*Technical Paper*

# Zinc and Alginate for Multipurpose Textiles

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## Abstract

The paper presents the possibility of applying zinc solutions on cotton fabrics. In a two-stage procedure a fabric is first impregnated with $ZnCl_2$ and then with alginate. The presence of zinc on impregnated samples is proved quantitatively and qualitatively. Absorption of water, overall flexural rigidity and UV transmittance of impregnated fabrics are measured and the UV protection factor (UPF) calculated. It has been stated that the absorption of water of the fabrics impregnated with $ZnCl_2$ depends on the concentration of $ZnCl_2$; the same applies to the combination of $ZnCl_2$ with alginate. An overall flexural rigidity of fabrics increases after impregnation with 0,5M, 1M and 3M solution of $ZnCl_2$; it increases even more after application of $ZnCl_2$ and alginate. Although the UPF of the fabrics improves after impregnation with $ZnCl_2$, it does not achieve good UV protection as per the AS/NZS 4399: 1996 standard; good UV protection can be achieved on fabrics dyed with a phthalocyanine dyestuff. By applying $ZnCl_2$ in combination with alginates on dyed fabrics, we can obtain differently absorbent materials which provide UV protection and have anti-microbial properties.

**Key words:** cotton, $ZnCl_2$, alginate, ultraviolet protection factor, SEM.

## Introduction

The consequences of modern living style when transportation means are widely used, when environment is daily polluted with Freon, when forests are radically cleared, are already noticed… The most serious consequence of the crumbled natural balance is fast and intense thinning of the ozone layer. For living beings, ozone represents the only real protection from ultraviolet rays. During last 20 years the number of patients with skin cancer has been growing.[1,2] The latest researches confirm perilous effect of UV-A rays (320-400 nm) on people and animals. Mutations of DNK triggered by UV-A rays lead to cancer diseases and skin ageing.[3] Being aware of these facts, we have been protecting ourselves by applying sun creams regularly and abundantly. Optimal UV protection is provided by creams, which do not transmit UV-A rays. Sun creams are divided into the creams containing chemical substance, which absorbs UV rays, and the creams the particles of which reflect, scatter and absorb UV rays. It has been stated as well that the ultraviolet protection factor (UPF) of sun creams is changing with the change of the light source. The UV protection can change even by 50%.[4] Some UV pigment-based sun creams contain titanium dioxide, zinc oxide and ferric dioxide. In the UV-A range from 340 to 380 nm, zinc oxide provides better protection than titanium dioxide.[5] Sun creams usually provide only protection, however, the creams, which contain zinc oxide have also the healing effect.

However, sun creams do not represent the only available protection from the sunbeams. Textiles can provide efficient protection, too. The higher the density, the better the protection. Dyestuffs and absorbers applied on textiles have positive effect on UV rays absorption. Big differences in protection capability can be noticed between different types of fibres. Polyester fibres with many aromatic rings in macromolecules provide the highest protection whereas cotton fibres provide the lowest protection. The researches are dealing with such lightweight summer cotton textiles, which provide low protection from the perilous effect of UV rays.

The purpose of our investigation was to develop multipurpose lightweight cotton fabrics, which would protect and heal the skin at the same time. We combined the healing effect of zinc with its capability to prevent transmittance of UV rays.[5] The anti-microbial effect of zinc has been proven; zinc preparations, which are available on market, shorten the time of sore throat during cold, which would otherwise last 14 days. Zicam (Zicam LLC Phoenix, Arizona), which contains zinc gluconate and zinc acetate is known and recognized. Most people have problems with the first sun exposure (allergies), others have permanent skin problems (seborrhoea, psoriasis); lightweight cotton fabrics which would provide at least moderate UV protection and would have healing effect would be highly welcomed by these people. In our research, we investigated the effect of $ZnCl_2$ and of the combination of $ZnCl_2$ with alginates, and of both in combination with the Procion Turquoise H-EXL dyestuff, on the UV protection of lightweight cotton fabrics for summer dresses, bed linen or even for compresses for wounds due to the ability of alginates to absorb water; alginates are well known absorbents on antiseptic gauzes.

## Experimental

*Fabric:*

Unmercerized, bleached lightweight cotton fabric (Aqua Sava, Kranj) with the following parameters: warp density: 25 threads/cm, weft density: 27 threads/cm, mass per unit area: 150 g/m$^2$, weave: plain weave.

*Identification of samples:*

The application of $ZnCl_2$ is identified by the solution molarity (1MZn) and the alginate percentage (1% A NV) or (0,5% A MV), and of the combination of both for example: 1MZn, 0,5% A MV.

*Used chemicals:*

$ZnCl_2$, purity >99 % (Fluka), Alginat,[6] medium viscosity MV (CHT, R. Beitlich), Alginat, low viscosity NV (CHT, R. Beitlich), Procion Turquoise H-EXL (BASF), Cibapon R (Ciba).

*Application of chemicals on cotton fabric:*

We prepared 0,5 M, 1M, 3M and 5M solutions of $ZnCl_2$. Impregnation of fabrics was carried out by applying $ZnCl_2$ solutions in a continuous impregnation process on the drying stenter's dye padder (Benz) at maximum squeezing effect. The samples were dried in a drier at 60 °C for 20 minutes, rinsed in distilled water for 3 minutes in order to remove residual zinc on the fibres surface, then dried again in the same way, and finally impregnated with alginates in another bath. If alginates are applied on a cotton fabric immediately after its impregnation, a layer of a gel-like, chipping off substance is formed on the fabric surface. To be able to apply both solutions on cotton fabrics, it was necessary to develop a proper technological procedure on the basis of many experiments. For a two-stage application only 0,5 M and 1M solution of $ZnCl_2$ could be used. Two concentrations of alginates, i.e. 0,5% in 1%, were used. The fabric was dipped into each bath for 5 minutes, so that it was totally impregnated with the agent.

*Determination of absorption of water of impregnated fabrics:*

Absorption of water of fabrics was determined by measuring the time required by a water droplet to spread to the edge of a circle with diameter 1 cm.

*Determination of stiffness of the fabric:*

The stiffness of the fabric and, consequently, its drape and touch was determined according to the ASTM D 1388 – 64 standard method which includes two options. We used the cantilever test.[7] From the measurements of overhanging lengths of the fabric strips, warp flexural rigidity ($U_w$), filling flexural rigidity ($U_f$) and an overall flexural rigidity ($U_o$) was calculated.

*Analysis of zinc content on impregnated cotton fabric:*

The presence of $Zn^{2+}$ ions in the extraction of the samples impregnated with $ZnCl_2$ and with $ZnCl_2$ and alginates was proved with $K_4Fe(CN)_6$.[8] The samples were extracted in distilled water for 30 minutes. In combination with $Zn^{2+}$, $K_4Fe(CN)_6$ produces white precipitate of $K_2Zn_3[Fe(CN)_6]_2$ which dissolves with NaOH. A quantitative analysis of zinc was carried out on the impregnated cotton fabric by using the ICP AES method. The method of optical emission spectrometry with inductively joined plasma was carried out on the samples of the cotton fabric impregnated with 3M $ZnCl_2$ and 3% Alginate NV. The method is based on the plasma effect, which is produced when the gas argon is passing through the radiofrequency field in which the gas particles get partly electrically charged. Plasma achieves the temperature to 10.000 $^0$C. At these temperatures, most elements emit the light of characteristic wavelengths.

*Dyeing:*

The non-impregnated and impregnated fabrics were dyed with the Procion Turquoise H-EXL dyestuff in 5 % concentration. We used Launder-o-meter. The liquor ratio 1:10 was preserved during dyeing. The dyeing bath was composed and the dyeing and rinsing procedures carried out in compliance with the dyestuff producer's (BASF) instructions;[9] Cibapon R (Ciba) was used for soaping.

*Measurement of UV transmittance and calculation of UPF:*

The UV transmittance of cotton fabrics impregnated in different ways was measured on the Varian CARY 1E UV/VIS spectrophotometer containing integration sphere. The measurements of transmittance and the calculation of the ultraviolet protection factor (UPF) were carried out in accordance with the AATCC standard.[10]

*Scanning electronic microscopy (SEM):*

The JEOL JSM 6060LV scanning electronic microscope was used to observe the surfaces of the impregnated fabrics. All samples were evaporated with carbon and Au/Pd and monitored at the accelerating voltage 10 kV and working distance 10 mm at proper magnifications.

## Results and discussion

The presence of $Zn^{2+}$ on the impregnated cotton fabric was confirmed with the qualitative analysis of the fabric water extraction with $K_4Fe(CN)_6$. In the extraction, $K_4Fe(CN)_6$ in combination with zinc produced white crystalline precipitate, which dissolved after addition of NaOH. By using the ICP AES method we proved that the sample impregnated with 3M $ZnCl_2$ and 3 % Alginate NV contained 107 mg of Zn per 1 g of sample. In this way, the presence of zinc on impregnated cotton fabrics was proved qualitatively and quantitatively.

In the SEM micrographs (Figure 1), a slight precipitate can be noticed on cotton fibres. At higher concentrations of zinc the layer of precipitate is thicker. The macrofibrillar structure, typical for raw unprocessed cotton fibres, is no more clearly visible on the surface of fibres.

When applied in combination with alginates, lower concentrations of $ZnCl_2$ were proved more adequate. 3M and 5M solutions of $ZnCl_2$ in combination with alginates produced a thicker, chipping off layer of gel on the fabric surface.


**Figure 1.** Cotton fibres impregnated with 3M $ZnCl_2$.

The results of the absorption of water measurements show that the application of $ZnCl_2$ considerably changes the absorbency of fabrics (Figure 2). When $ZnCl_2$ is applied in low concentrations, the absorption of water of the cotton fabric decreases at the beginning (longer times); only with higher concentrations (5M $ZnCl_2$) the absorption of water increases (shorter time). The solutions of $ZnCl_2$ trigger swelling of cotton - zinc chloride is known as one of the first agents for cotton mercerization.[11] The difference in absorption can be explained with the phenomenon that the solutions with low concentrations of $ZnCl_2$ diffuse into fibres and trigger swelling, whereas at higher concentrations, $ZnCl_2$ partly remains also on the fabric surface and, as we know, it absorbs water well. Diffusion of water molecules into fibres requires longer time than their reaction on the fibres surface. With the two-stage application of $ZnCl_2$ and alginate the absorption of water of fabrics decreases in comparison with non-impregnated fabrics (longer times). This also applies to the applications of 0,5M concentrations of $ZnCl_2$ and alginates (Figure 3) the wettability of which is lower; this is above all the film on fibres, which considerably reduces capillarity of fabrics and, consequently, additionally decreases their absorptivity.

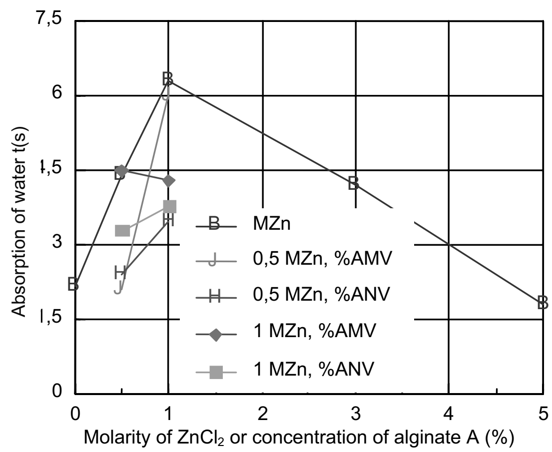


**Figure 2.** Absorbance of impregnated cotton fabrics.


**Figure 3.** Film of $ZnCl_2$ and alginate on fibres and between them.

Alginates are linear non-branched polymers, which contain 1,4 β bonded D-manuronic acids and 1,4 α bonded L-guluronic acids. These co-monomers are bonded in alginates in repeating blocs. Alginates are obtained from brown algae, species Phaeophyceae, mainly from Laminarrie hyperboree. In combination with water they produce viscose solutions, which are applied on antiseptic cotton gauzes for covering wounds. When dried, they absorb exudates from wounds. The necessity of differently absorbable alginate compresses for healing different kinds of wounds is high. The investigations of absorbency of two-stage applications of $ZnCl_2$ and alginate show that it is possible to prepare compresses with different capability of absorbing water. Since it has been proved that zinc in cooperation with calcium ions, which are present in the skin, expedites healing of wounds,[12] the combination of zinc and alginates would be more useful than alginates alone.

The application of $ZnCl_2$ and alginate on fabrics results also in the change of the overall flexural rigidity of fabrics. The values of overall flexural rigidity ($U_o$) of the non-impregnated fabric and the fabrics impregnated in different ways are presented in Figure 4.

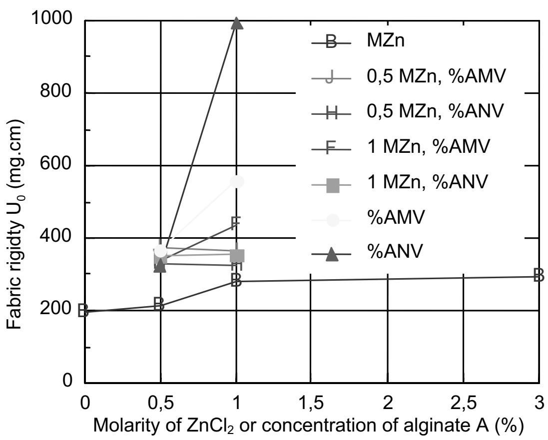


**Figure 4.** Overall flexural rigidity ($U_o$) of non-impregnated and in different ways impregnated fabrics.

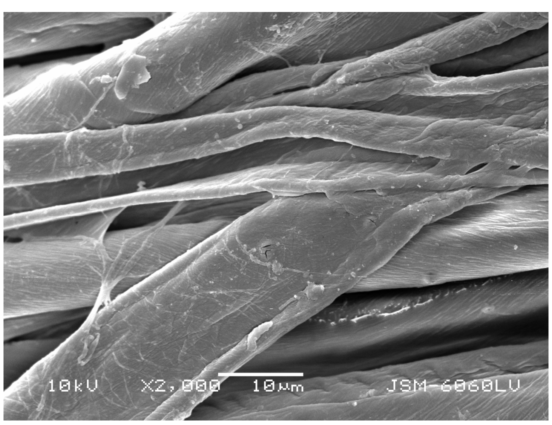


**Figure 5.** Surface of fibres coated with a layer of $ZnCl_2$ and alginate.

The measurements of overall flexural rigidity, i.e. bending capacity of fabrics due to fabric weight, show that the stiffness of fabrics increases with increasing concentration of $ZnCl_2$ on fabrics. This is not surprising because at higher concentration the film on fibres is thicker (Figure 1). Of course, the rigidity of fabrics impregnated with $ZnCl_2$ and then with alginate is even higher due to thicker film on fibres (Figures 4, 5).

After application of alginates (0,5% or 1%), an overall flexural rigidity of cotton fabrics increases also due to less interrupted bonding layer (Figures 4, 6), which means that the fibres in yarn are more closely bonded. Values of the overall flexural rigidity of fabrics and SEM micrographs taken after impregnation clearly show the bonding layer ($ZnCl_2$, alginate or both) between fibres; in the cases of applied alginates, it represents a larger bonding surface, which is evident in SEM micrograph in Figure 6.

The purpose of the investigation was to develop multipurpose textiles. The influence of different concentrations of $ZnCl_2$ and alginates on the properties, which are important for the fabrics providing anti-microbial effect used for compresses were investigated. Beside these properties, UV transmittance is also important for multipurpose textiles. The enhanced UPF of such fabrics can result in wider application for special purposes.

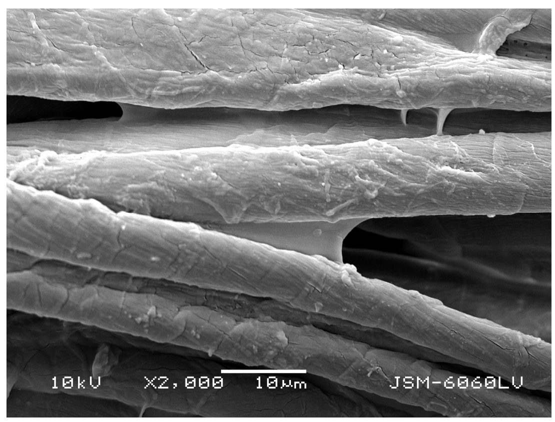


**Figure 6.** Better bonding of fibres in yarn by applying alginate.

On the fabrics impregnated with $ZnCl_2$, and with $ZnCl_2$ and alginate, the light transmittance was measured in the ranges 280-400 nm, 280-315 nm, 315-400 nm and 400-700 nm (Figure 7). The measurements were carried out in accordance with the AATCC standard for calculation of the ultraviolet protection factor (UPF). The values are the mean values of the UV transmittance measured on four different samples. The UV light transmittance of the samples impregnated with different concentrations of $ZnCl_2$ changes as expected (Figure 7). The higher is the concentration of $ZnCl_2$ in or on fibres, the lower is the UV light transmittance; the light transmittance is increasing proportionally in dependence of the wavelength.

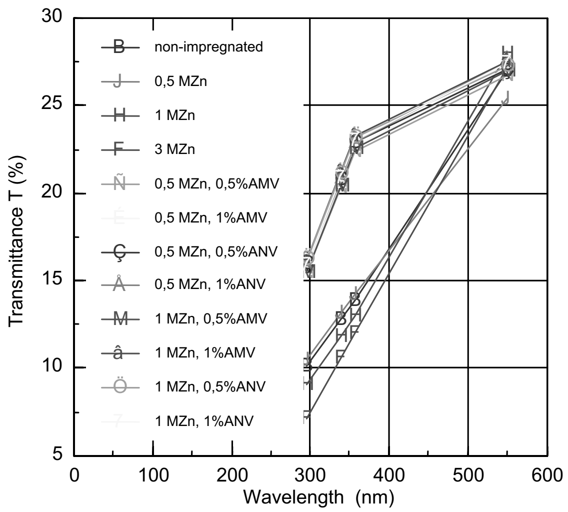


**Figure 7.** Light transmittance of impregnated cotton fabrics within the range 280-600 nm.

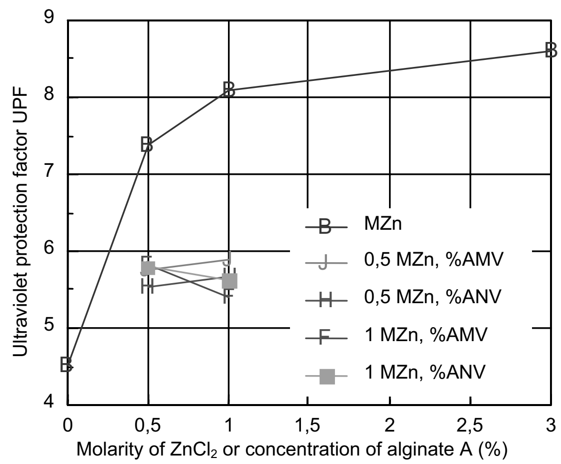


**Figure 8.** Ultraviolet protection factor (UPF) of impregnated cotton fabrics.

The transmittance of the samples with applied $ZnCl_2$ and alginate is higher due to removal of residual zinc from the fibres surface prior to applying alginate. With the self-absorbed quantity of zinc in fibres, the UV light transmittance does not depend either on 0,5% or 1% concentration of alginate but it increases with the wavelength.

The results of measurements of the UV protection factor (UPF) show that after application of 0,5 M $ZnCl_2$, 1 M $ZnCl_2$ and 3 M $ZnCl_2$ on a cotton fabric with high light transmittance having UPF 4.5, UPF increases to the value 8.6 (Figure 8). As per the AS/NZS 4399:1966 standard, this value does not represent good UV protection (good protection UZF>15, very good protection UZF>30, excellent protection UZF>40).[13] The fabrics, which were impregnated first with $ZnCl_2$ and then with alginate in low concentrations also exhibit low UV protection (Figure 8) due to high UV transmittance resulting from removal of residual zinc on the fibres surface.

In order to increase the UPF of cotton fabrics, we dyed them with 5 % Procion Turquoise H-EXL dyestuff. UPF of such dyed fabrics increases to UPF 377, which means that fabrics treated in this way provide more than excellent UV protection.

The results of impregnation of dyed cotton fabrics (Procion Turquoise H-EXL dyestuff) with $ZnCl_2$ and alginate show that it is possible to develop various products with high UV protection and different absorption of UV rays, which have also the anti-microbial effect due to the presence of zinc. Water solutions of $ZnCl_2$ represent a pleasant, slightly acid medium for the skin (pH 5-6). Zinc in the form of bivalent ions is also good antioxidant, which protect the skin from free radicals.[14]

## Conclusions

The results of the investigation of developing a multipurpose textile by impregnating a cotton fabric with $ZnCl_2$ and alginates can be summarized as follows.

The application of different concentrations of $ZnCl_2$ has the influence on the fabric water absorption. Lower concentrations of $ZnCl_2$ decrease absorption of water, whereas the application of 5M solution increases water absorption of impregnated fabrics. The water absorption of cotton fabrics after impregnation with $ZnCl_2$ and alginates is lower than the water absorption of untreated fabrics. The stiffness of fabrics is increasing with increasing concentrations of $ZnCl_2$. Fabrics are still more rigid after application of $ZnCl_2$ and alginate. Zinc, applied on the fabric in the form of $ZnCl_2$, increases the UV protection, but not sufficiently. Lightweight cotton fabrics dyed with Procion Turquoise H-EXL dyestuff provide excellent UV protection. By applying $ZnCl_2$ and alginates, differently absorbent materials are obtained, which have also the anti-microbial effect, and when dyed, also the UV protection.

The researches have proved that it is possible to develop multipurpose textiles by using zinc solutions. It is therefore possible to produce, by impregnating cotton fabrics with $ZnCl_2$, the textiles with at least a double effect – the healing and the anti-microbial effect. The two-stage application of $ZnCl_2$ and alginate is particularly important for compresses for wounds care. Zinc highly expedites healing whereas alginate improves adsorption of exudates.

## Acknowledgements

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## Povzetek


V prispevku je prikazana možnost aplikacije cinka na bombažnih tkaninah. Pri dvostopenjskem postopku je po impregnaciji z $ZnCl_2$ tkanina prepojena še z alginatom. Prisotnost cinka na impregniranih vzorcih je dokazana kvantitativno in kvalitativno. Izmerjene so vpojnosti tkanin, togost in UV transmisija ter izračunan ultravijolični zaščitni faktor (UZF). Ugotovljeno je, da je vpojnost tkanin impregniranih z $ZnCl_2$ odvisna od njegove koncentracije, kar se odraža tudi pri kombinaciji $ZnCl_2$ z alginatom. Togost tkanin se po impregnaciji z 0,5 M, 1M in s 3M raztopino $ZnCl_2$ poveča; še bolj po nanosu $ZnCl_2$ in alginata. UZF tkanin impregniranih z $ZnCl_2$ se izboljša, vendar ne doseže po AS/NZS 4399: 1996 standardu dobre UV zaščite, le-to je mogoče doseči na tkanini pobarvani s ftalocianinskim barvilom. Nanos $ZnCl_2$, v kombinaciji z alginati na pobarvanih tkaninah daje različno vpojne materiale, ki delujejo UV zaščitno kakor tudi proti mikrobno.