respiratory protection	2500 (lower and higher)	0	Self-contained breathing apparatus

Table 2. Threshold limit value for zinc oxide fumes according to OSHA and NIOSH, requirements for respiratory protection for zinc oxide fume.

2 Materials and methods

Several methods to examine an influence of the ALD treatment with DEZ, TMA and TTIP were applied. Due to positive dynamics using ZnO in paper deacidification from previous studies, samples treated with DEZ were widely analysed. All experiments were performed in Laboratory of Green Chemistry of Lappeenranta University of Technology.

2.1 ALD treatment

The treatment receipt was set accordingly to a film growing rate of ZnO, Al_2O_3 and TiO_2 [43]:
Al_2O_3 ~1.0 Å/cyc
ZnO ~1.5 Å/cyc
TiO_2 ~0.6 Å/cyc
Where the zinc and aluminium oxides had the same receipt where the one cycle were set at first to introduce DEZ (or TMA) 250ms followed by purge of N_2 3s, then pulse of H_2O 250 ms with

a following purging with N2 5s. Due to a slow reaction rate for the film growing, TiO_2 pulse time was increased and purging decreased: TTIP 1.5 s / N_2 1 s / H_2O 2 s / N_2 3 s. Temperature was set on 110° C for all runs. [43, 44]

2.2 pH examination

Cold extraction

Cold extraction method according to TAPPI Standard T-509 is used for pH value determination of an aqueous extract of the paper or cardboard. The method is destructive and required 1±0.01 g of dry sample cut on the size in 10x10 mm where the pieces are well mixed with each other. Then sample is placed into a flask and filled with 70 ml of MilliQ water (<11 µS/cm) where the temperature is varied at 20-25^{0}C (see Figure 5). Sample is mixed during 60 minutes on the rotary shaker with a speed in 100 rpm. [8]

Ready-made sample is examined by calibrated WTW electrode (pH-electrode SenTix 81) by buffer solution pH 4 and 7 (VWR AVS titronorm). During measurements, solution is analysed with the presence of paper pieces mixed by a magnet stirrer. Data is recorded after stabilization of pH value (or after 1 or 2 min) and averaged after 7 determinations. Deviation between each result was ±0.05. [8]

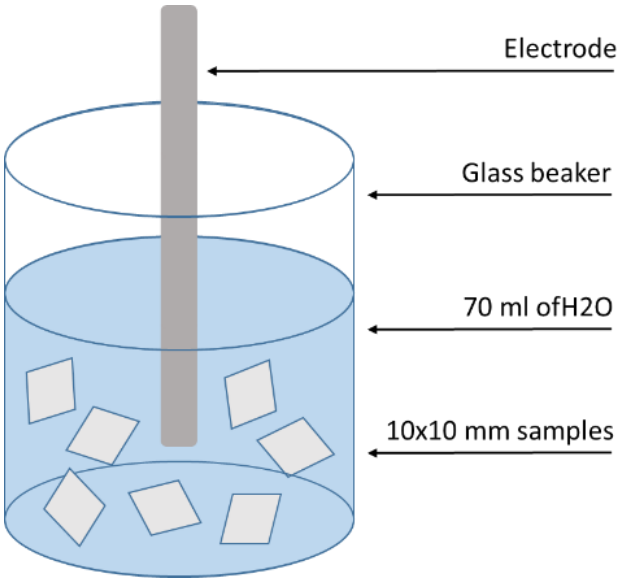


Figure 5. pH measurement by TAPPI Standard T-509

Contact method

Contact method is applied for pH value measurement by using flat tip electrode specifically designed for material surface pH analysis. HI99171 (Hanna Instruments, Inc) was used to perform pH examination of the samples. This method is non-destructive (Figure 6). Before measurement, under a sample is placed hydrophobic inert film to retain water on target area. Then the analysed surface of the sample is wetted ~10 µl with HI70960 electrolyte solution (30 mL) applied for sample preparation. Before each measurement, the flat tip probe was cleaned with HI700680P solution against cellulose deposits and rinsed with MilliQ water. [7, 45]

Figure 6. pH meter HI 99171.

2.3 Sample observation

Three types of samples were received from Finnish National Library to be analysed and treated. The samples were printed in 1891, 1937 and 1946. It is important to mention that between 1850-1985 paper manufactures have used a lot of acid containing sizing agents, which possibly defines the samples as acidic [22]. General condition of papers was deteriorated due to colour difference between the edge, middle and binding areas of the books. Mechanical strength and elasticity were low according to “first tough” during handling, papers were brittle. The books had specific smells, which represents a degradation of lignin and cellulose. Additionally, this acid hydrolysis process in the papers paper followed by distinctive smell could represent a presence of organic compounds such as benzaldehyde, toluene, ethyl benzene and ethyl hexanol.

[46]. Further, each sample was reviewed individually see Figures 7, 8 and 9 (images were taken by Sony Xperia Z3 with 20.7 MP camera).

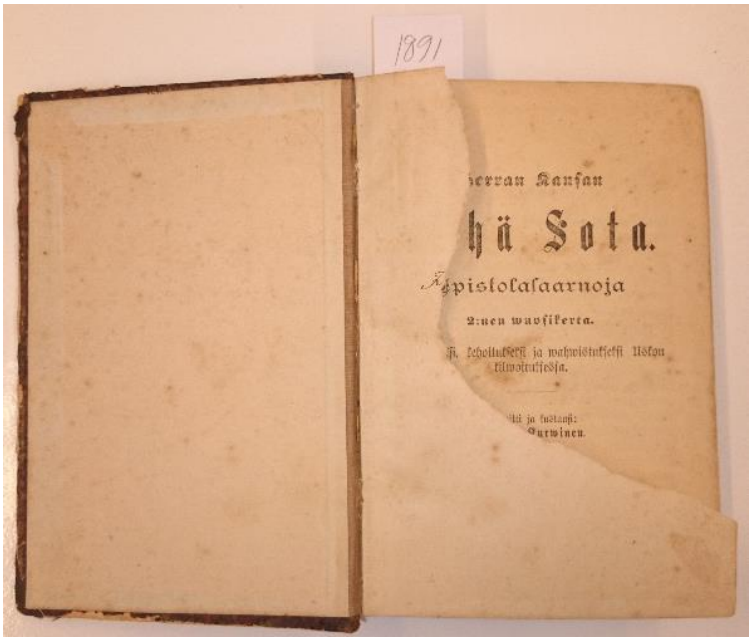


Figure 7. Sample 1 published in 1891

Sample “1891” was published in 1891. General condition of the book was worsened. Visually book papers were yellow with dark spots of potential fungi erosion. Yellowing was present on the margins and binding areas of the paper more intensely. Physically, the sample was brittle. Information about book manufacturing was limited. Suppositional pulping method is combined of chemical and mechanical pulping.

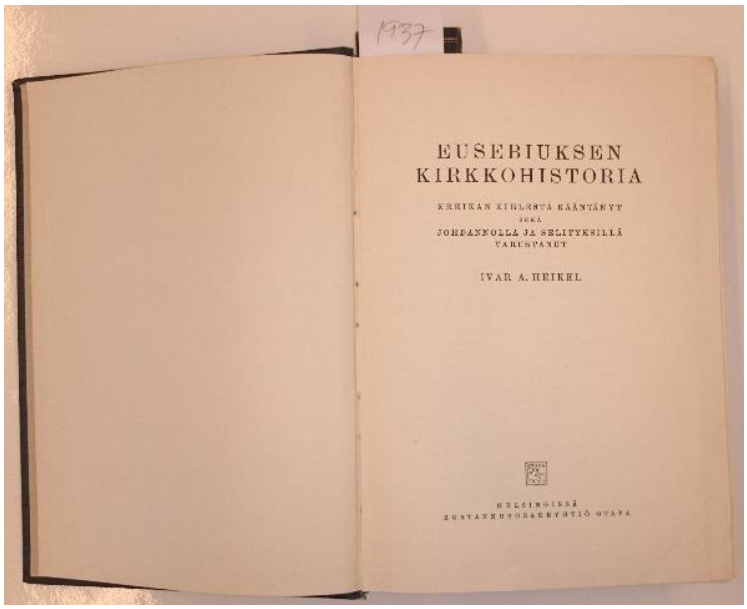


Figure 8. Sample 2 published in 1937

Sample “1937” was published in 1937. General condition of the book was worsened. Colour of papers was white. Yellowing was present on the margins and binding areas of paper. Physically, the sample was brittle. Suppositional pulping method is chemical pulping.

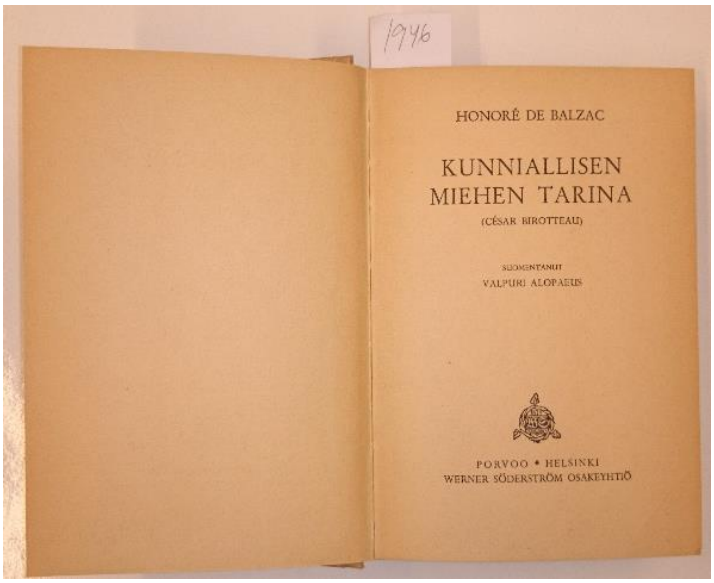


Figure 9. Sample 3 published in 1946

Sample "1946" was published in 1946. General condition of the book was worsened. Visually papers were yellow with more intense yellowing on the edges of the paper. Physically, the sample was brittle. Suppositional pulping method is mechanical pulping.

2.4 TFS 200 and TFS 500

Thin Film System (TFS) is ALD systems designed for coating of thin films on the substrate of choice, created by Finnish company Beneq. Applied ALD system TFS 200 (see Figure 10) TSF 500 (see Figure 11) has high flexibility to work with multi structural surfaces including porous materials, particles, wafers, 3D objects at temperature ranges from 25 till 500^0 C [13]. Various precursors can be used. Reactor size the both systems is 200 mm diameter, 5 mm height.

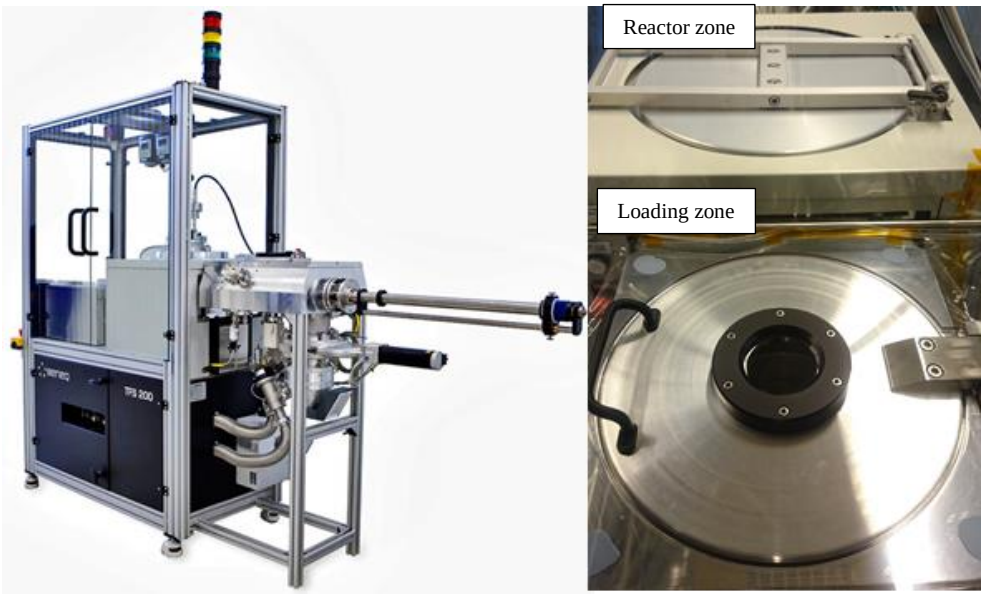


Figure 10. TFS 200 [12]

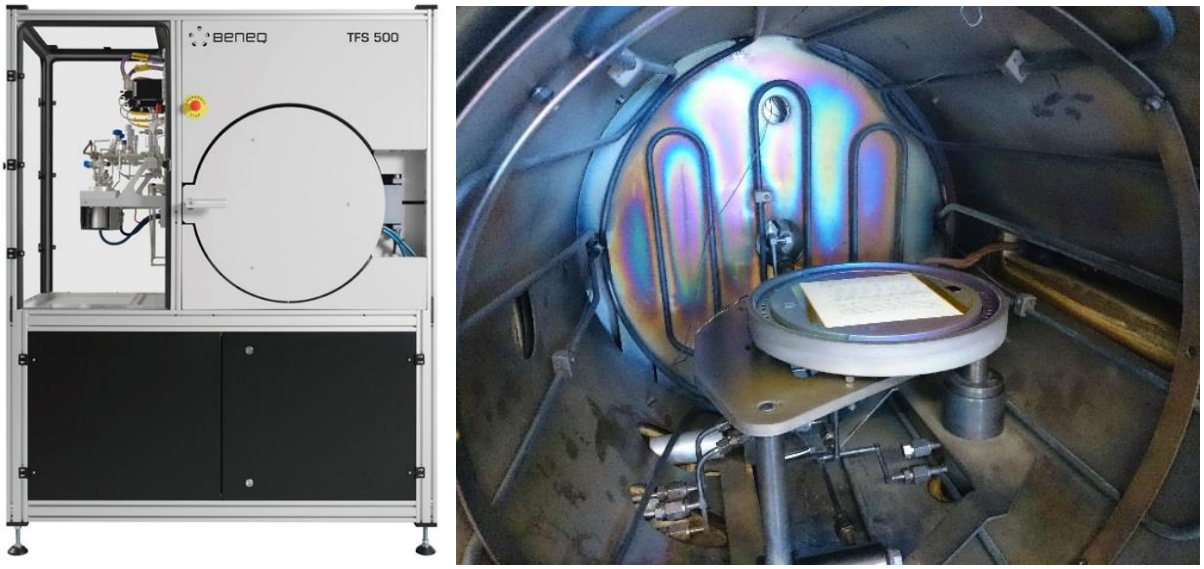
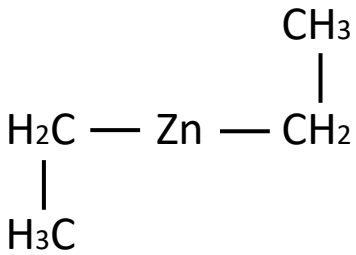


Figure 11. TFS 500 and its reactor (without lid) with a sample. [12]

2.5 Precursors

As the major objective of this studies is aimed to deliver an alkali agent onto a paper's structure to neutralize acidity and to create an alkali buffer. Therefore, the oxidation of organometallic compounds to produce basic oxide is required for the process.

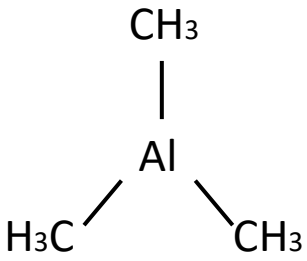
Diethylzinc (DEZ)



Diethylzinc is organozinc compound with a zinc in centre and two ethyl groups; abbreviated as $Zn(C_2H_5)_2$ or DEZ; oxidized to zinc oxide. The chemical nature of zinc is pyrophoric, corrosive, colourless liquid and slightly toxic for the environment. Areas of use are semiconductors, barrier films, deacidification, and aircraft fuel. [26, 47]

1) $Zn(C_2H_5)_2 + -O - H \rightarrow -O - Zn(C_2H_5) + C_2H_6$
2) $H_2O + -O - 2Zn(C_2H_5) \rightarrow -O - ZnO + 2C_2H_6$

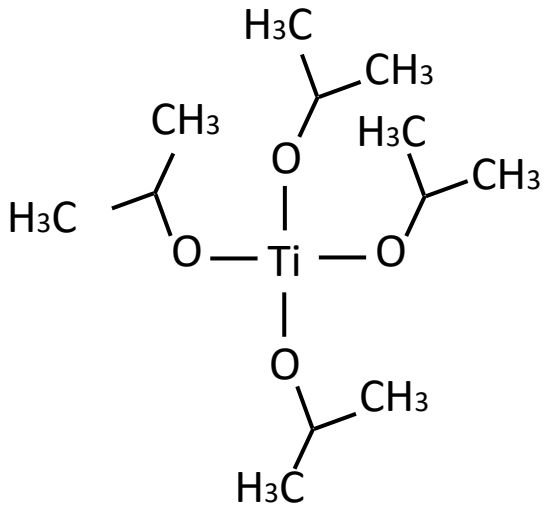
Trimethylaluminum (TMA)



Trimethylaluminum is organoaluminum compound with a two aluminum surrounded by three methyl groups; abbreviated as $Al_2(CH_3)_6$ or TMA; oxidized to aluminum oxide. The chemical nature of zinc is pyrophoric (highly reactive with water and air), corrosive, colourless liquid. Areas of use are semiconductor, barrier films, and aviation fuel. Al_2O_3 is a final product due to oxidation of TMA in ALD process. [43]

1) $Al_2(CH_3)_3 + -O - H \rightarrow -O - Al(CH_3)_2 + CH_4$
2) $2H_2O + -O - Al(CH_3)_2 \rightarrow -O - Al(OH)_2 + 2CH_4$

Titanium tetraisopropoxide (TTIP)



Titanium tetraisopropoxide (TTIP) is an alkoxode of titanium(IV). TTIP is non- pyrophoric, colourless or slightly yellow liquid, which is soluble in benzene, ethanol, and chloroform. Used in organic synthesis and material science. TiO_2 is the final product due to oxidation of TTIP in ALD process. [48]

2.6 Ellipsometer

Spectroscopic ellipsometry (Figure 12) was applied to characterize a layer thickness of deposited the precursors on silicon wafers by ALD. The purpose of use the ellipsometer was to evaluate a homogeneity of the reactants layer formation. Data were taken from the silicon wafers placed between the sample and in areas where the precursors injects and pumped away (see Figure 13).

Method uses polarized light to analyse its polarization changes due to interaction with the sample's surface. Ellipsometry can be applied to determine thin film properties such as film thickness, refractive index, optical constants and surface roughness. Data is represented in values Delta (Δ) and Psi (Ψ) which can define the material properties of choice only after applying a model with a number of algorithms and equations. [49]

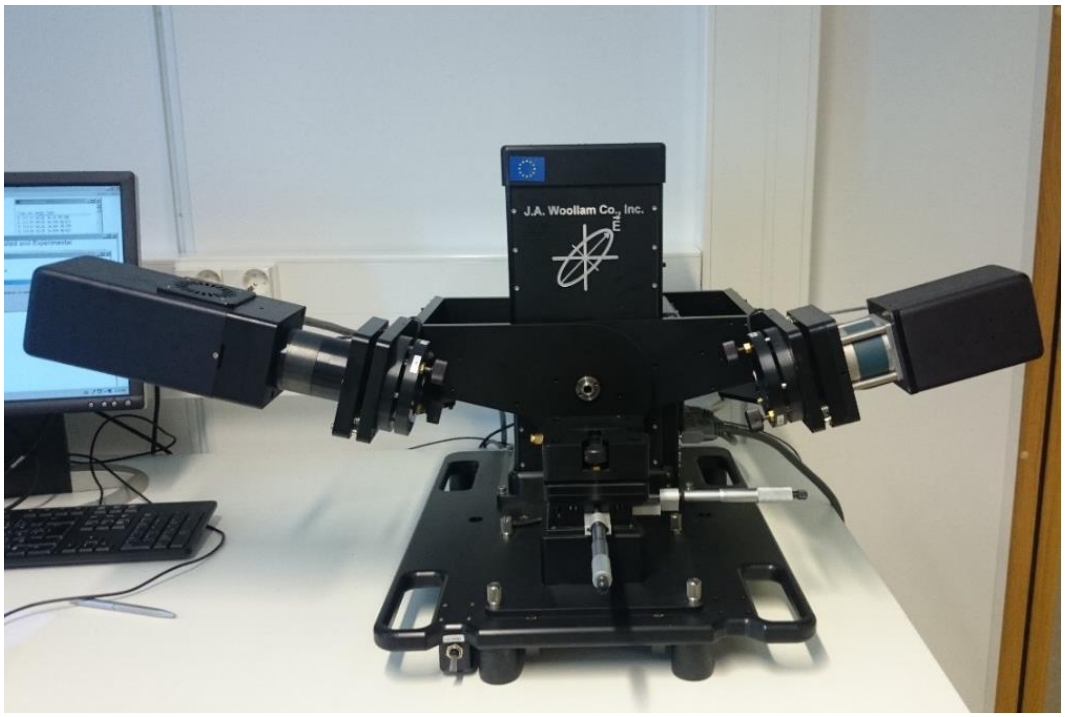


Figure 12. ESM-300, J.A. Woollam Co., Inc applied in this work.

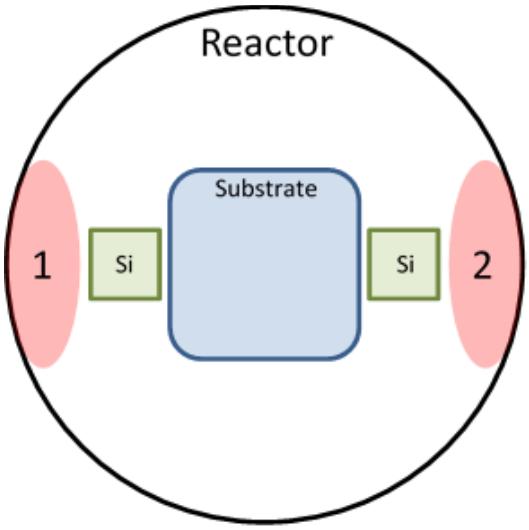


Figure 13. Allocation of substrates in the reactor of TFS 500. 1 is inject zone, zone 2 is exhaust.

2.7 SEM examination

Scanning electron microscope (SEM) is the electron microscope (see Figure 14) designed to image the surface of an object with a high (0.4 nm) spatial resolution and information on the composition, structure and other properties of the surface layers. The scanning is based on the principle of electron beam interaction with the study object. [11]

SEM phenomenon occurs at the surface of sample due to intense bombarding with ions in Focused Ion Beams (FIB) and electrons in SEM, which arises an accumulation of chargers. Therefore, this supports a creation of an electric potential, which consequently starts to growth in impacted area till the state of saturation. The condition is forcing electrons with a lower potential repel. Reflected electrons are directed to upper part of the chamber where the SEM's screen display converted image, which refers to chamber's plafond. [11]

Modern SEM allows working in a wide magnification range from about 10- to 1000000-fold, which is approximately 500 times larger than the top limit of optical microscopes. Currently, SEM is used virtually in all fields of science and industry, such as biology, material science. There is a huge number of companies produced a number of different designs and types of SEM equipped with detectors of various types. In this study, Hitachi S-4800 SEM was applied to examine the surface structure of the treated and non-treated samples.

Figure 14. Hitachi S-4800 scanning electron microscope (SEM) was used in this study [11]

2.8 Contact angle

Contact angle is an optical wettability examination of a solid surface characteristics where the liquid interface is locally introduced on the solid surface. Wetting is a physical interaction of the liquid with the surface of a solid body to define a CA Wetting properties are conventionally measured through the liquid's attachment to the surface and quantified by the Young equation. [9]

The possible scenarios when the liquid contacts a solid body:

- Liquid molecules are attracted to each other more than the molecules of a solid material, which results a retaining of spherical shape of the liquid drop due to the force of attraction. This explains hydrophobic nature of the solid surface where the surface cannot be wetted or it takes longer period of time.
- Molecules of fluid attract to each other less than the molecules of a solid substance. As a result, adhesion of the liquid is stronger with the surface and the liquid drop spreads out over hydrophilic surface.

In the frames of this research work, CA apparatus (see Figure 15) was applied to determine an increase of hydrophilicity of the samples after the ALD process.

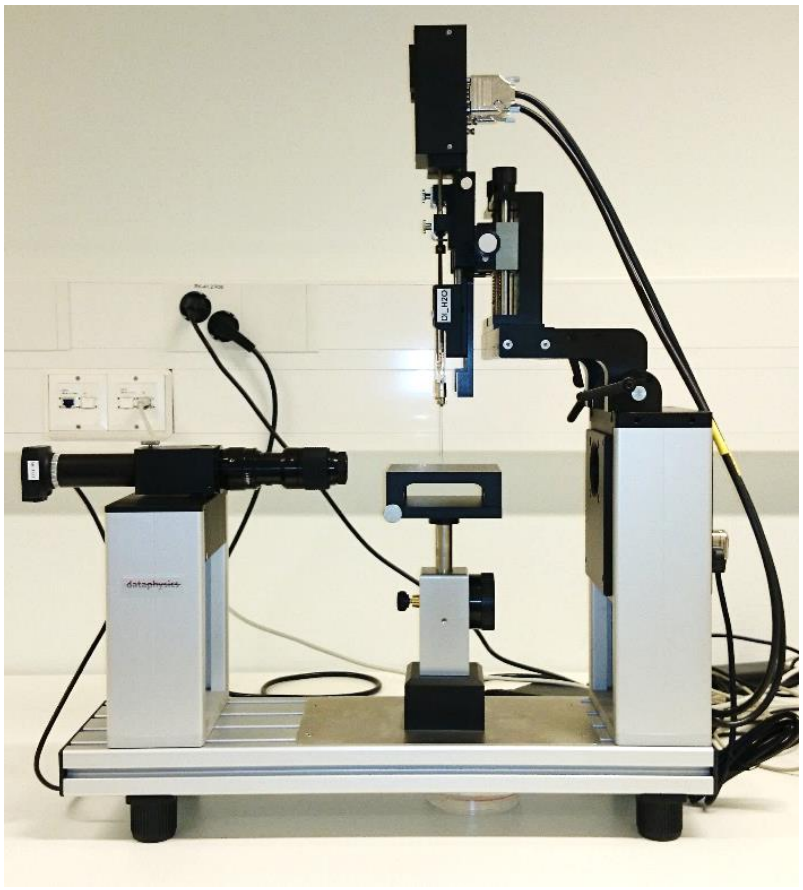


Figure 15. OCA 15EC (Dataphysics)

2.9 Mechanical strength

Paper's mechanical endurance were tested vie paper folding technique, which counts an amount of manual double folding of a paper stripe until its break. The method was partly based on ISO 5626:1993 which is used for paper endurance determination via folding. [10]

Samples have to be sized 50x100 mm. One complete folding was counted as a double fold of backwards and forwards from the middle of the sample.

3 Results and discussion

The experimental part of this study is aimed to define best paper preservation process by ALD in depositing alkali agents such as DEZ, TMA, and TTIP. Initial step of analysis starts with a pH value determination and continued with optical observations, mechanical strength and hydrophilicity evaluations. All samples manipulations are performed with worn gloves and in

clean conditions. Glass dishes for experiments were washed with concentrated nitric acid and rinsed with distilled water.

To identify a deacidification potential of the precursors sample 1937 was chosen. Untreated pH value of 1937 was 3.9 by cold extraction. ALD recipe for DEZ and TMA was the same: DEZ/TTIP 250ms / N_2 3s / H_2O 250 ms N_2 5s. Due to a slow reaction rate for the film growing, TiO_2 pulse time was increased and purging decreased: TTIP 1.5 s / N_2 1 s / H_2O 2 s / N_2 3 s. 2D reactors of TFS 200 and TFS 500 are capable to allocate one sample per treatment. The process temperature was chosen 110^0 C due to necessity in higher reaction rate and avoidance of CVD reaction. Set temperature has no significant effect onto cellulose paper, but leads to evaporating of physically bounded water in the temperature range between 90-150° C. Higher temperature ranges lead to a possible thermal depolymerisation process depending on cellulose paper composition. Active decomposition starts with a rapid loss of mass from 280-370° C. [22]. Samples were vacuumed under 1 mbar pressure and stored with a temperature in 100-110^0 C during one hour till the process was initiated. Together with the samples two silicon wafers were placed in areas where the precursor is injected and pumped away (Figure x bellow - several). It is necessary to analyse homogeneity of the deposition based on the film thickness on the silicon wafers. Amount of cycles was varied from 100 to 250.

Recorded data presented in Table 3 is showing that precursors TMA and TTIP has slightly increased pH value of the sample. TMA and TTIP have shown an increase of pH till 200 (pH 4.8) and 100 (pH 4.2) cycles, where after the value remained stable without further growth. DEZ represents a significant growth of pH value due to an alkali nature of zinc oxide, where neutral condition was reached below 150 (pH 7.1) cycles. Additionally, paper printed nowadays was examined as a comparable example with a pH value 9.6. Modern paper manufactures remove lignin and other additives which could decrease paper's brightness and general durability.

	1937			Paper 2015
Cycles	TMA	TTIP	DEZ	Untreated
	pH			
0	3.9	3.9	3.9	9.6
100	4.4	4.2	6.4	-
150	4.6	4.2	7.1	-
200	4.8	4.2	7.2	-
250	4.8	4.2	7.2	-

Table 3. Analyses of sample 1937 after treatment with TMA, TTIP and DEZ

Therefore, major analytical efforts will be directed to study deposition of ZnO due to its positive results in acid content deacidification in the papers. Precursors TMA and TTIP are excluded for further study due to a low deacidification capacity. Next experiments will be continued together with samples 1891 and 1946.

3.1 Deacidification

Acidity of samples 1891, 1937 and 1936 was analysed before and after deposition of zinc oxide. Cold extraction and contact methods were applied to measure pH value. TAPPI Standard T-509 requires samples weight in 1 g. Accordingly, received samples were sized to be equal 1 g [9]:

- 1891 size 120x150 mm
- 1937 size 105x106 mm
- 1946 size 122x122 mm

Cold extraction is a destructive method where a sample has to be reduced in 1 square cm as it is presented in Figure 16. Therefore, initial pH value determination was performed by contact method (see Figure 17) before grinding up the sample. Significant advantage of this methods comes from its ability of multi spot measurement, which supports a detection of a precursor's coating homogeneity against acidity. Nevertheless, several samples for TAPPI Standard T-509 were prepared separately in parallel to distinguish a possible pH value shift from an apply of electrolyte solution. Significant measurement data deviations were not detected. Each ALD receipt was repeated three times for precise pH examination. [8, 9, 45]

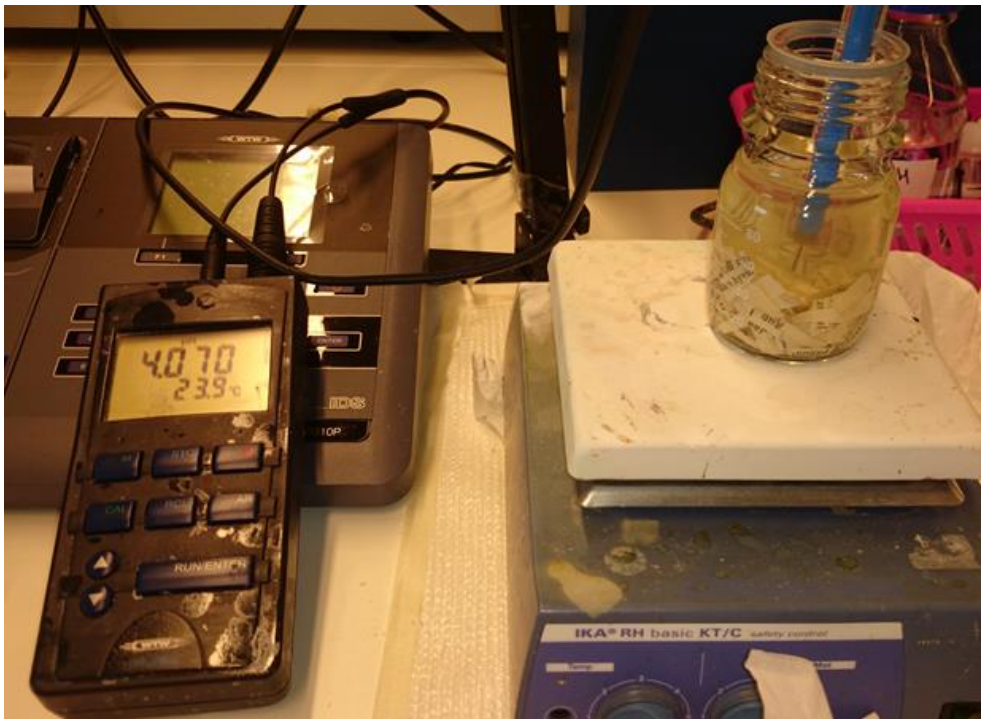


Figure 16. Measurement of pH by TAPPI Standard T-509. Sample is reduced on 1 square cm and mixed with water.

Figure 17. Examination of sample 1891 with contact method.

According to the results collected from the two methods of pH value measurement, paper deacidification with a use of ALD has to be set individually due to the differences in composition, density of the fibres, surface area, and acidification rate. Paper treatment was performed with a

use of DEZ at constant parameters (ALD receipt), only varying a number of cycles. Three samples were treated and analysed to determine pH value change. Table 4 presents the gathered results, which were observed on figures 18, 19 and 20.

Figure 18 shows the deacidification dynamics with a deposition of ZnO. According to results taken from cold extraction method, prompt pH value growth can be seen where from pH 5 (untreated) it raises till the target value with 75 cycles with DEZ and remains stable. Contact method represents more gradual growth, which starts from 4.3 (reference) and becomes neutral closer to 150 cycles.

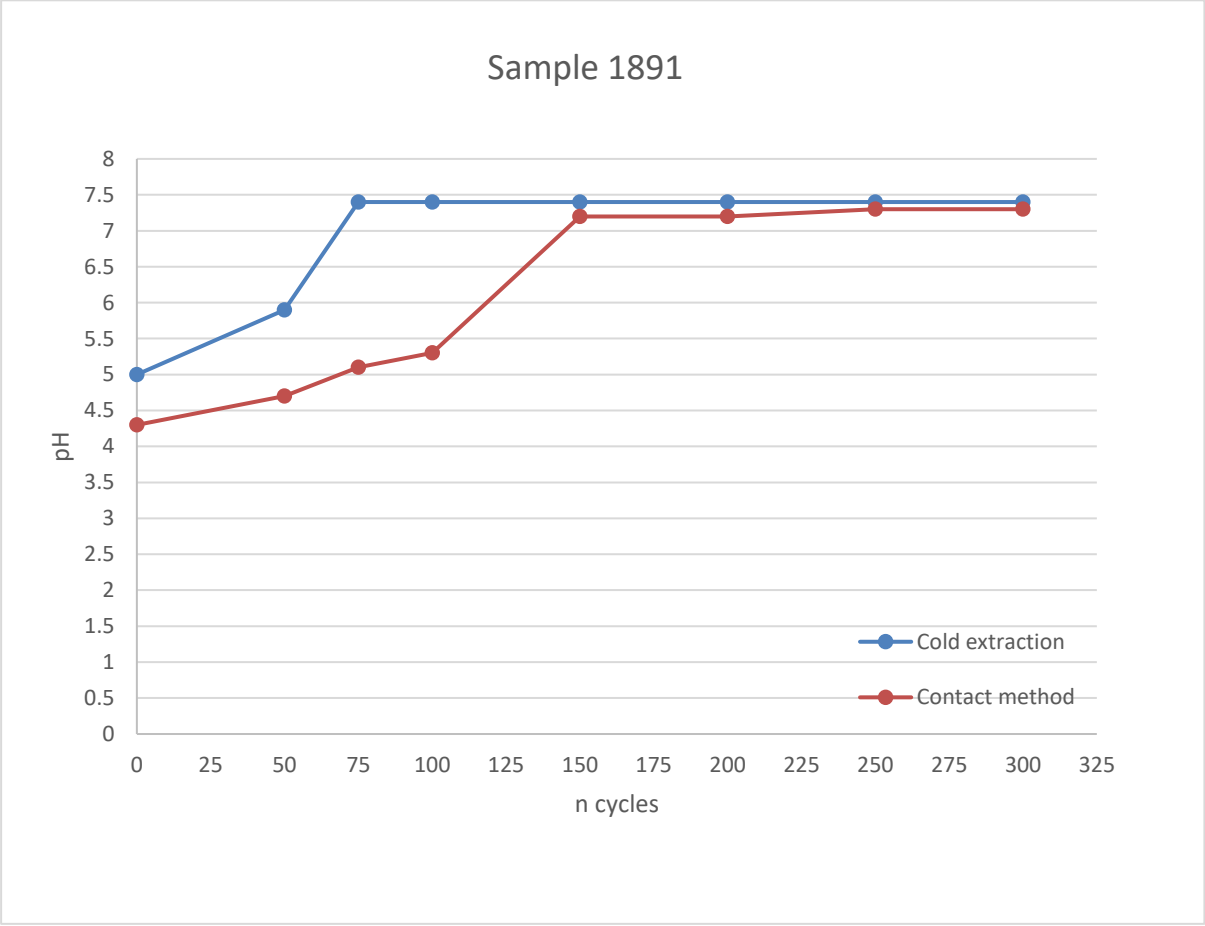


Figure 18. pH value determination of sample 1891 by cold extraction and contact methods after ALD treatment with DEZ

Figure 19 presents an acid neutralisation from sample 1937. Cold extraction method shows a gradual increase of pH which starts from 3.7 (untreated) until 7.0 with 100 cycles of DEZ. Contact methods has different picture, where until 100 cycles pH value stays in a small range

between 3.1 (untreated) to 3.5. Further, pH is significantly raising and 250 treatment cycles shows value in 7.1.

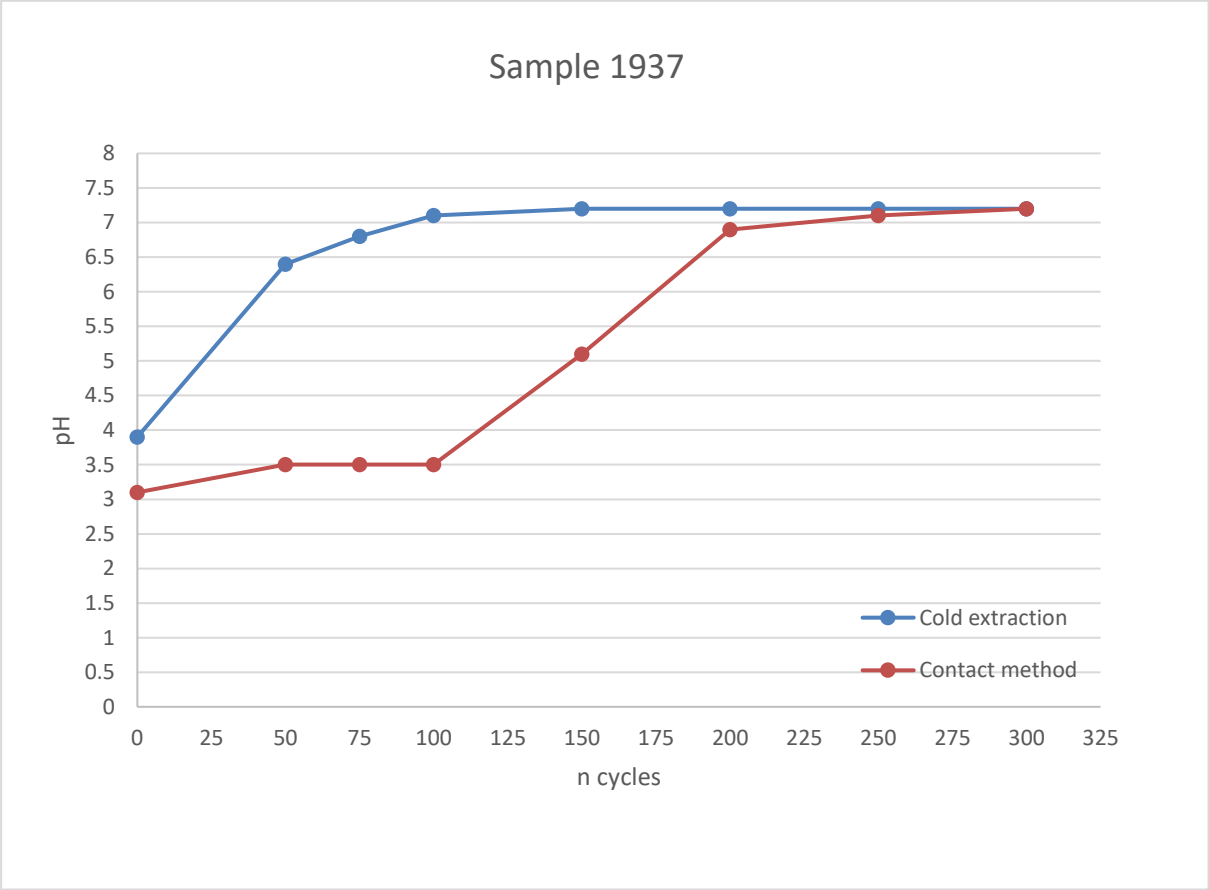


Figure 19. pH value determination of sample 1937 by cold extraction and contact methods after ALD treatment with DEZ

Figure 20 is representing deacidification dynamics of sample 1946. Cold extraction method shows a gradual increase of pH which starts from 3.9 (untreated) until 7.0. Contact methods has different picture, where until 150 cycles pH value stays in a small range between 3.1 to 3.4. Further, pH is significantly raising where complete deacidification according to both method results require 300 cycles of DEZ.

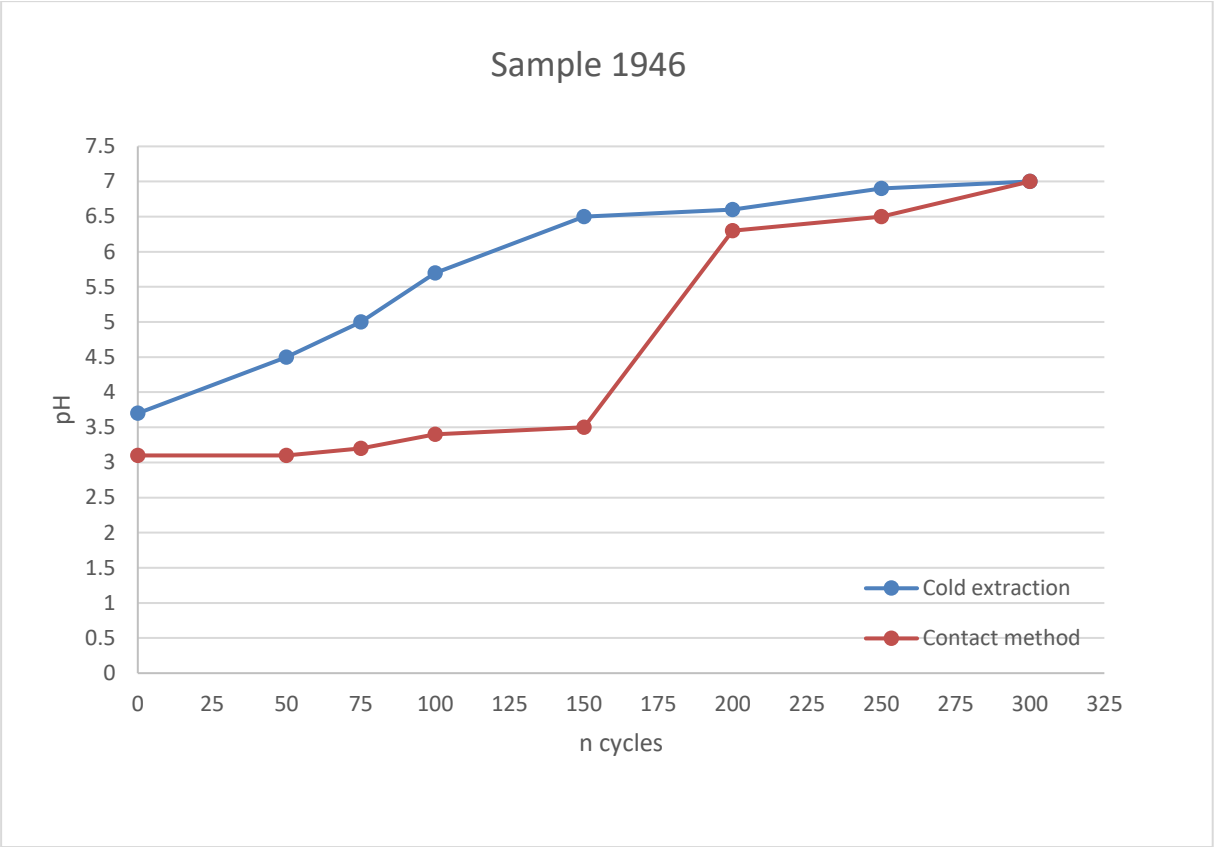


Figure 20. pH value determination of sample 1946 by cold extraction and contact methods after ALD treatment with DEZ

DEZ	Cold extraction			Contact method		
	1891	1937	1946	1891	1937	1946
Cycles	pH					
0 (ref)	5	3.9	3.7	4.3	3.1	3.1
50	5.9	6.4	4.5	4.7	3.5	3.1
75	7.4	6.8	5	5.1	3.5	3.2
100	7.4	7.1	5.7	5.3	3.5	3.4
150	7.4	7.2	6.5	7.2	5.1	3.5
200	7.4	7.2	6.6	7.2	6.9	6.3
250	7.4	7.2	6.9	7.3	7.1	6.5
300	7.4	7.2	7.0	7.3	7.2	7.0

Table 4. Results of pH examination

Visual observation of treated samples

Possible cosmetic impacts were observed from camera images. The observation was targeted to define any quality changes and deterioration of the colour or printing inks after ALD treatment. 200 cycles treatment was done with use of DEZ under 110^0 C. Samples on Figures 21,

22 and 23 remain readable and negative cosmetic impacts were not detected. ALD treatment do not have decolourisation and tinting effects to inks, dyes and adhesives.

Visually, samples were remained the same comparing with their reference. Sample 1946 (Figure 23) after treatment got a whitening effect, which can be clearly seen in Figure 24. The treated sample was attached to the reactor from the edges, 6-8 mm of the sample was covered with a tape which keeps area colour same as the reference. Additionally, two stripes of inert film were attached in parallel to tape to clarify whitening phenomena and surface reagent distribution. The red circles are highlighting the area of whitening effect.

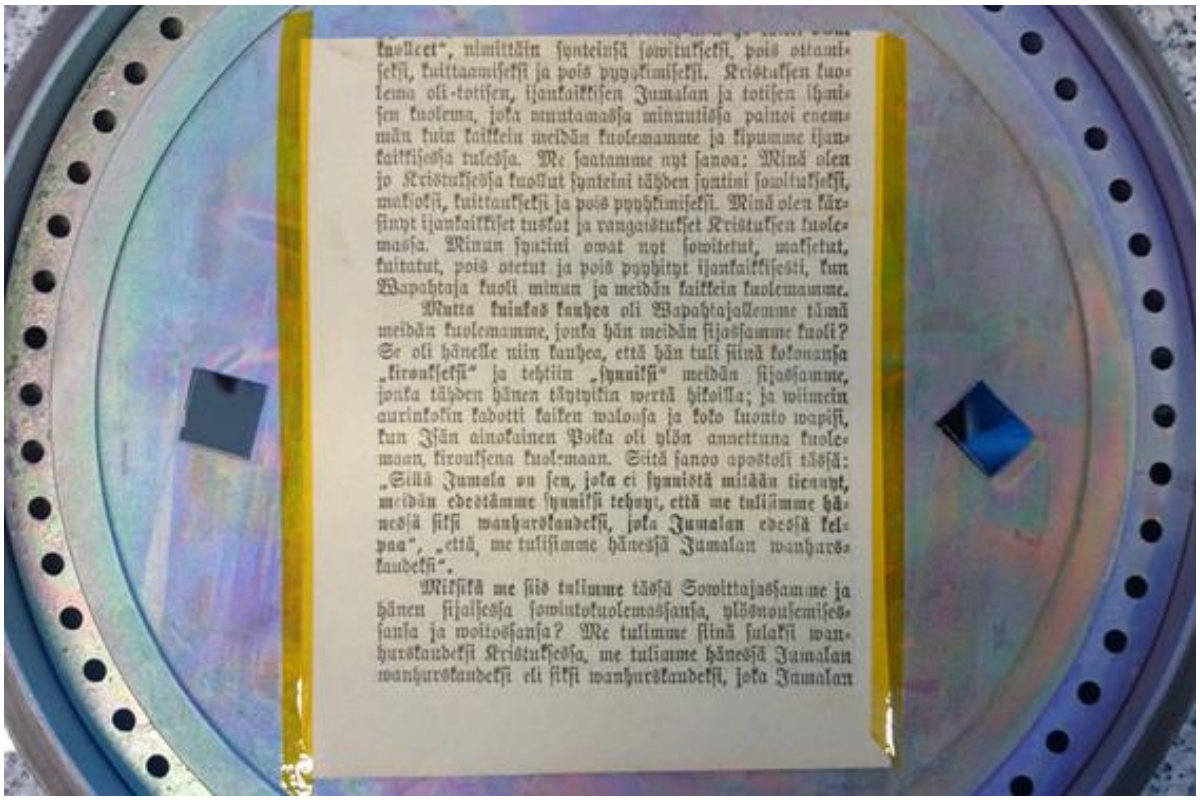
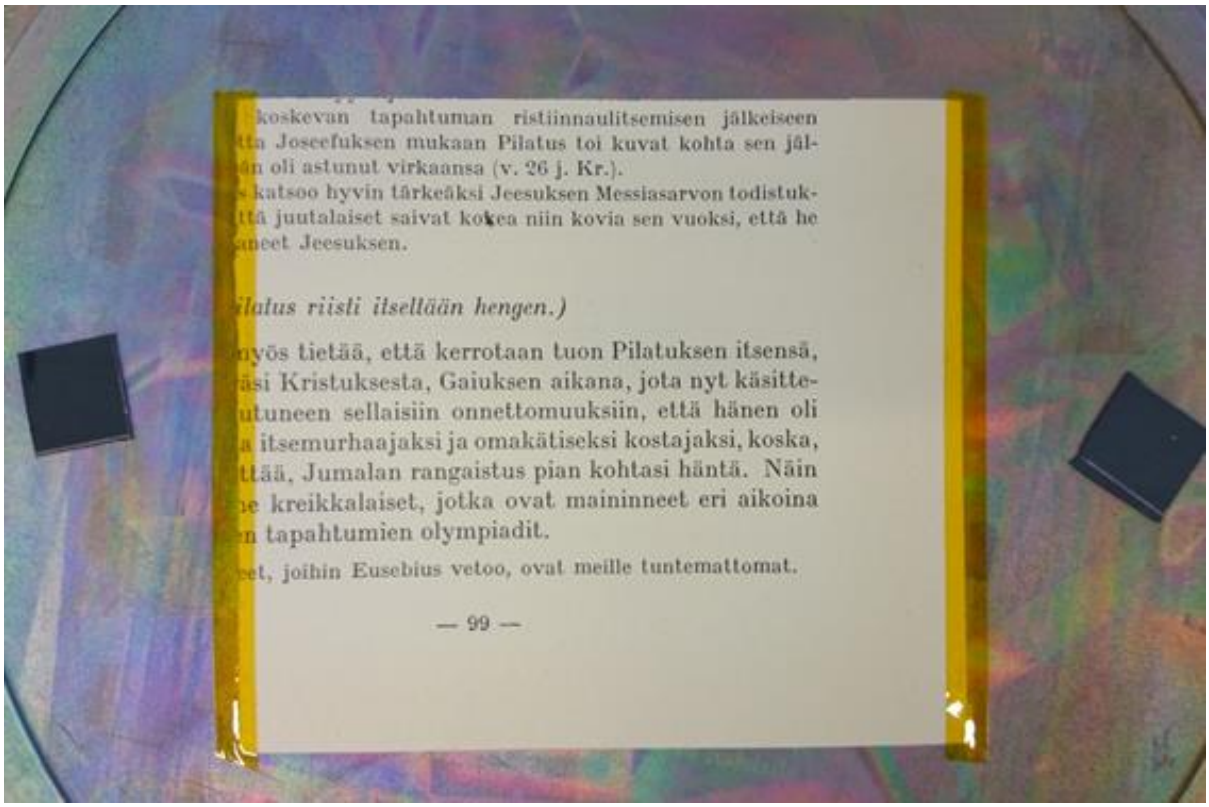


Figure 21. Sample 1891 treated with DEZ 200 cycles 110^0 C



koskevan tapahtuman ristiinnaulitsemisen jälkeiseen
tta Joosefuksen mukaan Pilatus toi kuvat kohta sen jäl-
n oli astunut virkaansa (v. 26 j. Kr.).
katsoo hyvin tärkeäksi Jeesuksen Messiasarvon todistuk-
ttä juutalaiset saivat kokea niin kovia sen vuoksi, että he
neet Jeesuksen.

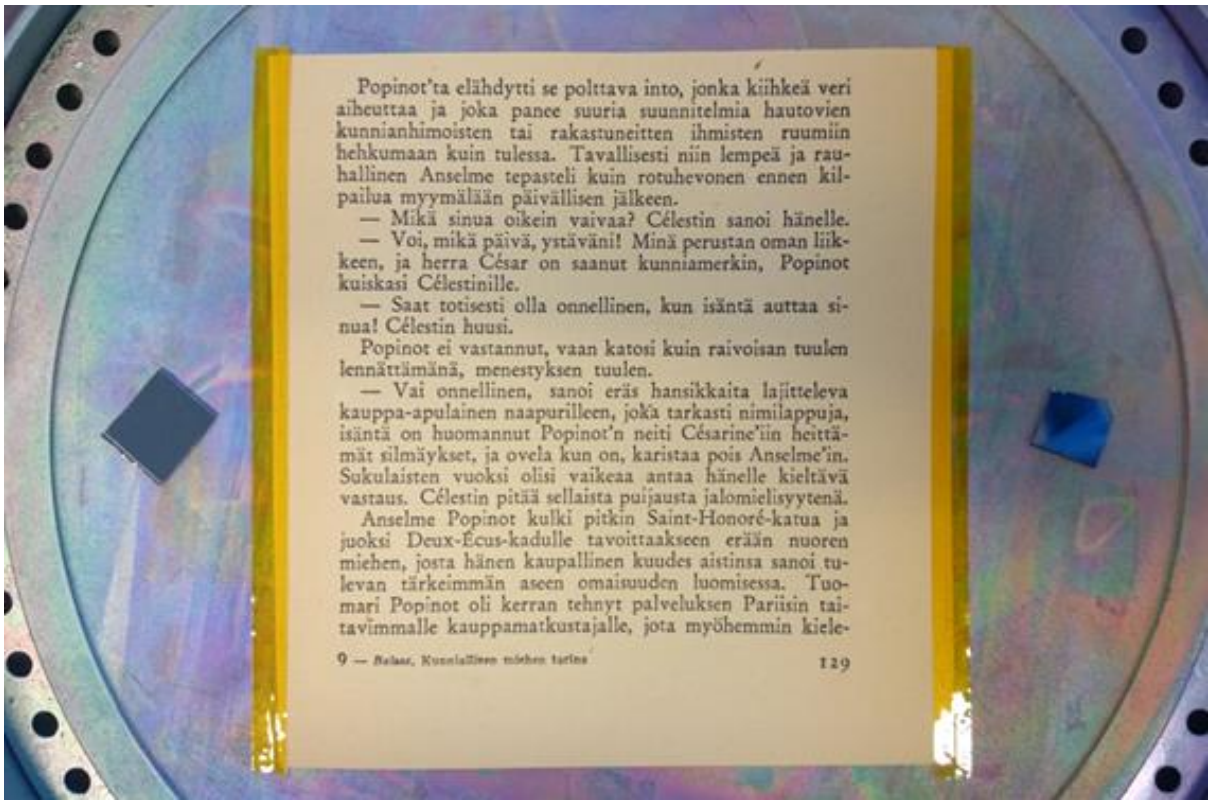
ilatus riisti itsellään hengen.)

myös tietää, että kerrotaan tuon Pilatuksen itsensä,
äsi Kristuksesta, Gaiuksen aikana, jota nyt käsitte-
utuneen sellaisiin onnettomuuksiin, että hänen oli
a itsemurhaajaksi ja omakätiseksi kostajaksi, koska,
ttää, Jumalan rangaistus pian kohtasi häntä. Näin
e kreikkalaiset, jotka ovat mainineet eri aikoina
n tapahtumien olympiadit.

et, joihin Eusebius vetoo, ovat meille tuntemattomat.

— 99 —

Figure 22. Sample 1937 treated with DEZ 200 cycles 110^0 C



Popinot'ta elähdytti se polttava into, jonka kiihkeä veri aiheuttaa ja joka panee suuria suunnitelmia hautovien kunnianhimoisten tai rakastuneitten ihmisten ruumiin hehkumaan kuin tulessa. Tavallisesti niin lempeä ja rauhallinen Anselme tepasteli kuin rotuhevonen ennen kilpailua myymälään päivällisen jälkeen.

— Mikä sinua oikein vaivaa? Célestin sanoi hänelle.

— Voi, mikä päivä, ystäväni! Minä perustan oman liikkeen, ja herra César on saanut kunniamerkin, Popinot kuiskasi Célestinille.

— Saat totisesti olla onnellinen, kun isäntä auttaa sinua! Célestin huusi.

Popinot ei vastannut, vaan katosi kuin raivoisan tuulen lennättämänä, menestyksen tuulen.

— Vai onnellinen, sanoi eräs hansikkaita lajitteleva kauppa-apulainen naapurilleen, jokä tarkasti nimilappuja, isäntä on huomannut Popinot'n neiti Césarine'iin heittämät silmäykset, ja ovela kun on, karistaa pois Anselme'in. Sukulaisten vuoksi olisi vaikeaa antaa hänelle kieltävä vastaus. Célestin pitää sellaista puijausta jalomielisyytenä.

Anselme Popinot kulki pitkin Saint-Honoré-katua ja juoksi Deux-Écus-kadulle tavoittaakseen erään nuoren miehen, josta hänen kaupallinen kuudes aistinsa sanoi tulevan tärkeimmän aseen omaisuuden luomisessa. Tuomari Popinot oli kerran tehnyt palveluksen Pariisin taitavimmalle kauppamatkustajalle, jota myöhemmin kiele-

9 — Balzac, Kunniallisen miehen tarina 129

Figure 23. Sample 1946 treated with DEZ 200 cycles 110^0 C

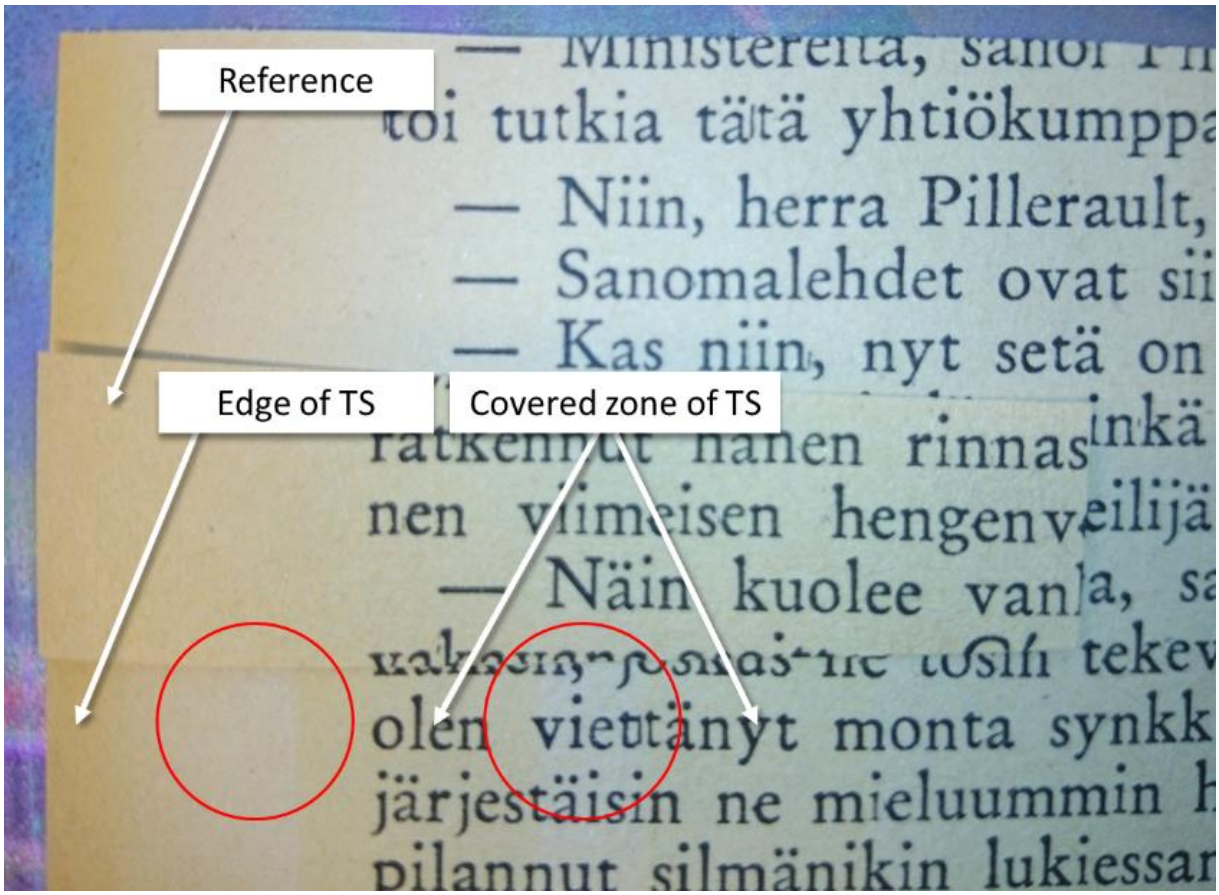


Figure 24. Whitening effect on sample 1946 after treated with DEZ 200 cycles 110^0 C

3.2 Ellipsometry and coating homogeneity

Ellipsometry helped to analyse a diffusion of the precursor over the samples via observation of the layer thickness deposited on silicon wafers. One silicon wafer was placed between the area precursors injection area and the sample, and another one in the same way in opposite place near exhaust zone (see Figure 25).

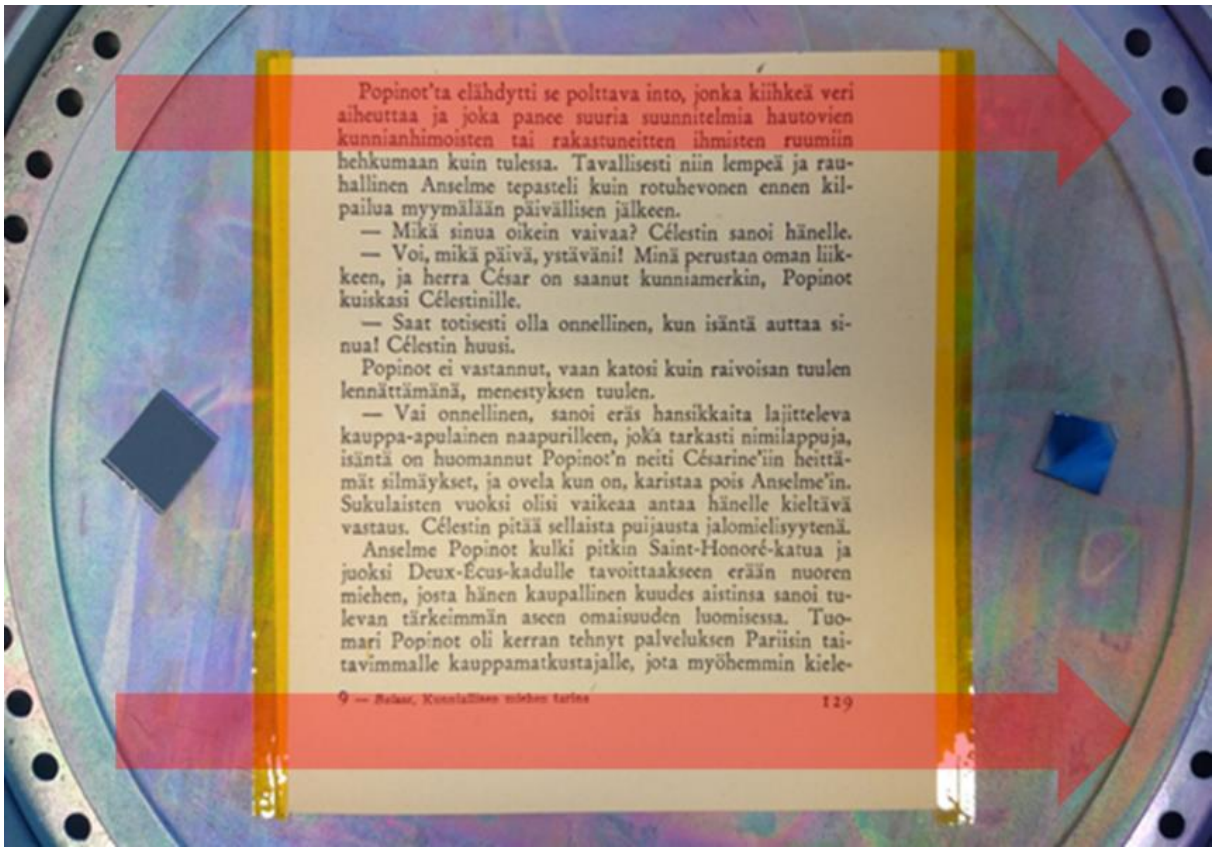


Figure 25. Sample 1946 and silicon wafers allocation in TFS 500 reactor, red arrows represent a direction of precursors flow.

Experimental set up was adjusted in TFS 500 under 110^0 C. Sample 1946 was examined. Data from the three times repeated ALD sessions was averaged in Figure 26, which shows thickness of the film over certain amount of cycles. Inject zone samples have a gradual film growth followed with amount cycles increase. Thickness of exhaust zone samples is remained insignificantly changed from 50 till 250 cycles. Abnormal layer stability of exhaust zone silicon wafers a reason of high paper's surface area with a high density of –OH groups, which are forcing DEZ to actively react through the sample's surface area. Concluding the results, high reactivity of paper with DEZ was detected due to a significant loss of film growth in the exhaust area. This condition is raising a question of a possible uneven deacidification.

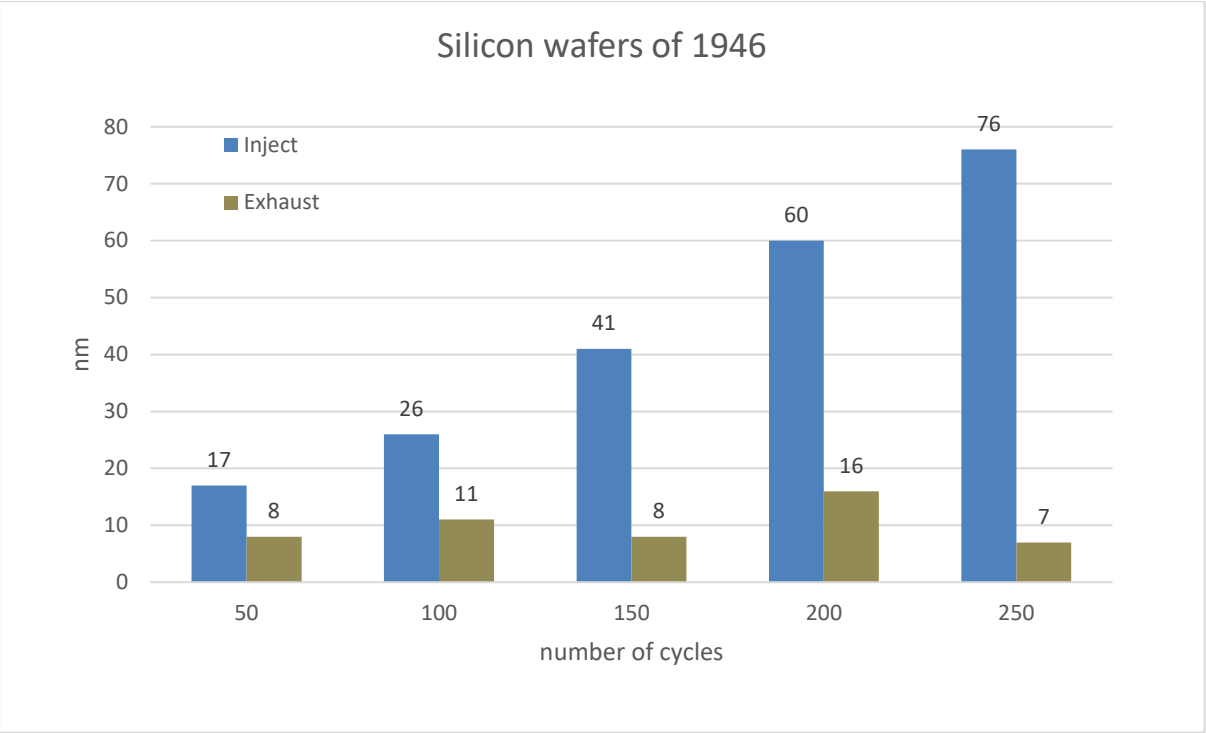


Figure 26. Analysis of silicon wafers placed between precursor inject zone and sample 1946, and another in exhaust zone.

Therefore, sample 1946 surface was observed in many points to identify homogeneity of paper deacidification with contact method. Figure 27 shows three measurement point in zones 1, 2 and 3. Precursor inject zone is on the left and exhaust is on the right. Initiated treatment had 200 cycles of DEZ under 110^0 C. Data from each zone was averaged and placed in Table 5. Samples 1891 and 1946 have shown a complete deacidification. Sample 1946 has pH value differences between paper edge 2.8 and middle 3.3. Sample 1937 is showing stable acidity neutralization until zone 3 which drops pH value to 4.5. General picture of deacidification homogeneity can be evaluated as good.

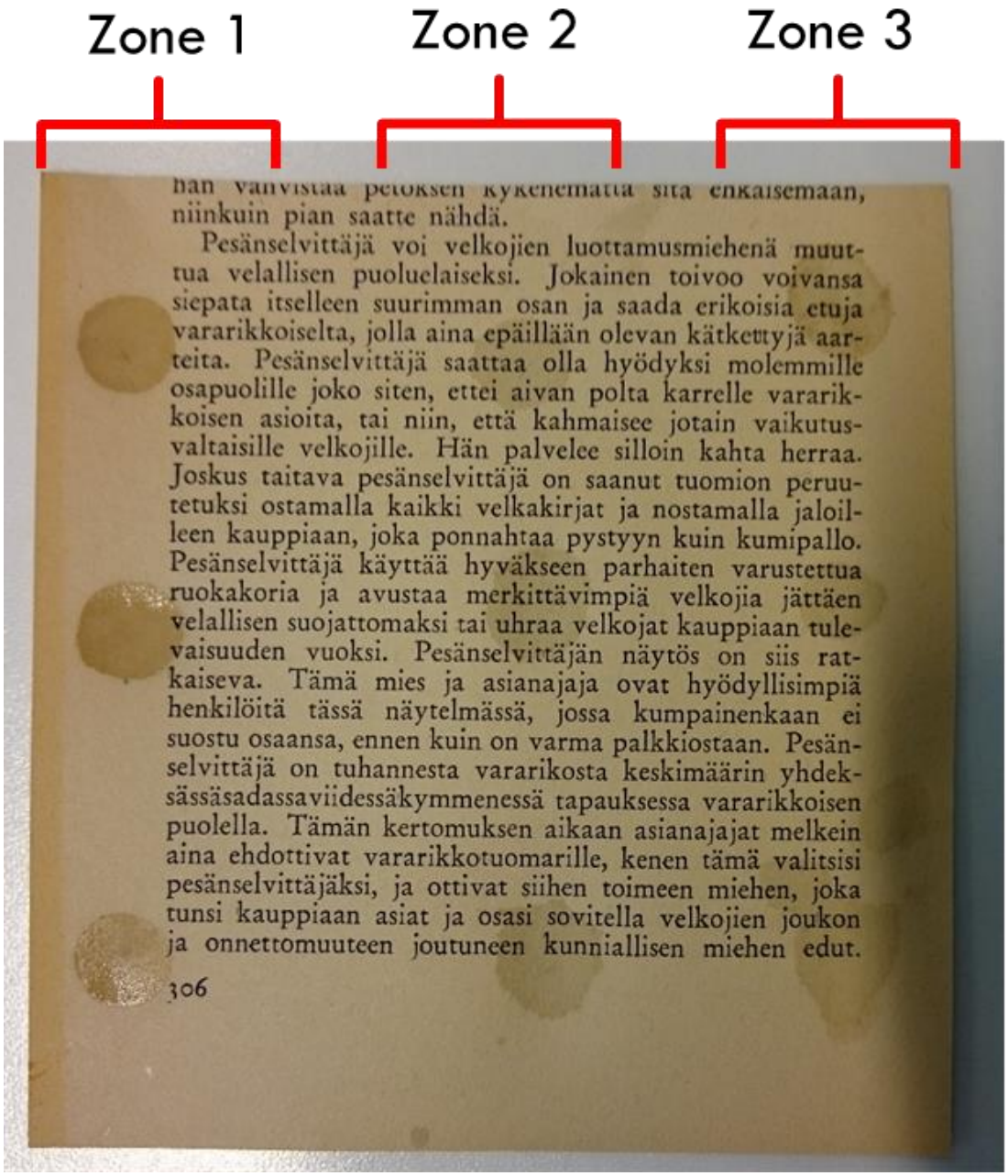


Figure 27. Image of sample 1946 right after pH examination by contact method over surface area.

Sample	Reference	Treated Z1	Treated Z2	Treated Z3
1891	4.3	7.2	7.2	7.2
1937	3.1	7.1	7.1	4.5
1946	2.8 (edge) 3.3 (mid)	7.0	7.0	6.9

Table 5. pH observation over sample 1946 surface. 200 cycles of DEZ.

3.3 SEM

The possible mechanical or chemical damage on the samples after ZnO deposition was observed with SEM. The analyse was aimed to determine physical and chemical impacts on the paper after ALD treatment. The samples (1891, 1937 and 1946) were treated with 200 cycles of DEZ under 110^0 C.

Figure 28 is presenting sample 1891. According to the result, paper fibres do not have any quality degradation. Comparison between the reference and the treated samples do not have critical differences. On each magnification level, fibre cracking, decay, volume loss and CVD were not detected.

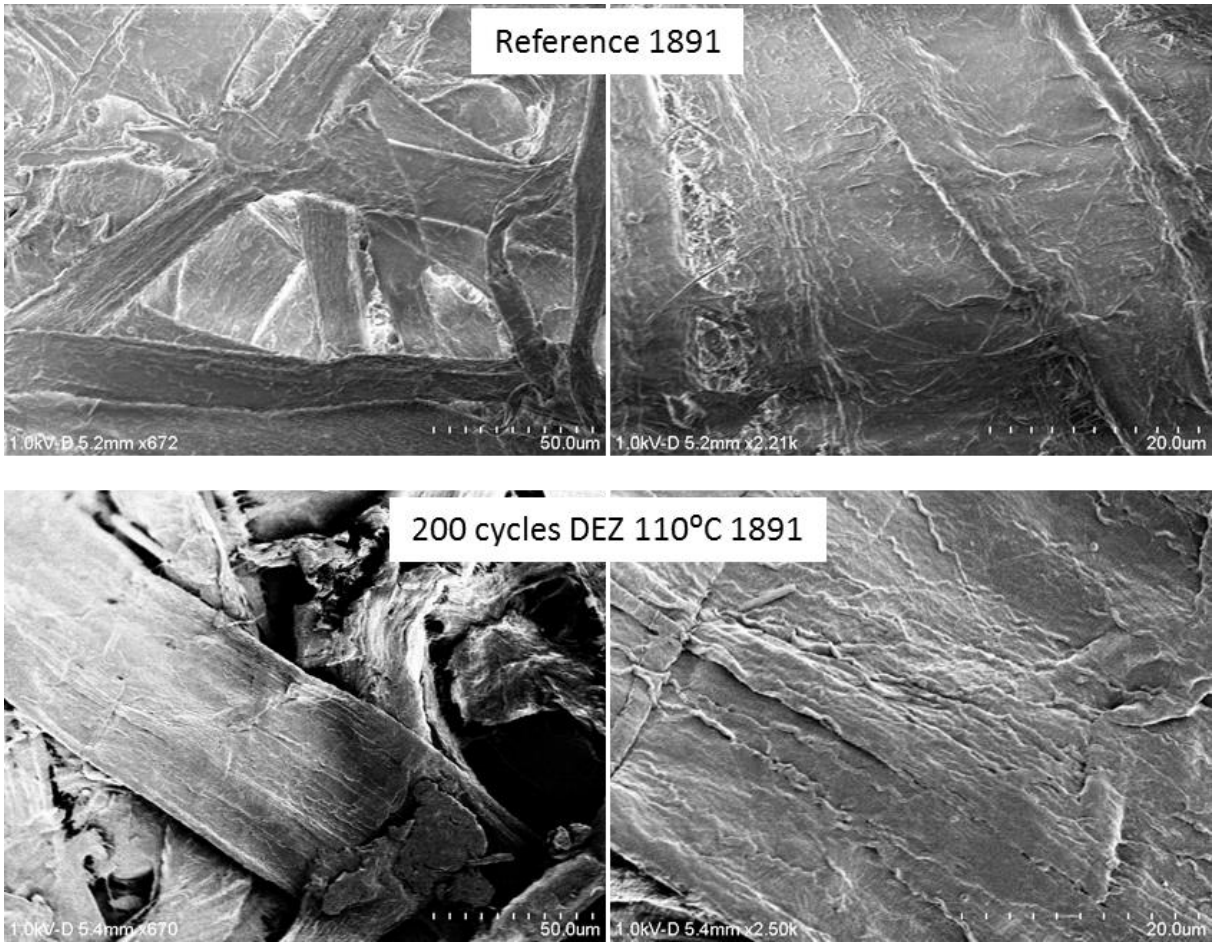


Figure 28. SEM images of sample 1891, reference and 200 cycles with DEZ treated under 110^0C.

Figure 29 is presenting sample 1937. According to the result, paper fibres do not have any quality degradation. Comparison between the reference and the treated samples do not have critical differences. Fibre thickening is present after the treatment. Reacted ZnO with a surface fibres has a smoothing effect. On each magnification level, fibre cracking, decay and CVD were not detected.

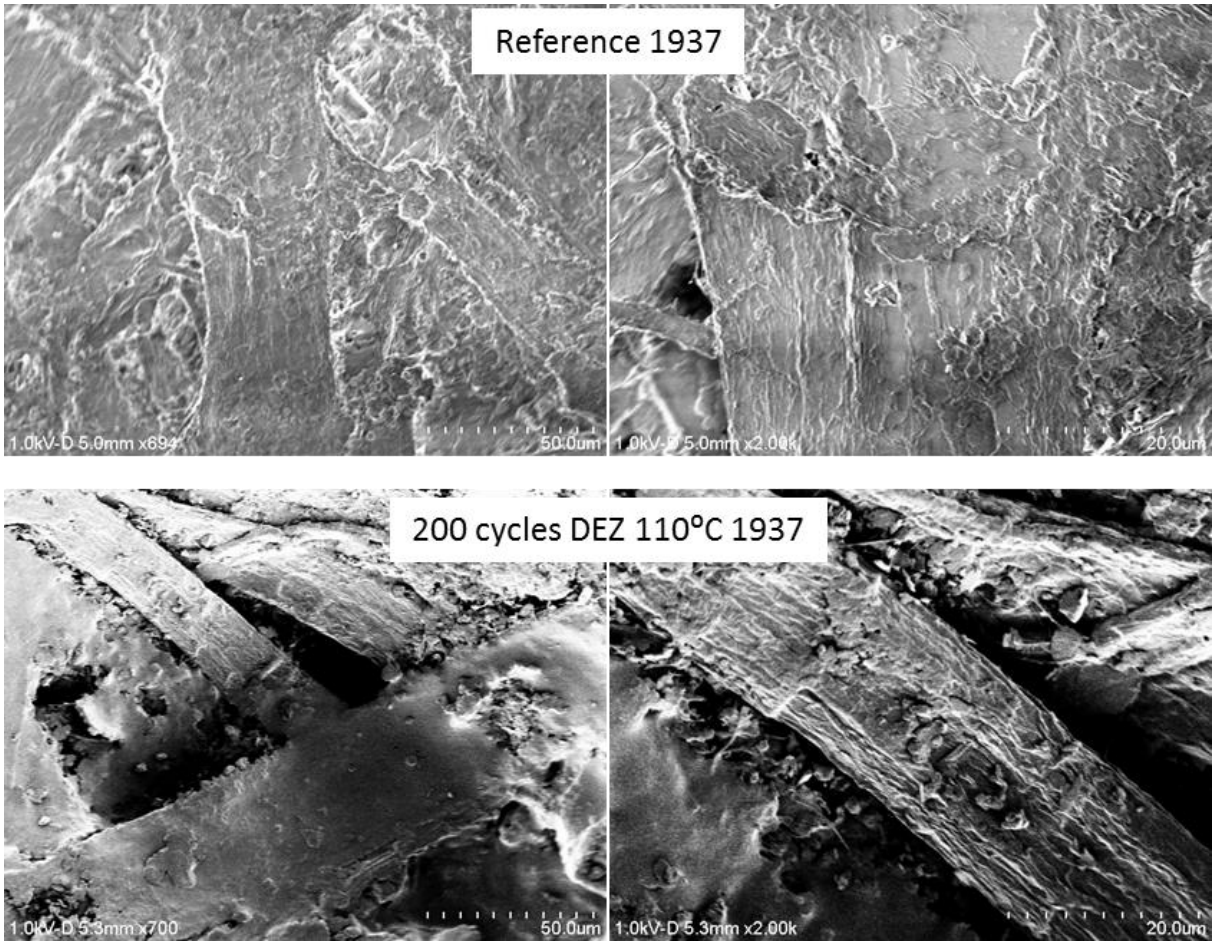


Figure 29. SEM images of sample 1937, reference and 200 cycles with DEZ treated under 110^0C.

Figure 30 is presenting sample 1946. According to the result, paper fibres do not have any quality degradation. Treated samples had a CVD reaction due to the presence of flocculation on the surface. Fibres remain undamaged after the treatment. On each magnification level, fibre cracking and decay were not detected.

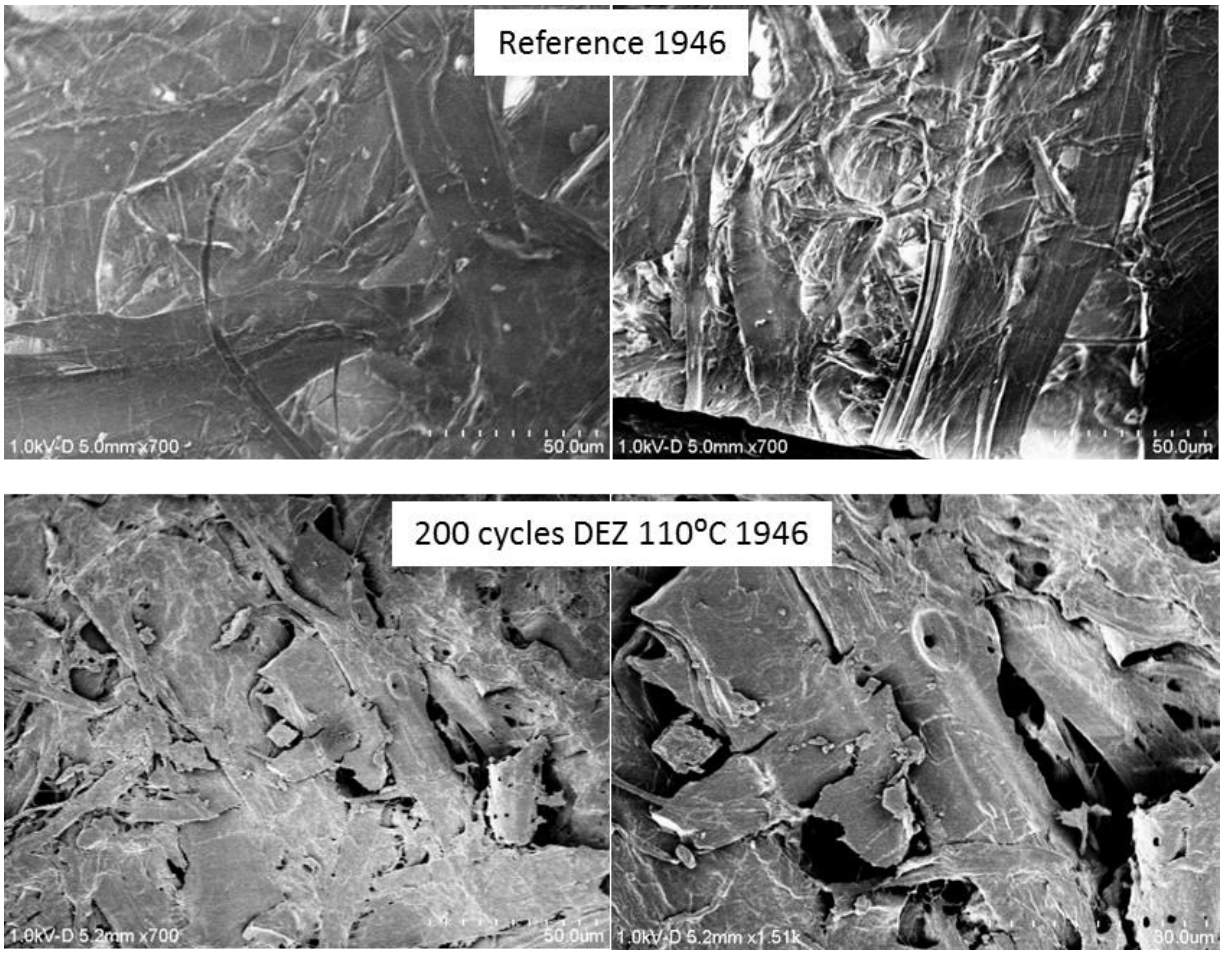


Figure 30. SEM images of sample 1946, reference and 200 cycles with DEZ treated under 110^0C.

3.4 Hydrophilicity test

Hydrophilicity of the samples was analysed with CA measurement before and after ALD treatment with DEZ. The samples (1891, 1937 and 1946) were treated with 100 cycles of DEZ under 110^0 C. The droplet angle examination was performed during 30 minutes after sample extraction from the reactor of TSF 500. Applied liquid was distilled water with amount of droplet in 2 μl. Temperature in the room was 20^0 C. CA measurements were repeated 10 times and the results were averaged.

Figure 31 is representing the results of hydrophilicity change after ALD treatment. Samples 1891 and 1946 are significantly increased hydrophilicity on 70%. Sample 1937 has lower hydrophilicity value which equals 31%. Reasons of the result shifting come from differences of the paper composition and the rate of paper acidification. These results are confirming that ALD

treatment considerably dehydrates the samples. Repetition of the experiment after 24 hours has proved a gradual CA increase due to a paper saturation by the presence of relative humidity in the laboratory.

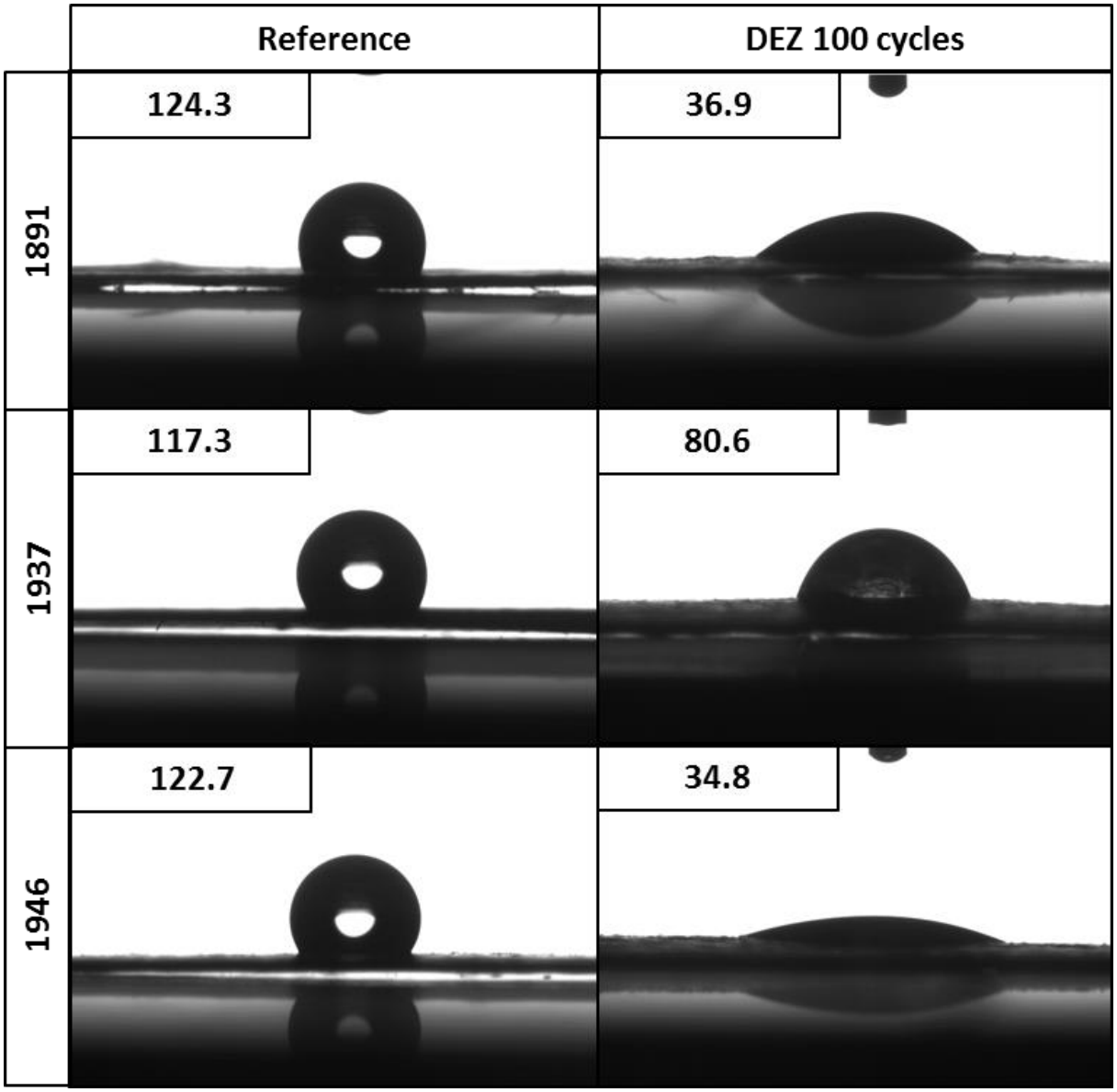


Figure 31. Contact angle results

3.5 Folding test

Folding test is aimed to determine paper embrittlement. Method is based on paper folding expertise due to the counting of the amount of folding at certain area till the crack. Double fold on 90^0 with a gentle press at the folded line is counted as one complete folding. Table 6 is

representing amount of folding applied on samples 1891, 1937 and 1947 before and after deposition of zinc oxide. Hydrophilicity test represents a significant vaporisation of physically bounded water, which leads to an increase of brittleness. Therefore, 15-20 seconds of vapor impact was applied to restore water content in treated papers. As the result, it restored for flexibility for 1891 sample on 5 folds, sample 1937 was restored completely with a slight improve from untreated. Sample 1946 remained unchanged.

ALD treatment parameters:

- DEZ 200 cycles
- 110^0 C

Vapor treatment parameters:

- H_20 100^0 C
- 15-20 sec

Sample	Reference	Treated Z1	Vapor
1891	<30	15	20
1937	4-5	2	3-7
1946	2	2	2

Table 6. Folding test results

3.6 Treatment technique

Treatment consequence is shown on Figure 32, which starts from a sample examination to detect a level of acidity. Secondly, an actual treatment procedure is performed to deposit ZnO. Finally, post-treatment humidification to moisturise the sample has to be applied. Samples moisturizing was applied aiming to decrease embrittlement which occurs under vacuum and thermal condition. ALD treatment deacidification of books with DEZ has proved its effectiveness to stop paper organic degradation. Designed treatment conditions according to applied reactor size can handle one sample per treatment which is 150x150 cm. Homogeneity of treatment is high and ensuring whole surface area coverage with zinc oxide. TFS 200 has a technical advantage in samples treatment due to its ability to keep reactor warm during sample's injection

and extraction. Basing on TFS 200, ALD system can be designed specifically aiming to deacidify papers or book. Reactor size has to be scaled up to handle several books per treatment. Further development is required in area of applying ALD system for paper deacidification.

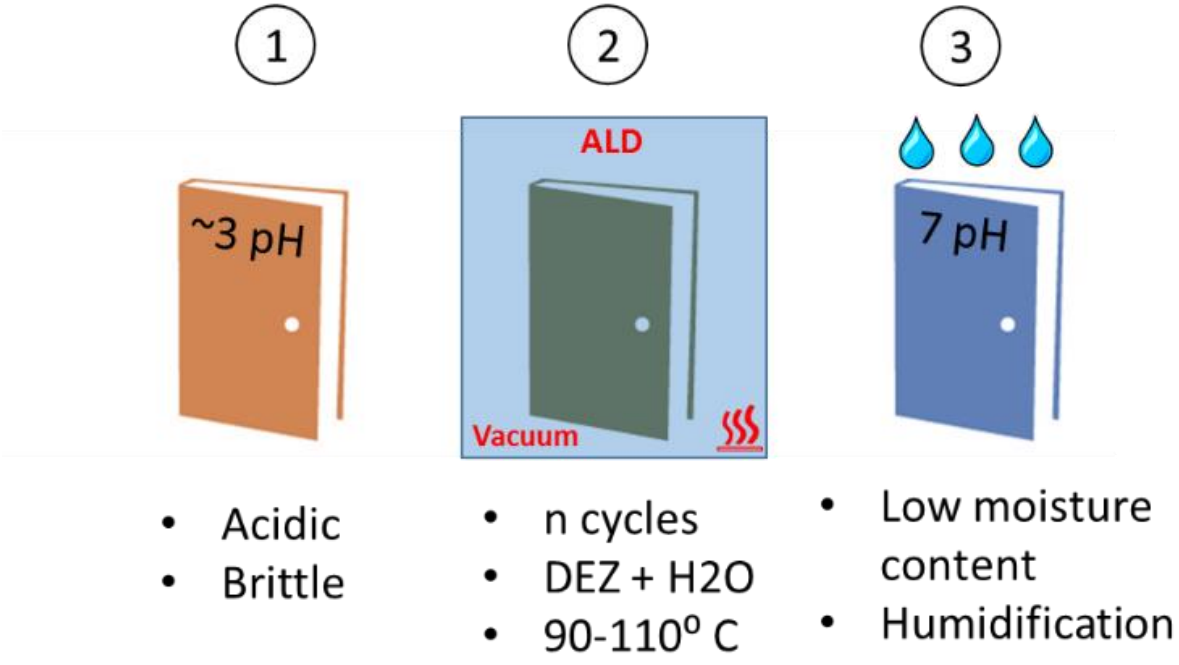


Figure 32. Deacidification treatment consequence

4 Conclusions

This thesis work was aimed to enhance atomic layer deposition of ZnO used for paper deacidification. ALD treatment with DEZ has shown positive dynamics in paper deacidification. TMA and TTIP did not neutralize an acid content in the studied papers. ZnO introduced by ALD has been analysed in a wide range including pH, SEM, CA, folding method of examinations. The general picture gives promising results for further ALD treatment with DEZ development for paper deacidification. ZnO does not damaging a paper structure and does not causing any visual effects to a colour and prints. Whitening effect was noted in decreasing a paper yellowing. Preciseness of the active compound distribution into a paper structure is high according to complete surface observation. The method disadvantages have been detected as well. Where the complete reagent chemisorption requires thermal and vacuum environment, which is causing an increase of paper's embrittlement due to it dehydrating. By returning back a papers moisture content, it is possible to restore a paper's flexibility on approximately 70%.

Nevertheless, the treatment conditions were designed to treat exceptionally small sizes and weights of the studied material per treatment. According to a scale of ALD treatment, the method requires further development to be scale up and capable of quantitative material handling. Investments towards designing specialized engineering machinery is needed. Additionally, pyrophoric nature of DEZ requires extra attention in safeness. It raises a question, on the one hand to invest towards safety in handling DEZ or to study non-pyrophoric reagents for paper deacidification. Ecotoxicological profile review of ZnO, as the objective compound, has determined possible negative effects to the environment, which requires an extra attention for further recycling.

Nevertheless, the applied experimental parameters are able to neutralize acid content in the single piece of paper in approximately 10-minute process. It could be practically used to treat single paper documentation. Possible solution is to create a reactor with a loading capacity which is capable for example to handle 1-3 kg or 3-7 books per treatment, which possibly will give an advantage in reagent diffusion preciseness and a lower demand in DEZ which supports higher safety. Designed machinery in such frames could have an interest around national libraries all over the world. All and all, ZnO deposited by ALD has a good potential to be used for paper deacidification, but further research in this area is required.

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