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MULTIVARIATE ANALYSIS OF THE PHYSICO MECHANICAL PARAMETERS VARIATION FOR HYDROPHOBIC TEXTILE

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Abstract: *This work presents a multivariate analyse regarding textile surfaces treated with fluorocarbon chemicals in order to obtain hydrophobic effect. The hydrophobic characteristics of the textile samples (cotton 100%) were obtained after hydrophobization treatement in the laboratory, by using chemicals based on fluorocarbon and by process parameters variation (temperature, time). Experimental data were evaluated by means of laboratory tests and multivariate analysis in order to observe covariance and the connections between the process parameters and the final characteristics of the fabric hydrophobizated.*
For evaluating the hydrophobic effect, some investigations were performed by qualitative method Spraytest for determinating the resistance to surface wetting in accordance with the standard SR EN ISO 4920-2013, air permeability according to SR EN ISO 9237:1999 standard and contact angle computing by using the device VCA Optima for contact angle measuring, in accordance to the standard ASTM D7490-2008. In order to highlight the morphological changes that appear on the cotton fibers, samples were examined using scanning electron microscopy device (SEM) with the magnitude of X2000 X4000, X8000.
The purpose of multivariate analysis for parameters and influence factors for hydrophobization process, based on fluorocarbon, is to obtain information relating to the dependent variables and independent, which influence the process.
We establish some dependence between parameters (contact angle, spray test resistance, air permeability) by using covariance matrix analysis.
This analysis shows that contact angle and the resistance to spray test are in direct dependence and in reverse dependence with the air permeability.

Key words: *hydrophobic, textiles, multivariate, impact, environment.*

1. INTRODUCTION

The multivariate approach enables to explore the joint performance of the variables and determine the effect of each variablein the presence of the others. Multivariate analysis provides both descriptive and inferential and allow searching for pattern and test hypotheses about pattern [1].

In the scientific literature there are information regarding hydrophobization agents used for cotton, such as bifunctional polysiloxanes with various contents of functional groups [2], maleic-anhydride grafted poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymer solutions based on calcium carbonate particles [3] . In case of addition of W/V $CaCO_3$ 6% was obtain the highest contact angle value of 154° [3].

The fluorinated polymeric products gases are used for a large number of articles (clothing and household linen stofe furniture, bedspreads, gaskets earth) because the ultimate effect increases, in general, the value of use and provide the maintenance process. Now, on the market are available commercial products with water-repellent properties, most of them being protection materials anti-staining, such as StainSmart (Milliken), Advanced Dual action and ultra Teflon launched by Invista, Scotchgard Protector (3M). Almost all the finishing treatments provide the repellency of water and oils, such as Crypton®, TEFLON®, Gore TM, and Scotchguard TM, because are based on fluorocarbon. Fabrics treated in this way are used for clothing active, travel, clothing and protective equipment; military uniform, medical and school, equipment for hospitals, public places, tents for emergency situations etc. The hydrophobic properties are produced by covering with nanoparticule [4] and polymers as the NanoSphere technology. For super-hydrophobic effect novel approaches to decrease the surface free energy of fibers was studied in the last years, such as silane chemistry, nanocomposite structures, or physically applied thin layers [5, 6, 7].

Fabrics that are coated with nanosferele created by Schoeller are used for sports equipment, rucksacks, t-shirts, slacks and other products by companies as well as the Cloudveil, Granite Gear, Mammut, Outdoor Research, Beyond Fleece and Westcomb.

2. EXPERIMENTAL PART

For obtaining the hydrophobic characteristics, the textile samples made from cotton 100% and with the mass 401g/m^2, were treated by using chemicals based on fluorocarbon and by process parameters variation (temperature, time) in the laboratory.

Experimental data, obtained in the laboratory processes, were investigated by means of laboratory tests and multivariate analysis in order to observe the joint variability of two random variables and the connections between the process parameters and the final characteristics of the fabric hydrophobizated.

The multivariate analysis was based on bivariate random variable (x, y) in order to observe the tendence of x and y to covary [1]. The population covariance is defined as cov(x, y) (1).

$$Cov(x,y) = \sigma_{xy} = E[(x - \mu_x)(y - \mu_y)] \quad \textbf{(1)}$$

Where:
μ_x is the mean of x.
μ_y is the mean y.

In table 1 are presented information about process parameters used for hydrophobization and the results for spray tests and contact angle in order to evaluate the hydrophobization. The sample P0 is the untreated textile surface. In Fig. 1 is presented the contact angle in function of air permeability and spray test resistance.

Table 1: *Hydrophobic textile samples parameters and results*

		Samples				Standard
		P0	**P1**	**P2**	**P3**	
Spray test resistance	Grade scale ISO	0	3.5	4.5	4	SR EN ISO 4920/2013
	Photographic scale AATCC	0	85	95	90	
Contact angle		<1	150.20	148.10	153	ASTM D7490-08
Temperature		-	140 °C	150 °C	160 °C	
Condensation time [minutes]		-	2	4	2	

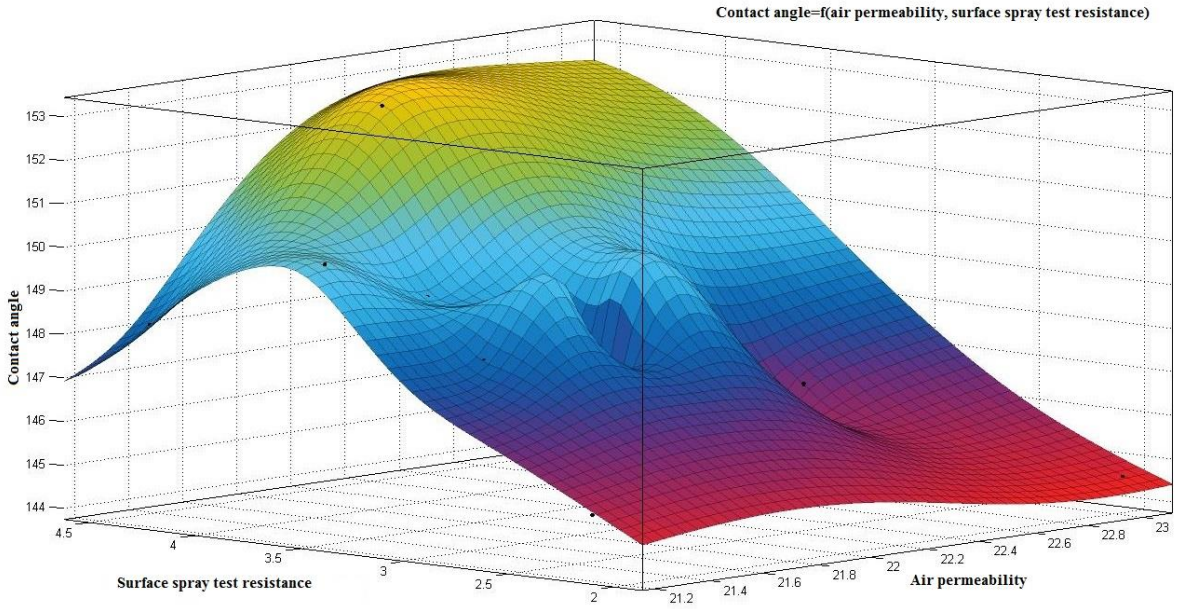


Fig.1: *3D prepresentation – Contact angle in function of surface spray test resistance and air permeability*

By mapping of 2D contact angle depending on the air permeability and surface spray test resistance (Fig. 2) we can observe that the values for which they have the best spray test resistance have the air permeability less than 22l/m^3/sec. For the samples with the air permeability exceeding 22l/m^3/sec have not been obtained good resistance to spray surface tension.

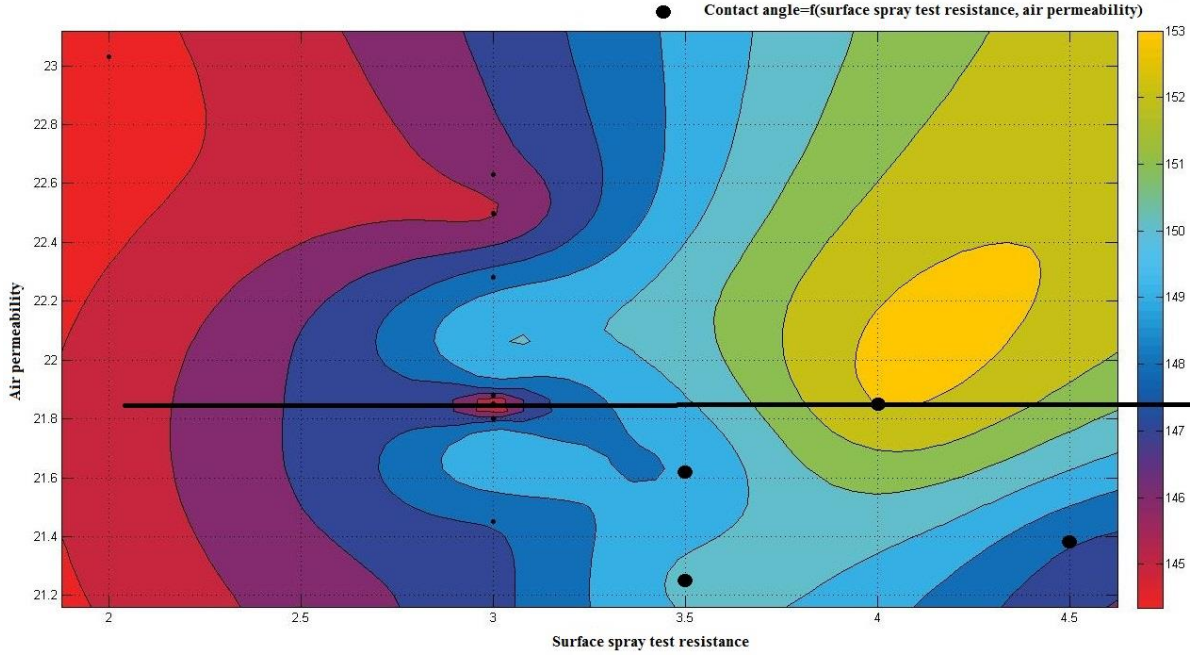


Fig. 2: *2D mapping –Contact angle in function of surface spray test resistance and air permeability*

In table 2 are presented the contact angle obtained for samples P1, P2 and P3 by OPTIMA VCA. In table 3 are presented the images with samples P0, P1, P2, P3 using scanning electron microscopy (SEM) with magnitude X2000, X4000, X8000.

Table 2: *Contact angle values*

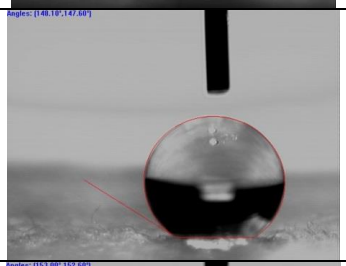
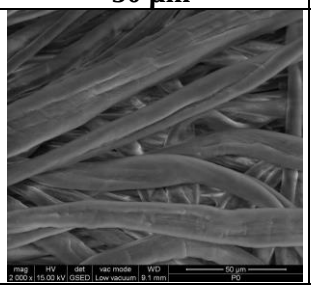
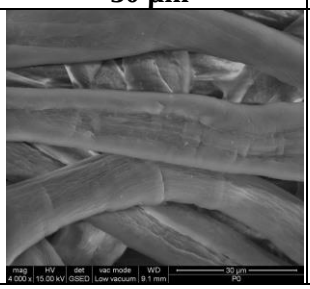
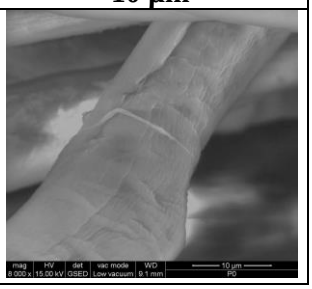
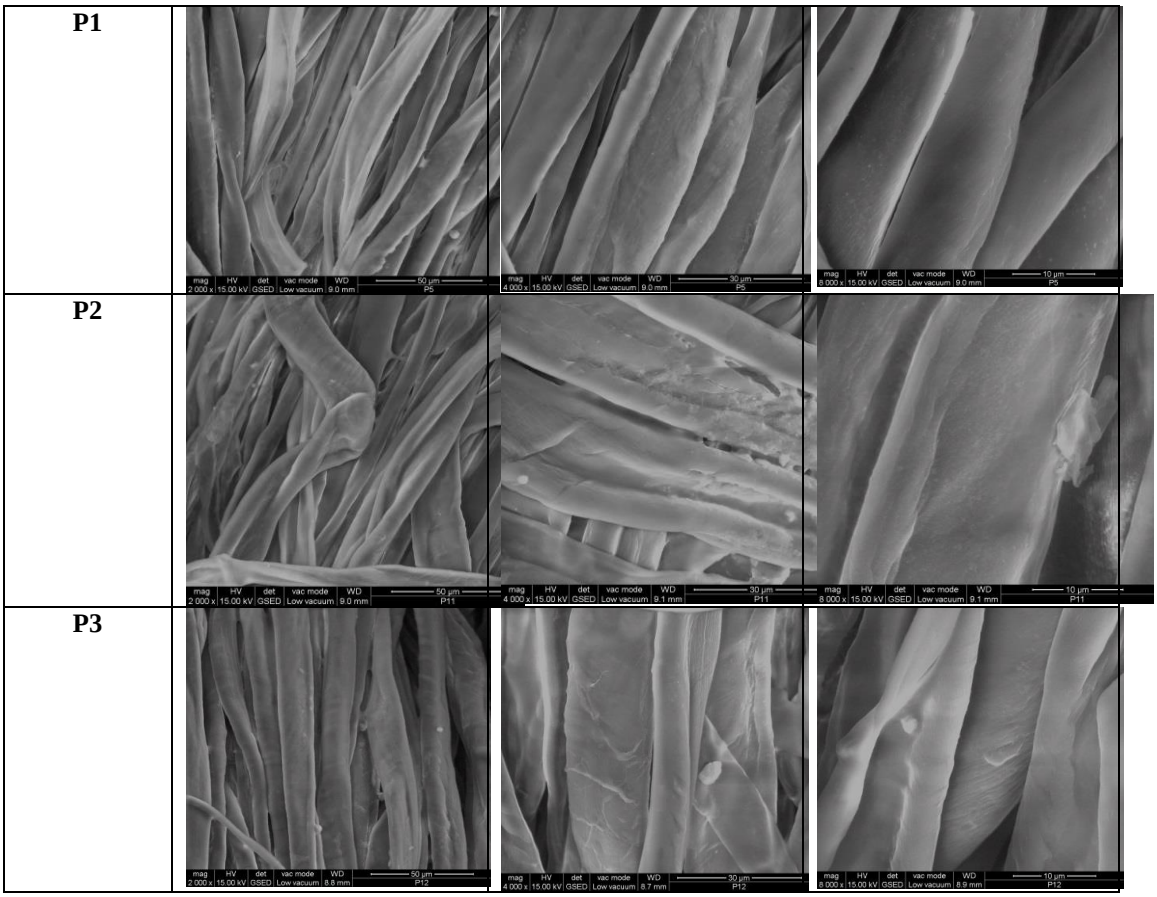
Samples	Contact angle value [°]	Image
P0	-	-
P1	150.20	
P2	148.10	
P3	153	

Table 3: *Scanning electron microscope images for textile samples*

Samples	50 µm	30 µm	10 µm
P0			



3. DISCUSSIONS AND RESULTS

We observed that the contact angle higher value is for sample P3, which has resistance at the surface spray test less than the value obtained for the sample P2. By analysing the covariation between the resistance at the surface spray (SS) and the angle of the contract (UC) (1) it can be said that they are in direct dependence and the increase of the value contact angle by hidrophobization determines the increasing of the spray test resistance).

$$\text{Cov}(SS, UC)=\begin{vmatrix} 0.3845 & 0.9841 \\ 0.9841 & 5.8427 \end{vmatrix} \Rightarrow \text{Cov}_{1,2}(SS,UC)=\text{Cov}_{2,1}(SS, UC)=0.9841\approx 1 \quad \textbf{(2)}$$

Taking into account the values obtained to the permeability to air and the resistance to the superficial spraying, it can be said that the contact angle is in direct proportionality with resistance to the spray superficial test and in reverse proportionality with the permeability to air (Fig. 1).

By analysing the covariation coefficients of the covariance matrix (2, 3) it can be concluded that the resistance at the superficila spray (SS), namely the contact angle (UC) are in a relationship of proportionality reverse with the permeability to air (PA).

$$\text{Cov}(UC,PA)=\begin{vmatrix} 5.8427 & -0.6971 \\ -0.6971 & 0.2958 \end{vmatrix} \Rightarrow \text{Cov}_{1,2}=\text{Cov}_{2,1}=-0.6971 \quad \textbf{(3)}$$

$$\text{Cov(SS,PA)}=\begin{vmatrix} 0.3845 & -0.2338 \\ -0.2338 & 0.2958 \end{vmatrix} \Rightarrow \text{Cov}_{1,2}=\text{Cov}_{2,1}=0.2338 \quad \textbf{(4)}$$

5. CONCLUSIONS

By multivariate analysis can be observed the independent or dependent variable, how they covary.

We can conclude that contact angle and the resistance to spray test are in direct dependence and in reverse dependence with the air permeability.

The knowledge about dependent and independent variable which influence the hydrophobization process is important for advanced material designers in order to create a new material stating from the parameters already known.

ACKNOWLEDGMENTS

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECTS OF ULTRASONIC WASHING ON COTTON TEXTILES

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Abstract: *The idea of employing ultrasonic energy to textiles has been commenced since 1990s. It can be seen that the use of ultrasonic energy in textile washing processes has some advantages such as energy conservation, reducing the duration of the processes, and improving the parameters of the product quality. For this reason, ultrasonic energy can be an alternative to conventional washing methods. More recently, ultrasonic energy has been used on the dyeing of cellulose nanofibres. However in generally, researchers have been used ultrasonic energy on the wet finishing processes rather than the effects of mechanical properties of the yarns.*
In this work, we aimed to study the mechanical properties of the cotton textiles after being washed with the help of ultrasonic energy. 100% cotton yarns and knitted fabrics produced from these yarns were washed by both ultrasonic and conventional methods. The two techniques were compared in terms of yarn breaking strength, yarn breaking elongation, pilling of fabrics and lightness (L) values of the fabrics. The results showed that ultrasonic washing can present slightly higher mechanical properties than the conventional washing of the cotton yarns. It was observed that ultrasonically washed fabrics have better pilling values than the conventionally washed fabrics. Cotton fabric appearances were also examined under JEOL-JSM 5910 LV model scanning electron microscope.*

Key words: *Ultrasonic energy, conventional washing, pilling, cotton, tenacity, SEM.*

1. INTRODUCTION

Textiles can be in various forms i.e. loose fibres, spun and filament yarns, fabrics or non-woven materials. Even though a particular form of the material may state the type of machinery best can be used on an industrial scale, it is the nature of the fibre itself that determines the procedure to be used. Amongst textile technologies, numerous methods have been established and used to improve the properties of cotton yarns and textiles; ultrasonic energy is one of that methods where is applied in textiles. The ultrasonic energy has been adapted to textiles in wet finishing processes, almost the past twenty years; yet in all these works ultrasonic energy was generally applied to dyeing of textiles [1],[2],[3],[4],[5]. In some studies, the utility of ultrasonic methods has been considered in regards of the dyeability properties of bleached cotton yarns and woven fabrics, medical surgery gowns were successfully washed and cleaned with ultrasonic energy where the fabrics treated by ultrasonically have shown less tenacity when compared to fabric treated by conventional methods [6],[7],[8],[9]. Recently ultrasonic energy technique was applied to wool

dyeing process where wool woven fabrics were dyed well with the ultrasonic probe by reducing the amount of time more than an hour than the conventional dyeing technique [10]. Also the ultrasonic energy has been used for removing undesirable materials on textiles and improving effectiveness of enzyme molecules [11]. In another study, conventionally washed fibres within the cotton yarns were extensively deformed and it was thought that this is due to the changes between the distances of fibre macromolecules where evident [12]. The aim of this study was to wash cotton yarn and fabrics by means of ultrasonic energy and compare their mechanical properties with those washed by a conventional method. In this study, both conventional washing and ultrasonic washing methods reduced the breaking tenacity of yarns. However, ultrasonic washing method caused less loss of breaking tenacity than conventional washing method. It is expected that the textile industry will benefit more from the ultrasonic energy on a commercial scale.

2. MATERIALS

2.1. Yarn Samples Production

In this study, 15 tex cotton ring-spun yarns were produced with a twist factor of α_{tex} 31.5. All of the yarns were tested in standard atmospheric conditions (20 ± 2 ^{0}C and 65% ± 2 RH) after 48 hours of equilibrium was reached. Fibre properties were measured on the SPINLAB HVI 900 instrument; yarn evenness and hairiness were both measured on the Uster Tester 3. The properties of fibres and yarns are given in Tables 1 and 2 respectively.

Table 1: *Fibre properties*

Fibre properties	
Micronaire	4.7
%50 spun length (mm)	26.7
%2.5 spun length (mm)	30.5
Strength (g/tex)	33.8
Elongation (%)	7.7
Rd	76.7
+b	8.4
Colour grade	31-2

Table 2: *Yarn properties*

Yarn properties	
Yarn linear density (tex)	15
Twist factor (α_{tex})	31.5
Yarn irregularity (U %)	11.1
Hairiness (H)	5.4

2.2. Fabric Production

To determine the effect of washing technique on the pilling of fabrics, the cotton yarns were knitted into a stocking fabric on a Harry Lucas machine (E 20 and total of 240 needles).

2.3. Detergent

In this study, 1g/L commercial detergent was used. The content of this detergent is:
‹5% nonionic active, polycarboxysilicate, phosphanate, soap, cation active substance,
5-15 % anionic active, oxygen-based bleaching,
15-30 % phosphate and enzyme.

2.4. Methods

2.4.1. Ultrasonic Washing Method

In this study, Branson 2200-F-4 model ultrasonic cleaner (47 kHz ± 6%) was used in the ultrasonic washing. 1L of deionised water containing 1g of commercial detergent placed in an ultrasonic bath. 600 mm long cotton yarns and 150x150 mm squares of knitted fabrics were immersed into heated bath. The yarns and fabrics were kept for 30 min durations in the ultrasonic vibrated bath at 40 ^{0}C of water. The ultrasonic washing process was repeated 10 times for each sample. After the washing process, the ultrasonically washed samples were rinsed twice in a 1l deionised water bath and left out to dry at room temperature.

2.4.2. Conventional Washing Method

1L of deionised water containing 1g of commercial detergent was placed into a Gyrowash lab-size washing machine. Temperature was maintained at 40 ^{0}C throughout the washing. 600 mm long cotton yarns and 150x150 mm squares of knitted fabrics were placed in the machine and washed for 30 min intervals. After being washed 10 times repeatedly, the samples were rinsed twice in a 1l deionised water bath and left out to dry at a room temperature.

2.4.3. Determination of Pilling Washing Method

The fabric samples were left to conditioning under the standard atmosphere which is 20 ± 2 ^{0}C and 65% ± 2 RH for 48 hours. 4 samples from each fabric were tested for pilling on a nu-martindale abrasion tester. 2000 rubs were considered for the pilling tests and the comparison was made according to ASTM D 4970-89 (12).

2.4.4. Mechanical Testing

Both conventionally and ultrasonically washed yarns were tested for their breaking tenacity and elongation according to ASTM D 2256-97 standard [13] by using a Instron 4411 model testing instrument. The mechanical testing instrument was calibrated just prior to the tests according to the instructions given in the equipment's manual. All the yarns were tested in standard atmospheric conditions after 48 hours of equilibrium was reached.

2.4.5 Colour Measurement of the Washing Samples

The colour of untreated fabric, ultrasonically washed and conventionally washed fabrics was measured using a Datacolor SF 600 PLUS spectrophotometer with the CIELab system D 65 and 10^0 observer USAV 6.6 mm.

2.4.6. Evaluation of the SEM Photographs

In this study, a JEOL JSM-5910 LV model scanning electron microscope was used. Samples of untreated cotton fabrics, fabrics washed in conventional method and fabrics washed by ultrasonic method was cut into small pieces and bonded onto a conductive mount. These samples were then gold coated for 90 seconds with 18 mA current under vacuum. The magnification was 25 kW with x60.

3. RESULTS AND DISCUSSION

3.1. Pilling Values of the Produced Fabrics

The pilling values of the cotton knitted fabrics are given in Table 3; the related standard [14] gives pilling values of the fabrics as 1, 2, 3, 4, 5 from the worst to the best.

Table 3: *Pilling values of knitted fabrics*

Fabrics	Pilling values of untreated fabric	Pilling values after ultrasonic washing	Pilling values after conventional washing
Coton (100 %)	3	4	3

3.2. Breaking Tenacity and Breaking Elongation Values of the Yarns

As can be seen in the tables, both ultrasonic washing and conventional washing methods resulted in a decrease in yarn breaking tenacity values with respect to unwashed cotton yarns. However, when the two washing methods were compared to one another it is obvious that ultrasonic washing method caused less deterioration in breaking tenacity of yarns than conventional method. Due to the discrepancies in the values of yarn elongation, the situation seems to be not very clear in the case of the elongation values. But again ultrasonic washing method gave rise to higher elongation values compared with conventional washing method. It is thought that by the interlocking effect, the fibres were reduced leading to an increase in the elongation values. The yarn tensile parameters are tabulated in Table 4.

Table 4: *Yarn tensile parameters*

Yarn Parameters	Untreated Yarn	Sd	Washed by Ultrasonic Method	Sd	Washed by Conventional Method	Sd
Yarn Breaking Tenacity (cN/tex)	14.5	0.53	13.8	0.49	13.0	0.51
Yarn Breaking Elongation (%)	4.10	0.46	3.40	0.52	3.20	0.48

3.3. Lightness (L*) Values of the Fabrics

The results of these colour measurements are presented as lightness (L*) in Table 5. As can be seen in the table, conventional washing method resulted in lower lightness (L*) values than that of ultrasound process.

Table 5: *Lightness (L*) values of the fabrics*

L* Values of Untreated Fabric	L* Values after Conventional Washing	L* Values after Ultrasonic Washing
83.99	87.00	88.58

3.4. Interpretation of the SEM Photographs

Ultrasonic washing led to less reduction in yarn strength when compared with conventional washing. The reason for this is superior performance of that the cavitation energy, which is formed by ultrasonic vibration, was evenly distributed among fibres. This was demonstrated by the SEM micrographs shown in the Figs 1–3. In these micrographs, the yarn twists can be clearly observed on the ultrasonically washed fabrics. In the comparison of ultrasonic washing with conventional

washing, less harm was demonstrated to the yarns of the fabrics. As mentioned earlier, the protruding ends of the fibres were visualized through scanning electron microscopy on the fabric surface to correlate a relationship with number of these ends of the yarns and surface of the knitted fabrics which are made of from these yarns.

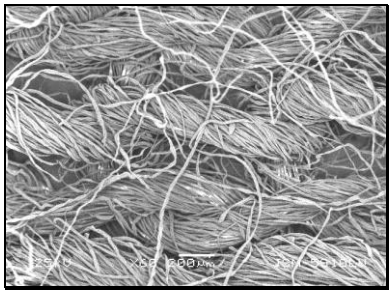

Fig.1: *Untreated fabric*

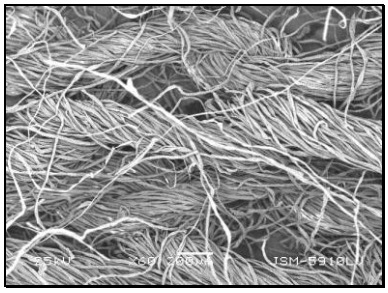

Fig.2: *Conventionally washed fabric fabric*

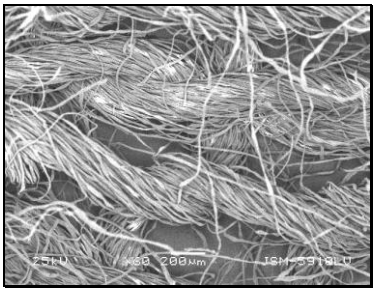

Fig.3: *Ultrasonically washed*

3. CONCLUSION

1. The breaking tenacity and elongation of washed and dried yarns were lower than the untreated yarns.

2. Both breaking tenacity of yarns and elongations were slightly lower than the ultrasonic washing methods.

3. Better lightness (L*) can be achieved by using the ultrasonically washed knitted fabrics than by using a conventional washing method.

4. Ultrasonically washed fabric has shown better pilling values than conventionally washed fabrics.

5. Conventionally washed fabrics have shown more protruding ends on the surface of the knitted fabrics than the ultrasonically washed fabrics.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EMISSION REDUCTION OF COLORED WASTE WATER AFTER CONTACT WITH A NATURAL SORBENT WITH A SPECIAL FOCUS ON THE THERMODYNAMICS OF ADSORPTION

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Abstract: *The possibilities of using an inexpensive sorbent for dyes removal from waste waters after textile dyeing were investigated in this work. Ashes from city heating plant that arise as a by-product in the burning process during the city central heating operated were sorbent. After chemical modification of the ashes it were transformed to the efficient sorbent. Based on the results from this paper, it can be said that the sorbent produced from ashes has potential for the textile dyes removal from aqueous solutions and emission reduction of toxic dyes. A metal complex textile dye was used and the adsorption thermodynamics were studied. On the basis of obtained results, it can be concluded that the natural sorbent is an efficient sorbent for metal complex removal dye from aqueous solution and has a potential for use on an industrial scale. Characterization of other similar, solid waste materials can help explain adsorbate–sorbent interactions in order to optimize and increase efficiency of adsorption process as an environmentally acceptable process. Negative values of free energy change indicate a spontaneous nature of adsorption, negative values of free enthalpy change indicate an exothermic adsorption process and negative values of free entropy change indicate a decrease of disordered system at solid – liquid interface during adsorption. Based on adsorption, kinetic and thermodynamic parameters it can be concluded that chemisorption of the dye on the sorbent is also present together with physical adsorption.*

Keywords: *ashes, dyeing, metal complex dye, enthalpy, entropy, free energy.*

1. INTRODUCTION

Last few decades several decolorization methods were reported, some of them adopted in textile industry. Among many dye removal techniques, adsorption procedures give the best results because they can be used to remove various coloration materials. The most of commercial systems use activated carbon as a sorbent for dye removal from waste water due to its excellent adsorption abilities. Although activated carbon has advantages as a sorbent, its widespread use is limited due to high costs. To reduce treatment costs attempts are made to find cheap alternative sorbent [1].

Dye removal with various sorbents is subject of some recent research works. Waste agriculture materials, sugar cane pith, wood sawdust, pine bark, corncob, rice bran, rice husk, coconut shell fibers, walnut shell, and soy and cotton seed hull were investigated for their adsorption properties and it was reported that these materials can adsorb various pollutants including dyes. Waste sawdust and sugar cane pith are also able to adsorb significant quantities of wastewater dyes while palm tree particles were used in basic dyes adsorption [2, 3].

This paper attempts to explain the absorption of metal complex dye on sorbent from ashes obtained after burning of brown coal in the city heating plant using thermodynamic principles. This can impact on a better understanding of the adsorption of waste dye to a waste solid sorbents to reach a wider and more practical application on a larger scale.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and methods

The sample, city heating plant ashes, used in the experiments, was obtained after burning of brown coal. One of the reasons for the use of ash as adsorbent, lies in the fact that it is a waste material that is easy to find and practically it is very inexpensive means. After collecting and drying the ash was sieved to 0.7 mm particle size. After combustion the ash contains many metal salts, especially oxides making basic pH of ash solution in distilled water. In this form the ash has not a satisfactory adsorption power (tested practically), and its modification is necessary by treatment with 8 % sulfuric acid for 40 min. The treatment is repeated until ash water extracts become neutral or slightly acidic with pH 6-7. The treatment is followed by distilled water rinse and air drying. The constant amount of ashes of 1-4 g was used, and 100 cm^3 of solution contained dye concentrations of 10-100 mg/dm^3, while the equlibrium time was 30 min. The procedure is based on similar research [3].

Models of waste water after dyeing were prepared with metal complex dye C.I. Acid Blue 193. Preliminary results showed the most efficient adsorption occurred at pH 10.

Thermodynamic parameters for adsorption systems were calculated using following equations [4]:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \quad \textbf{(1)}$$

$$\Delta G = \Delta H - T \cdot \Delta S \quad \textbf{(2)}$$

where: k_2 (g/mg min) is second order adsorption rate constant; T (K) is temperature; k_b ($1.38065 \cdot 10^{-23}$ J/K) is Boltzmann's constant; h ($6.626 \cdot 10^{-34}$ J·s) is Planck's constant; ΔS (J/K·mol) is entropy change; R (8.314 J/Kmol) is universal gas constant; ΔH (J/mol) is enthalpy change; ΔG (J/mol) is Gibbs free energy change.

Plot $ln(k_2/T)$ vs. $1/T$ gives a straight line from where enthalpy and entropy changes can be calculated.

Thermodynamic parameter values are actual indicators for practical application of the process. In some adsorption processes entropy and enthalpy are considered in evaluation of spontaneous process.

Rate constant is also expressed as a temperature function with Arrhenius type equation [5]:

$$k_2 = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \qquad \ln k_2 = \ln A - \frac{E_a}{R \cdot T} \quad \textbf{(3)}$$

where: k_2 is second order adsorption rate equilibrium constant, g/mg min; A is sorption frequency factor; E_A is Arrhenius activation energy, J/mol; R is gas constant equal 8.314 J/mol K; T is process temperature, K.

The plot lnk_2 vs. $1/T$ is a straight line with slope $-E_a/R$. Activation energy gives an idea on adsorption type which is mostly physical or chemical.

3. RESULTS AND DISCUSSIONS

The H_2SO_4 treatment of ashes increases the surface area and pore volume, while decreases its average pore diameter. The adsorption capacity of the ash enhances with increasing pH value in basic solution, which may be explained by surface condition of the ashes and by the changes of the dye in the basic solution [3].

SEM tests of sorbent samples has shown finely scattered material consisting of heterogeneous particles with irregular shape originating from agglomerates, probably from particular minerals, mostly below 5 μm in size. Micrograph in Fig. 1a shows magnification of 1000× and in Fig. 1b it is 5000× (Fig. 1).

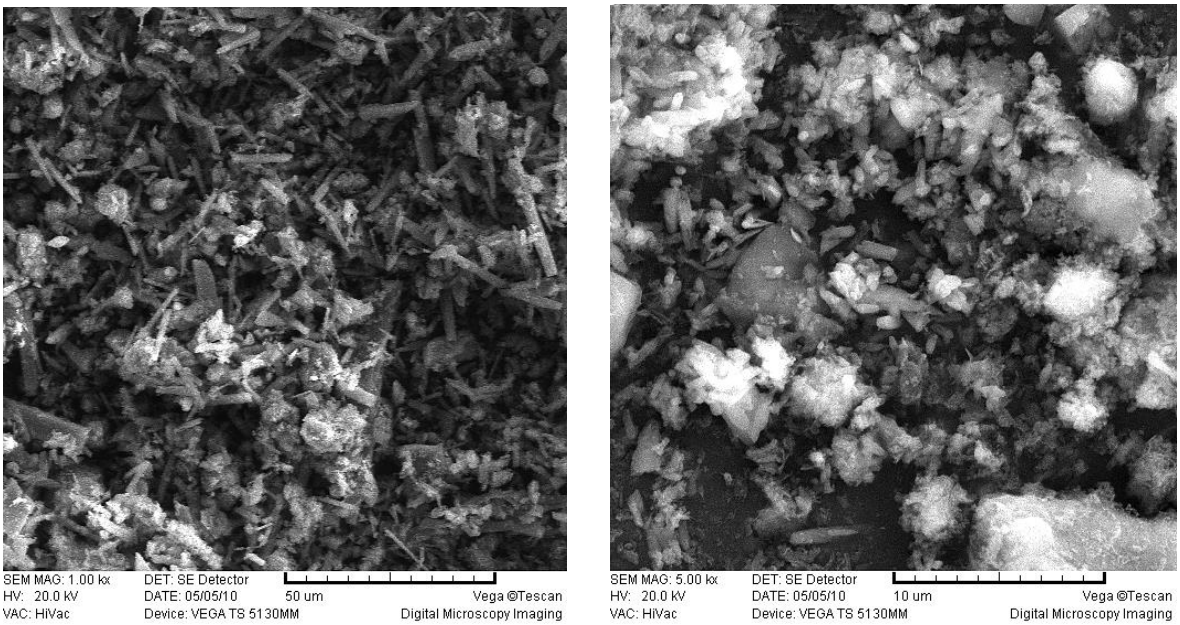

Fig. 1: *Micrographs of studied sorbent, 1000× to the left, b) 5000× to the right*

Temperature has two main effects on adsorption process. It is known that higher temperature increases diffusion rate of bound molecules over outer boundary layers into pores of sorbent particle. Moreover, adsorption equilibrium capacity of particular sorbent–adsorbate system is changed [3, 4].

Fig. 2 shows adsorption plots of used dye and all sorbent doses and on the bases of them (slope and intercept), major thermodynamic parameters, as adsorption process enthalpy and entropy were determined and on their basis the change of *Gibbs* free energy is calculated.

Graphs in Fig. 3 represents *Arrhenius* adsorption graphs for dye and serve for determination of process activation energy of all sorbent doses.

From these diagrams (figs. 2 and 3) it calculated values of thermodynamic parameters, entropy, enthalpy, Gibbs free energy and activation energy for studied dye, all sorbent doses, all initial concentrations and all studied temperatures of adsorption.

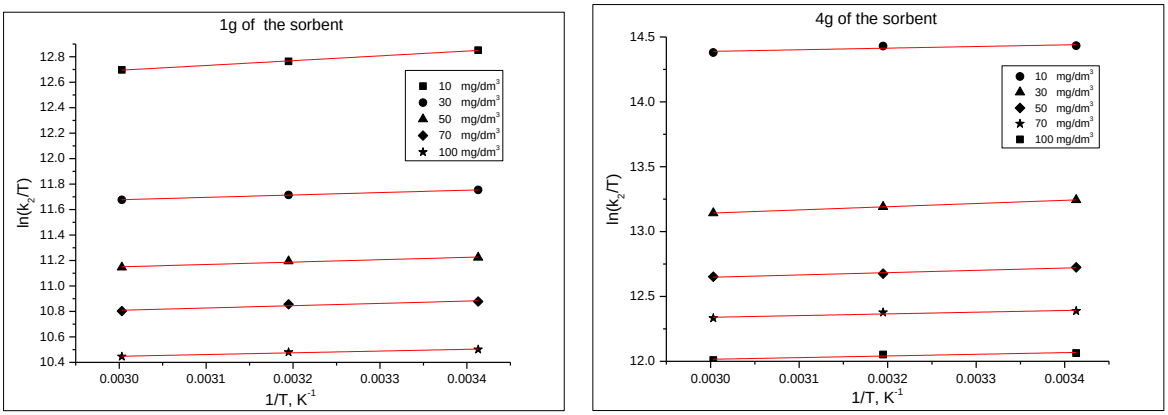

Fig. 2: *Plots ln(k_2/T) vs. 1/T for adsorption of the dye on sorbent*

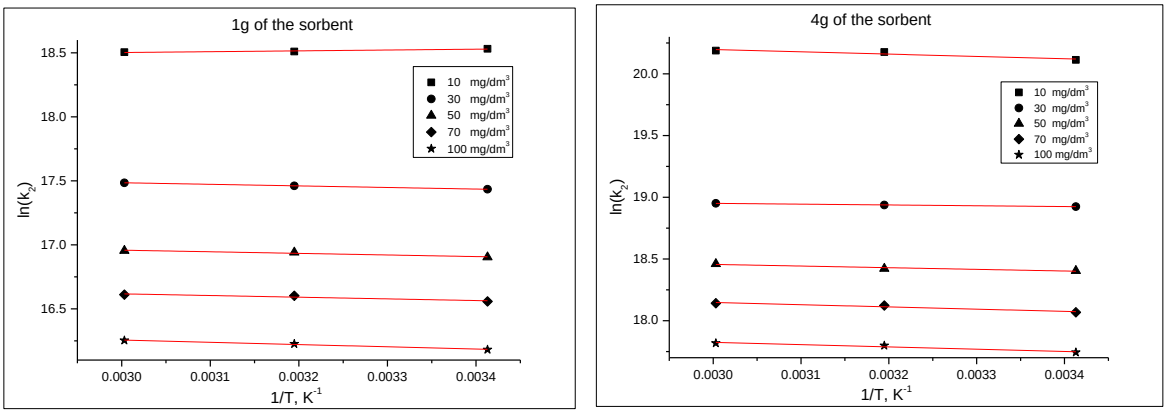

Fig. 3: *Arrhenius graphs of the dye adsorption on sorbent*

The results confirm the fact that activation energy of surface reaction has positive values. In our case, E_a has small values indicating fast reactions which can be affected also by the fact that some structurally different parts of sorbent may take a role of a catalyst decreasing activation energy. It is also known that, when reaction occurs in more steps, molecularity is decreased reducing activation energy. On the other hand, when association mechanism is considered, reaction rate is increased because of facilitated electron transfer, rearrangement of some reactant atoms into more favorable positions, better orientation etc. When considering these mechanisms, superposition of adsorption and desorption processes should also be taken into account [6].

Entropy is decreased when initial adsorbate concentration is increased, but increased when sorbent quantity is increased. Energy released during adsorption process compensates entropy loss of adsorbed molecules, i.e. stronger forces release more energy [7].

As entropy is a state function that can be considered as a measure of "bound" energy of an isolated system, i.e. energy that, contrary to "free" energy, cannot be converted to work, negative changes of entropy (-1.17 to -1.65 J/K·mol) correspond to reduced degree of freedom of adsorbed dye; that indicates decreasing of disordered system at solid-liquid interface during dye adsorption on sorbent. Moreover, reaction rate depends also on the probability of forming of activated complex having adequate configuration. If the structure of activated complex is more ordered then entropy reduction is higher and reaction rate is also lowered due to the effect of entropy factor. Adsorption entropy can be changed in two directions during forming of monolayer. First, entropy is decreased

due to increasing of adsorbed molecules order; when some surface covering is reached, increased movements of loosely bound particles may bring about the entropy increase. Entropy is an extensive state property of a system and its value depends on the substance quantity in the system [5].

Gibbs free energy is increased discontinuously with adsorbate quantity but continuously with temperature increase. By increasing sorbent mass the free energy is changed discontinuously showing similar and highest values with 1 and 3 g of sorbent. Since adsorption reaction can occur only if the change of total Gibbs free energy is negative, then negative values of free energy indicate spontaneity of adsorption process, i.e. favoring dye adsorption at 20, 40 and 60°C. Thereby, feasibility and spontaneous nature of adsorption process is confirmed at applied temperatures with good affinity of dye molecules to sorbent surface [8].

Negative values of enthalpy change (between -0.3 and -3.13 kJ/mol) indicate exothermic nature of adsorption interactions of studied dye and sorbent and the process is therefore energetically stable. It could be also concluded that breaking of bonds between adsorbate molecules and sorbent surface occurred because adsorbed molecules were not bound strongly on sorbent surface. They are in dynamic equilibrium with other molecules in bulk phase and can move only two dimensionally on the surface itself. When it is compared to three dimensional movements in bulk phase, this means enthalpy loss, indicating an exothermal process of adsorption [9].

Similar investigation reveal different results. The negative values of ΔG and positive ΔH obtained indicate that the black dye adsorption by sorbent is a spontaneous and endothermic process. The positive value of ΔS suggests that increased randomness at the solid/solution interface occurs in the internal structure of the adsorption of black dye onto sorbent [10].

Next, the negative ΔG suggests that the sorption of metal complex textile dye onto agro-residue is feasible and spontaneous thermodynamically. The positive ΔH suggests that this process is endothermic in nature while the positive ΔS indicates the increased randomness at the solid/liquid interface during the sorption process. The activation energy for the metal complex textile dye sorption by agro-residue was 45.84 kJ/mol indicating the physisorption process is predominant [11].

Also, molecuIs of the metal complex textile dye can remove by fungi, so the negative values of ΔG confirm the feasibility and spontaneous nature of the fungal biosorption processes at 25°C with a high degree of affinity of the dye ions for each biosorbent surface. The positive value of ΔH for *A. niger* biosorption (50.96 kJ/mol) suggests the endothermic nature of adsorption process favourable at higher temperatures and possible strong bonding between dye and the sorbent while the negative value of ΔS (-0.17 kJ/mol·K) revealed the decreased randomness at the solid/solution interface and no structural modification in *A. niger* during the adsorption of dye. The negative ΔH values of (-39.70) and (-14.48 kJ/mol) confirmed the exothermic nature of dye biosorptions on *R. arrhizus* and *T. versicolor* while positive ΔS values of 0.12 and 0.04 kJ/mol·K reflected the affinity of these biosorbents to dye in solution and some structural changes in sorbate and biosorbents, respectively. Generally, the change in adsorption enthalpy for physisorption is between 20 and 40 kJ/mol, but chemisorption is in the range of 80 - 400 kJ/mol. The values of the change in enthalpy indicated that each adsorption process is physical in nature [12].

4. CONCLUSIONS

On the basis of obtained results, it can be concluded that the natural sorbent is an efficient sorbent for removal of metal complex dye from aqueous solution and has a potential for use on an industrial scale. Characterization of other similar, solid waste materials can help explain adsorbate–sorbent interactions in order to optimize and increase efficiency of adsorption process as an environmentally acceptable process.

On the basis of experimental results the following conclusions are made:

- Negative values of free energy change indicate a spontaneous nature of adsorption.
- Negative values of free enthalpy change indicate an exothermic adsorption process.
- Negative values of free entropy change indicate a decrease of disordered system at solid – liquid interface during adsorption.
- Values of activation energy explain the type of adsorption.
- Based on adsorption, kinetic and thermodynamic parameters it can be concluded that chemisorption of the dye on sorbent is also present together with physical adsorption.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY ON THE BIOSCOURING TREATMENT OF 50 % OF HEMP + 50 % OF COTTON FABRICS

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Abstract: *This work presents the study of the Bioscouring treatment applied on 50 % of hemp + 50 % of cotton blended materials. The goal of the treatment was the removing of morphological impurities present in cotton and hemp fibers in order to obtain cleaner materials with better properties.*
For enzymatic treatments different concentrations (1-3 % o.w.f) from a commercial product named Beisol PRO (a mixture of enzymes pectinases) were used. The reaction media was made of phosfate buffer solution of 0.1 M and pH 8. (sodium phosfate/disodium phosphate), 2 g/L sodium citrate (complexing agent) and 0.5 % Denimcol Wash RGN (wetting agent). All the experiments were carried out after a central, rotatable second order compound program with two independent variables: enzyme concentration (concentrations between 1-3 % o.w.f) and treatment time (15-55 minutes) at 20:1 liquid to fabric ratio and a temperature of 55 ^{0}C.
The reatment efficiency has been verified by the following analyses: weight loss, hydrophilicity, whiteness degree, yellowness degree, crystallinity, tensile strength, elongation at break, Scanning Electron Microscopy (SEM), spectrophotometric analysis in CIELAB system of the samples dyed with alizarin dye.
After all the investigations it was found that the bioscouring procedure of 50 % of hemp + 50 % of cotton blended materials conducted to a proper removal of the morphological impurities without affecting the internal structure of cellulose or any significant degradation of the material.

Key words: *hemp/cotton material, bioscouring treatment, enzymatic commercial product, weight loss, hydrophilicity, whiteness degree*

1. INTRODUCTION

The cotton and hemp fibers mainly consist of cellulose. In addition to cellulose, natural attendants like pectins, waxes, extractable substances, minerals, etc. are present in the fibers structure.

The pectin is mainly present in median lamella, accompanying the fiber in the growth process and giving elasticity to the fibers. It contains cycles of methylated D-galacturonic acid. D-galacturonic acid partially esterified is called pectic acid and has the following structure as shown in Fig. 1 [1].

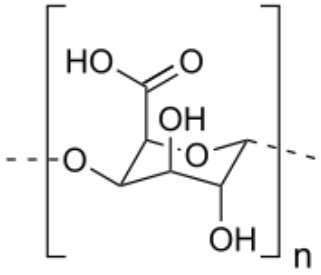


Fig. 1*: The structure of pectic acid*

By scouring treatment, the removal of natural attendances of cellulose is done by using sodium hydroxide which is usually replaced by enzymes, normally pectinases in the bioscouring treatment. Besides these agents, other auxiliaries are used: surfactants (anionic or non-ionic) and sequestrant agents in order to obtain a complete and uniform cleaning treatment. The role of the surfactants is to emulsify the unsaponifiable substances. The sequestrant agents bind the Ca^{2+} and Mg^{2+} ions which are present both in fiber's structure and water treatment, thus the detergent precipitation and staining of the fabric in the process is prevented. The sodium citrate belongs to the group of the hydroxycarboxylic acids and shows a very good sequestering activity [2].

Ideally, the scouring treatments have to be conducted in such a way that, the removal of natural attendants does not affect the structure of cellulosic fibers. Without these attendants, the material becomes hydrophilic and whiteness degree, crystallinity and mechanical properties are improved [3].

Still, over chemical or enzymatic treatments of textiles, different cellulose degradations may occur by hydrolysis or oxidation reactions, thermal, biochemical and photochemical actions, resulting hydrocelluloses, oxicelluloses, photocelluloses by the convertion of alcohol groups in the carbonyl or carboxyl groups [4].

2. EXPERIMANTAL PART

14 samples (13 for the enzymatic treatments and 1 for the conventional alkaline scouring treatment) were prepared from a fabric with the following characteristics: width (120 ± 3 cm), weight (220 ± 10 g/m^2), warp density (10 fibers/cm), weft density B (10 fibers/cm), 100 % of cotton yarn, Nm 14 for warp direction and 50 % of hemp + 50 % of cotton yarn, Nm 14 for weft direction.

Before the cleaning treatments, the samples were were washed with hot water at 100°C using a AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company - USA, followed by: drying, conditioning, weighing [5]

After drying, conditioning and weighing, the samples were subjected to Bioscouring and alkaline treatments. For enzymatic treatments concentrations between 1-3 % from the commercial enzymatic product Beisol PRO were used in phosfate buffer solution of 0.1 M and pH 8. (sodium phosfate/disodium phosphate) with the addition of 2 g/L sodium citrate and 0.5 % Denimcol Wash RGN. The liquid to fabric ratio was 20:1 and the temperature 55 ^{0}C for Bioscouring treatments and 100 ^{0}C for alkaline treatment, respectively. The variation of enzyme concentration (1-3 % o.w.f.)

and treatment time (15-55 minutes) was made by using a central, rotatable second order compound program with two independent variables. The alkaline treatment was done with 10 g/L sodium hydroxide, 5 g/L sodium carbonate, 1 g/L sodium bisulfite, 2 g/L sodium silicate and 2 g/L Sulfolen 148 (S-148, alkyl polyglicol ether) as a wetting agent.

Treatments efficiency was verified by the following analyses: weight loss, hydrophilicity, whiteness degree, yellowness degree, crystallinity, tensile strength, elongation at break, Scanning Electron Microscopy (SEM), spectrophotometric analysis in CIELAB system of the samples dyed with alizarin dye.

The results for weight loss and hydrophilicity after enzymatic and alkaline treatments are presented in Table 1.

Table 1: *Weight loss and hydrophilicity obtained for the samples subjected to the alkaline and bioscouring treatments for different conditions*

Sample	Enzyme concentration [%]	Treatment time [minutes]	Weight loss [%]	Hydrophilicity [s]
1	1.30	21.00	0.53	0.68
2	2.70	21.00	0.43	0.58
3	1.30	49.00	0.68	0.56
4	2.70	49.00	0.80	0.55
5	1.00	35.00	0.98	0.44
6	3.00	35.00	1.04	0.42
7	2.00	15.00	1.10	0.50
8	2.00	55.00	0.85	0.51
9	2.00	35.00	1.16	0.44
10	2.00	35.00	1.25	0.43
11	2.00	35.00	1.09	0.44
12	2.00	35.00	1.53	0.43
13	2.00	35.00	1.32	0.53
Alkaline	-	60.00	4.71	0.52
Control	-	-	-	>500

By analyzing the data presented in Table 1 it can be seen that for all coditions of enzymatic treatments, the weight loss does not exceed 2 %, which proves that the material was not degraded during treatments. For classic alkaline treatment, a higher weight loss of 5 % is observed, caused by the possible degradation of the fibers.

Regarding the hydrophilicity, for all 14 different treatments, values under 1 second were obtained, which show a good wettability of the treated material as a result of a proper cleaning. The wettability of the fabric being very important for further finishing processes.

The degree of structural organization of cellulose from treated fabric was evaluated by XRD analysis. A MiniFlex 600 diffractometer (Rigaku Corporation, Japan) was used. The operating conditions were: 40 kV, 15 mA, with CuKα monochromatic radiation, and using SC-70 detector and the automatic 6 position sample changer, ASC-6. The scan range was 5°-45°, with step width 0.05°, scan speed 1.2° / min. at room temperature and humidity. The PDXL2 Version 2.4.2.0 containing powder diffraction analysis package, PDXL Comprehensive Analysis, was used to analyze and calculate the cristallinity procent based on the diffraction intensity of the crystalline and amorphous phases.

For a better characterization of the treated samples from 50 % of cotton + 50 % of hemp material, determinations for tensile strength and elongation at break were made according to ASTM D 5035 – 06 "*Standard Test Method for Breaking Force and Elongation of Textile Fabrics (Strip Method)*" [6]. A testing machine 5KT from Tinius Olsen – United States with an interface running on a connected PC by Horizon software was used.

The crystallinity, tensile strength and elongation at break of the 50 % of cotton + 50 % of hemp analyzed samples are presented in Table 2.

Table 2: *The crystallinity, tensile strength and elongation at break of the treated samples*

Sample	Enzyme [%]	Treatment time [s]	Crystallinity	Tensile strength [N]	Elongation at break [%]
1	1.30	21.00	67.4	325.00	10.00
2	2.70	21.00	66.0	320.00	10.00
3	1.30	49.00	67.0	323.00	10.00
4	2.70	49.00	67.0	324.00	10.00
5	1.00	35.00	66.1	306.00	10.00
6	3.00	35.00	61.0	280.00	9.00
7	2.00	15.00	68.0	305.00	10.00
8	2.00	55.00	62.2	283.00	9.00
9	2.00	35.00	72.0	345.00	11.00
10	2.00	35.00	69.1	335.00	10.00
11	2.00	35.00	64.4	331.00	10.00
12	2.00	35.00	66.5	334.00	10.00
13	2.00	35.00	82.0	360.00	10.00
Alkaline	-	60.00	63.4	287.00	9.00
Control	-	-	65.0	333.00	10.00

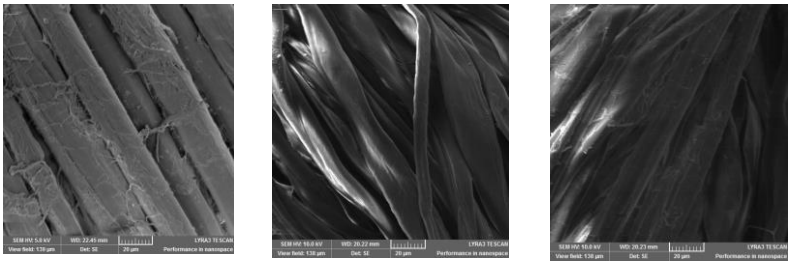
From data presented in Table 2 it can be seen as crystallinity varies depending on the treatment conditions, so that there was an increasing for concentrations up to 2.7 and 49 minutes and a decreasing of crystallinity for concentrations greater than 2.7 % and a higher duration of treatment (55 minutes). A good crystallinity seems to be at a concentration of 2 % enzyme and 35 minutes for treatment time. With the decreasing of crystallinity, the tensile strength of the material is decreasing.

For the majority of the treated samples, a slightly decreasing in tensile strength is observed compared to control (18 %), without significant changes in elongation at break. An increase in tensile strength of the material appears for the treatment with 2 % concentration of enzyme for 35 minutes.

The aspect of the fibre surface and structural changes were investigated by using Scanning Electron Microscopy (SEM). The samples were placed on a specimen support, then coated with Au using an auto fine coater (JFC-1200, JEOL Co., Japan). Observations were conducted using a SEM (LYRA 3, Tescan, Czech Republic) at 5 kV or 10 kV.

Figure 2 presents the SEM micrograph of 50 % of cotton + 50 % of hemp material for untreated sample (1), enzymatically treated sample at 2 % enzyme concentration and 35 minutes (2) and alkaline treated sample (3).

The SEM image (1) shows for untreated sample the presence of non-cellulosic cementing materials binding the fiber bundles together. No fiber damage was noticed for enzymatic treatment (2). The impurities were removed and the fiber surface is smooth and clean. The image of alkaline treated sample (3) presents peeling effect and some fibers degradations.



(1) (2) (3)

Fig. 2*: SEM micrographs for untreated sample (1), enzymatically treated sample (2% enzyme-35 minutes) (2), alkaline treated sample (3).*

Also, the treated samples were measured for whiteness and yellowness degree using a Datacolor 500 spectrophotometer. The reflectance (R %) at 420 nm was measured in comparison with a standard from barium sulphate of absolute white. The Hunter Whiteness Index and DIN 6170 Yellowness Index were calculated automatically by Datacolor Tools 2.0 software [7]. Bioscouring treatments led to a lower yellowness degree and to a 15 % enhancement of whiteness degree of the samples compared to control. A significant increase in whiteness degree of approximately 45 % appears for classic alkaline treated sample.

An effective cleaning of the material is also given by the removing of Ca^{2+} ions present in the pectin structure. Spectrophotometric analyses in CIELAB system were used for measuring the reflectance (R %) at 540 nm of the alizarin dyed samples in comparison to the control and K/S values were calculated. The color strength K/S value is a number related to the amount of the dyestuff present in a substrate. From these values, the percentage of residual calcium was used to establish the degree of Ca^{2+} ions removal. The results obtained for whiteness degree, yellowness degree and color strength (K/S) is shown in Table 3.

Table 3: *The whiteness degree, yellowness degree and color strength (K/S) of the treated samples*

Sample	Enzyme [%]	Treatment time [s]	Whiteness degree	Yellowness degree	Color strength (K/S) Alizarin
1	1.30	21.00	58.38	10.49	0.86
2	2.70	21.00	61.23	13.73	0.83
3	1.30	49.00	59.82	14.44	0.87
4	2.70	49.00	59.32	14.67	0.80
5	1.00	35.00	59.17	14.83	0.88
6	3.00	35.00	59.25	14.86	0.80
7	2.00	15.00	59.09	14.86	0.85
8	2.00	55.00	58.23	15.23	0.88
9	2.00	35.00	58.06	15.37	0.79
10	2.00	35.00	58.02	15.43	0.84
11	2.00	35.00	58.02	15.17	0.83
12	2.00	35.00	58.34	15.25	0.82
13	2.00	35.00	58.13	15.29	0.85
Alkaline			75.60	7.31	0.66
Control			52.00	16.45	1.01

A decreasing of the color strength (K/S) is observed for both enzymatically and alkaline treated samples, which demonstrates the removal of calcium ions from the system. For enzymatically treated samples, the color strength (K/S) was decreasing with 14-22 % compared to control. A 35 % decreasing of the color strength (K/S) is observed for alkaline treated sample.

5. CONCLUSIONS

After all the ivestigations carried out it was found that:

- For all enzymatic treatments, the weight loss does not exceed 2 %, what proves that the material has not suffered any degradation. For the alkaline treatment, a higher weight loss of 5 % is noticed, possible to some degradation of the fibres. The hydrophilicity values are under 1 second for all 14 different treatments, which show a good wettability of the treated material as a result of a proper cleaning.
- The crystallinity was varied depending on the treatment conditions, so that there was an increasing for concentrations up to 2.7 and 49 minutes and a decreasing of crystallinity for concentrations greater than 2.7 % and a higher duration of treatment (55 minutes). A good crystallinity was registered at a concentration of 2 % enzyme and 35 minutes for treatment time.
- With the decreasing of crystallinity, the tensile strength of the material was decreasing. For the majority of the treated samples, a slightly decreasing in tensile strength was observed compared to control (18 %), without significant changes in elongation at break. An increase in tensile strength of the material appeared for the treatment with 2 % concentration of enzyme and 35 minutes.
- Bioscouring treatments led to a lower yellowness degree and to a 15 % enhancement of whiteness degree of the samples compared to control. A significant increase in whiteness degree of approximately 45 % appeared for classic alkaline treated sample.
- A decreasing of the color strength (K/S) was observed for both enzymatically and alkaline treated samples, which demonstrates the removal of calcium ions from the system. For enzymatically treated samples, the color strength (K/S) was decreasing with 14-22 % compared to control. A 35 % decreasing of the color strength (K/S) was noticed for alkaline treated sample.

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ANNALS OF THE UNIVERSITY OF ORADEA
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METAL OXIDE DOPED ANTIBACTERIAL POLYMERIC COATED TEXTILE MATERIALS AND ASSESSEMENT OF ANTIBACTERIAL ACTIVITY WITH ELECTRON SPIN RESONANCE

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Abstract: *Antibacterial activity of a food conveyor belt is an essential property in some cases. However, every antibacterial chemical is not suitable to contact with food materials. Many metal oxides are suitable option for this purpose. The aim of this study was to investigate antibacterial properties of zinc oxide doped PVC polymer coated with electron spin resonance technique. Therefore, optimum zinc oxide containing PVC paste was prepared and applied to textile surface. Coating construction was designed as double layered, first layer did not contain antibacterial agent, thin second layer contained zinc oxide at 10-35% concentration. Oxygen radicals released from zinc oxide containing polymeric coated surface were spin trapped with DMPO (dimethylpyrroline-N-oxide) spin trap and measured with Electron Spin Resonance (ESR). Besides conveyor belt samples, oxygen radical release from zinc oxide surface was measured with ESR under UV light and dark conditions. Oxygen radical release was determined even at dark conditions. Antibacterial properties were tested with ISO 22196 standard using Listeria innocua species. Measured antibacterial properties were related with ESR results. Higher concentration of zinc oxide resulted in higher antibacterial efficiency. DCFH-DA flourometric assay was carried out to determine oxidative stress insidebacteria. It is tought that, this technique will lead to decrease on the labour and time needed for conventional antibacterial tests.*

Keywords**:** *Antibacterial, conveyor belt, Electron Spin Resonance, zinc oxide, spin trapping*

1. INTRODUCTION

A conveyor system is a very important part of an industrial facility with regard to continuous production. A conveyor belt has to fulfil some special expectations of the industry branch that it is used. From this point of view, food carrying conveyor belts are generally produced with antibacterial properties. Since those are in direct contact with food products, the antibacterial agents should be chosen form a very narrow list. Metal oxides, such as zinc oxide, magnesium oxide, calcium oxide, are very suitable option for an antibacterial addition for food conveyor belts due to non-toxic and durable properties [1-3]. Besides, with their low prices, metal oxides will be feasible alternative.

Though there are still some different thoughts about the antibacterial mechanisms of metal oxides, current researches concentrated on antibacterial effect with oxygen radical releasing of these chemicals. The electronic structure of metal oxides allows them to produce oxygen radicals such as $^{\bullet}OH$, $O_2^{\bullet-}$, $^1O_2$ [4-10]. Especially with UV light photons, the excitation and motion of electrons from valance band to conduction band leads to hole and electron couple formation. Electrons react with molecular

oxygen to form superoxide anion, holes take electrons from hydroxyl ions or water to form hydroxyl radical and superoxide anion reacts with water and singlet oxygen occurs [11].

Since oxygen radicals are highly unstable, it is difficult to detect these radicals under normal environmental conditions. Therefore, oxygen radicals must be reacted with special chemicals to obtain more stable and detectable compounds. Electron Spin Resonance (ESR) is one of the most important techniques to study with these oxygen containing compounds that have one or more unpaired electrons. The physical concept of ESR technique depends on the orientation of unpaired electron spins in the magnetic field. Under specific conditions, radicals have characteristic ESR spectrum. Signal intensities change with the radical concentration, thus, it is possible to predict about radical concentration [12, 13].

Spin traps are used in ESR to detect oxygen radicals. Spin traps react with oxygen radicals to form a stable radical which have a lifetime that at least let to take an ESR measurement. DMPO (dimethylpyrroline-N-oxide) is a suitable spin trap to detect $^{\bullet}OH$ radical [13]. The reaction between $^{\bullet}OH$ radical and DMPO spin trap is shown on Figure 1.

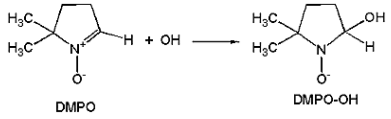

Fig. 1. *The reaction of $^{\bullet}OH$ radical and DMPO*

DCFH-DA is not a fluorescent compound, it can be pass through cell membrane and it is decomposed to DCFH inside the cell by intercellular esterases. When DCFH molecule reacts with oxygen radicals, it turns into DCF which is highly fluorescent. By this way, oxidative stress inside the cell can be detected [14-19].

The aim of this study is to confirm a relation between the radical formation that is detected by ESR measurements and antibacterial activity of textile materials. By this way, the labour and time (at least four days) which is spent for antibacterial test will be eliminated. Also, it will be possible to predict the antibacterial activity without pausing the production of the food producing facility.

2. EXPERIMENTAL

Zinc oxide (Sigma-Aldrich) was used as the antibacterial agent. Aqueous suspensions of 1, 10 and 100 g/L zinc oxide concentrations were investigated. Conveyor belts were produced with %10 and %35 zinc oxide concentration. Knife coating method was carried out and PVC polymer was used. Two layer of coating was carried out, top layer (0,05-0,1 mm) was the antibacterial layer. Oxygen radical releasing was observed under UV light and in dark conditions for zinc oxide powders and under UV light for conveyor belt samples. UV light exposure was 15 minutes.

ISO 22196-2011-*Measurement of antibacterial activity on plastics surfaces and other non-porous surfaces* standart was performed for antibacterial tests and *Listeria innocua* was used as the test bacteria.

ESR measurements were performed with Bruker e-scan model X-band spectrometer with following conditions: Microwave frequency, 9.80 GHz; scan width 65G; receiver gain $1.26x10^2$; resolution 512; conversion time, 81.92 msec; time constant 655 msec; scans, 4; modulation frequency, 86 kHz. 0.02 M DMPO (Sigma-Aldrich) was used as a spin trap. 360nm UV light was used for UV excitation of zinc oxide.

The concentration of released oxygen radical was calculated by the comparison of spin-adduct signals with signals of the known concentrations (1-30 µM) of stable TEMPO radical (Sigma-Aldrich) [20-22]. A calibration curve was built with the double integration of the ESR spectrum (signals only) of TEMPO ((2,2,6,6-Tetramethylpiperidin-1-yl)oxyl) in different concentrations. The bottom point of each signal was set to zero for area calculation.

Oxidative stress inside the bacterial cells was monitored under florescent microscobe using 100 µM DCFH-DA (Fluka). Bacteria culture in soy broth was incubated with 100g/L zinc oxide at 37ºC for 3 hours. After 3 hours of incubation, DCFH-DA solution was added to the culture media and incubation was continued for 1 hour. After 4 hours of total incubation, samples were analized under fluorescent microscobe. Excitation and emission wavelengths were λex= 498 nm and λem=522 nm, respectively

3. RESULTS AND DISCUSSION

The antibacterial efficiency is a very complicated phenomenon since there are countless parameters to be taken into account depending on the used antibacterial agent. As for metal oxides, such as zinc oxide, it is important to understand the mechanism of antibacterial activity in order to predict possible antibacterial effects and design a zinc oxide containing antibacterial product considering these properties. In this study, oxygen release from zinc oxide surface and the relation between antibacterial activity was studied and possible usage of zinc oxide in food conveyor belts was evaluated.

The ESR spectra of 100 g/L zinc oxide under UV light and in dark conditions are, shown on Figure 3. Specific signals for DMPO-OH adduct were obtained for ESR measurement of zinc oxide – DMPO solution interaction. As seen in Figure 2, even in dark conditions, the existence of oxygen radicals was seen in Fig.2B and C.

Effect of UV light on zinc oxide is clearly seen in Fig.2D. Electron-hole pairs created by electron excitation led to high amount of oxygen radical formation.

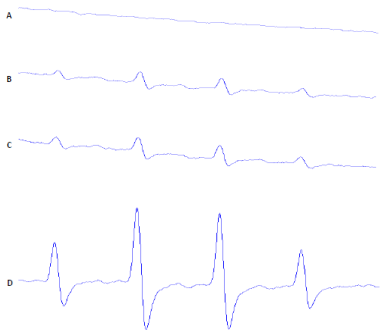

Fig 2: *ESR spectra of 100 g/l zinc oxide samples (A: Only DMPO solution, B: DMPO + zinc oxide under dark conditions, C: Pre-exposure of zinc oxide than mixing with DMPO solution, D: UV exposure of DMPO + zinc oxide suspension)*

As mentioned above, oxygen radical concentrations were determined by the comparison of DMPO-OH spin adduct ESR signals with the stable radical TEMPO's signal. The calibration curve obtained with signal area and concentration of TEMPO is shown in Figure 3.

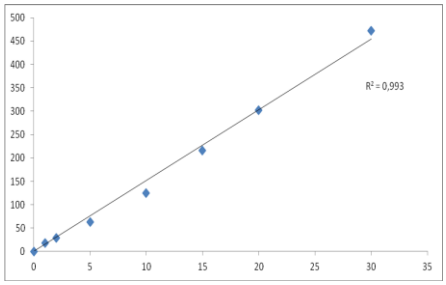

Fig. 3: *Calibration curve obtained with known concentrations of TEMPO stable radical*

Oxygen radical concentrations indicate that there is no dramatic change on oxygen radical release depending on the zinc oxide concentration. The lowest oxygen radical concentration (0.3 µM) was detected for 1 g/L zinc oxide concentration without UV light. Oxygen radical amounts detected with DMPO spin trap under dark conditions were 1.15 and 0.82 µM for 10 g/L and 100 g/L zinc oxide concentrations, respectively. On the other hand, zinc oxide exhibited antibacterial activity at much lower concentrations in dark conditions. Small amount of oxygen radical could be adequate for the antibacterial effect. Thus, increasing the zinc oxide concentration is not necessary for antibacterial efficiency due to slight changes of oxygen radical amount depending on concentration.

During UV exposure, oxygen radical releasing increases dramatically. Under UV light, there is almost no difference on oxygen radical concentration between 1, 10 and 100 g/L zinc oxide concentrations (7.78 µM, 7.67 µM, 7.82 µM, respectively). There are two situations conceivable; since zinc oxide release oxygen radicals via catalytic reaction, the potential of the medium for catalytic reaction might be limited or since zinc oxide is not water soluble, the UV exposure area of zinc oxide powder could be limited.

0.03 µM oxygen radical releasing was detected in 15 minutes of DMPO solution interaction with %10 zinc oxide containing conveyor belt material. On the other hand, 0,72 µM oxygen radical releasing was determined for 35% ZnO containing belt material. ESR signals of conveyor belt samples are shown on Figure 5.

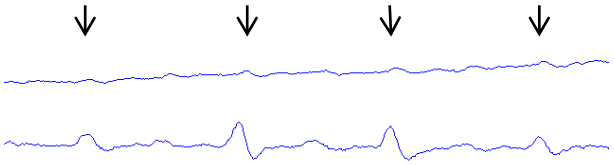

Fig. 4: *ESR signals of DMPO interaction with zinc oxide containing conveyor belts (10% ZnO: above, 35% ZnO: below)*

Very low concentration of oxygen radical was released from the surface of %10 ZnO containing belt material. The antibacterial activity of this belt material was 86.84%. 35% ZnO containing conveyor belt material exhibited % 99.99 antibacterial activity. These results are consistent with the calculated oxygen radical concentrations by using ESR measurements. The oxidative stress related ZnO inside the cells is shown in Fig.5. ZnO related oxidative stress inside the cells is seen on Figure 5.

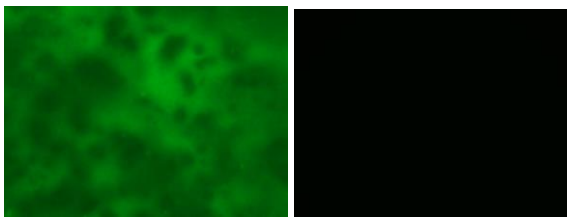

Fig. 5: *Fluorescent microscobe images of DCFH-DA treated bacteria (ZnO treated bacteria on the left, only bacteria and DCFH-DA on the right)*

Fluorescent microscope images belong to DCFH-DA assay was confirmed that ZnO caused an oxidative stress inside *Listeria innocua.*

4. CONCLUSION

Since the antibacterial activity arises from the oxygen radicals, determination of the radical quantity through the signal area of DMPO-OH spin adduct is a suitable way for the assessment of antibacterial activity. Even at low oxygen radical concentrations, antibacterial activity occurred.

In light of the information derived from this study, the concentration of the zinc oxide does not have a dramatic effect on antibacterial activity in the powder form. The released oxygen radical amounts for different concentrations were close to each other. UV light exposure created a significant effect on oxygen radical formation.

It can be told that, if a metal oxide (zinc oxide) will be used as an antibacterial agent in a conveyor belt, small amount of metal oxide usage will be effective. The important point is the contact of metal oxide powders with bacteria, otherwise, since the oxygen radicals have a very short time and might be fade and cause a decrease of antibacterial activity. At this point, the construction of the conveyor belt has an important role. Metal oxides should not be buried inside the polymer coating. Double layered coating with a higher concentration of ZnO on top layer would be an appliciable construction.

UV light usage is an important factor to increase antibacterial activity of zinc oxide. Oxygen radical amount increased nearly 20 times for 1 g/L ZnO concentration with UV light exposure. A facility that uses a zinc oxide containing antibacterial conveyor belt can use UV light in a point of the production and by this way, the antibacterial activity will be raised.

ACKNOWLEDGEMENT

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

VISCOSE BASED MAGNETIC YARNS – PHYSICAL AND MECHANICAL CHARACTERIZATION

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Abstract: *In the context of the rapid growth in the number of electrical and electronic devices and accessories that emit electromagnetic energy in different frequency bands we present and characterize here several magnetic functionalized viscose twisted yarns. A 100% viscose twisted staple yarn was covered through an in-house developed process with a polymeric solution containing micrometric sized barium hexaferrite magnetic powder. The in-house developed process allows deposition of micrometric thickness polymeric paste layer on the yarn surface. Barium hexaferrite is a hard magnetic material exhibiting high chemical stability and corrosion resistivity, relatively large saturation and residual magnetization and microwave absorbing properties. Five different percentages of the magnetic powder in the polymer solution were used, i.e. ranging from 15 wt% to 45 wt%. Physical characterization shows a very good adherence between the highly hygroscopic viscose staple fibers and the polymeric solution that contains polyvinyl acetate and polyurethane as binders. SEM images evidenced the fact that the polymeric solution penetrated more than 1/3 of the yarn diameter. The concentration of magnetic powder in the polymeric solution has a direct influence on the coating amount, diameter and density. The mechanical characterization of the coated yarns revealed that the breaking force is increasing with increasing magnetic powder content up to o certain value and then decreased because the magnetic layer became stiffer. At the same time, the elongation at brake is decreasing.*

Key words: *viscose coated yarn, magnetic particles, polymeric coating solutions, adherence, mechanical properties*

1. INTRODUCTION

Nowadays textiles find a myriad of applications in almost all fields. Textiles are everywhere around us, influencing our mood, protecting us, helping us to increase our performance, etc. Ensuring functional performance correlated with comfort characteristics, sustainability and environment protection is a priority in our current society [1], [2]. Increasing textile value through the integration of multifunctional elements in domestic textiles is a familiar trend line today. Development of textile elements, obtained by functionalization offers a wide range of applications [3]. Special emphasis is

placed nowadays on developing eco and human friendly products which lead to reduced harmful materials consumption from non-renewable resources and minimize the need for landfills.

There is a growing interest in the field of intelligent textiles, which are sensitive to changes in the environment, through a series of features such as: electrical conductivity, photo-luminescence, UV protection, catalytic and antistatic characteristics, antimicrobial and self-cleaning characteristics, that prevent or limit the spread of fire, magnetic characteristics and electromagnetic protection [4], [5]. The growth and advancement of the electronics industry or the widespread use of various electronic and communications equipment, information technology and automation, aerospace and medicine, etc. are leading to many problems of electromagnetic interference (EMI). With the rapid growth in the number of electrical and electronic devices and accessories that emit electromagnetic energy in different frequency bands, it becomes essential to limit and protect electronic equipment against all these sources of electromagnetic interference [6]. Textiles are dielectric materials which can acquire magnetic properties thanks to magnetic functionalizing particles attached to them [7]. Magnetic textile yarns are composite yarns exhibiting properties which are specific to magnetic materials (anisotropy, attraction / rejection, magnetic flux, electromagnetic shielding properties at very high frequencies (microwave)). There are various ways to obtain magnetic textile, as outlined in references [8] and [9]. One of these ways is through coating with a polymer solution containing magnetic inclusions. This article is presenting our studies on the effect of optimizing the polymeric coating solution (paste type) with different percentage of functionalizing magnetic powder on an artificial twisted staple yarn support [10], [11].

2. MATERIALS AND METHOD

2.1. Materials used

A 100% viscose twisted staple yarn with fineness 70/2 (metric count) has been selected for this study which was performed in a similar manner to the one in reference [10] involving cotton yarns. Viscose was chose for its hygroscopicity and a high degree of retention of aqueous solutions. The main physical characteristics detailed in Table 1 were determined according to the SR 13231-95 and SR ISO 1833-95 standards.

Table 1: *Physical characteristics of viscose yarn support*

Characteristic	**Uncoated yarn - (A) - 100% viscose**	
	Single yarn	**Twist yarn**
Measured diameter (µm)	-	200.8
CV of diameter (%)	-	6.69
Fineness Nm (m/g)	-	70/2
CV (%)	-	1.45
Twist/meter	846.0	483.0
CV (%)	3.68	5.45
Twist direction	Z	S
Hairiness/10 cm	-	187

The selected support yarn was analyzed from structural point of view (scanning electron microscopy) with a FEI Quanta 200 equipment with a GSED detector. The analysis was performed both along the longitudinal direction (Figure 1a) as well as in the cross section (Figure 1b).

For the functionalization, we prepared five polymeric solutions (paste type) containing different percentages of magnetic powder as described in [12]. These exhibited different densities. The densities of polymeric solutions increased from 1.26 g/cm^3 for a content of 15 wt% magnetic

powder up to 1.69 g/cm^3 for a content of 45 wt%. We used polyvinyl acetate (PVA) and polyurethane (PUR) as binding polymers, micrometric sized barium ferrite powder ($BaFe_{12}O_{19}$) - BF as functionalizing hard magnetic material and glycerine (G) as recipe plasticizer. BF has magnetic residual in the absence of an applied magnetic field in addition to excellent chemical stability and corrosion resistance [13], [14], [15], [16]. The mixtures were used for coating of viscose support yarn. In accordance with experimental optimization plan described in [10] and followed in the preparation of the coating solutions, coating of the viscose support yarn A lead to the following magnetic inclusions: A1-15 wt%; A2-20 wt%; A3-30 wt%; A4-40 wt%; A5-45 wt%.

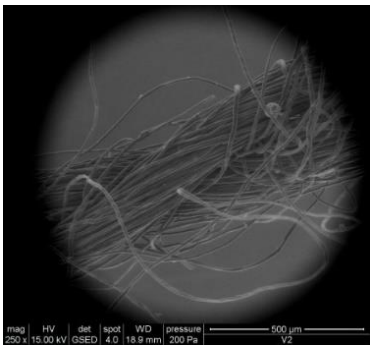

Fig. 1a: *Support yarn - SEM longitudinal position*

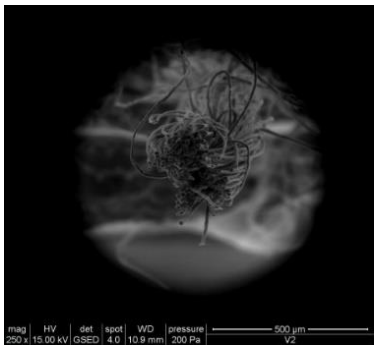

Fig. 1b: *Support yarn - SEM cross section*

2.2. Methodology

The viscose yarn was coated using an in-house setup which allows deposition of micrometric thickness polymeric paste layer on the yarn surface. An applied magnetic field is inducing orientation of the magnetic particles included in the paste. The constant magnetic field is generated by a DC electromagnetic induction bobbin with air gap [11]. The coating process was performed at ambient temperature. After coating, the yarn leaves the deposition room through a calibration system of spinneret type and arrives at the hot air dryer and fixing system.

3.RESULTS AND DISCUSSION

3.1. The adhesion mechanism

The physical characterization using SEM showed a strong adherence between the polymeric solution and the viscose support yarn. Compared to our previous research, where we used cotton as support yarn, the use of viscose allows a deeper penetration of the polymeric solution in the yarn fibers [10]. This is due to higher hygroscopicity and hairiness of the yarn. SEM images evidenced the fact that the polymeric solution penetrated more than 1/3 of the yarn diameter. The air gaps between fibers that were not bonded by coating solution were present only in the center of the yarn. The coating layer was eccentric to the yarn axis. Figures 2 a-e show SEM images of the cross sections of the coated yarns: A1 (Figure 2a), A2 (Figure 2b), A3 (Figure 2c), A4 (Figure 2d), A5 (Figure 2e).

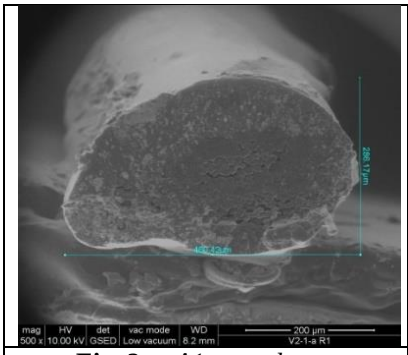

Fig. 2.a: *A1 coated yarn*

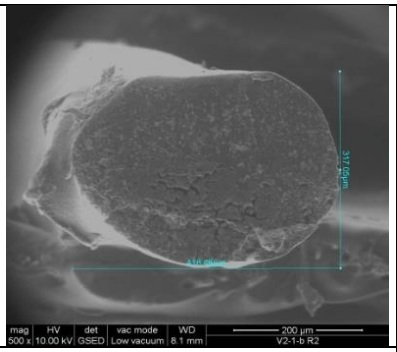

Fig. 2.b: *A2 coated yarn*

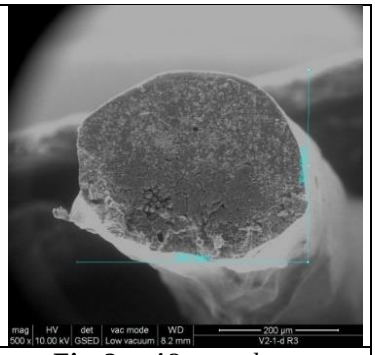

Fig. 2.c: *A3 coated yarn*

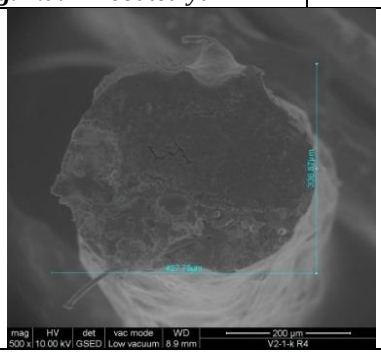

Fig. 2.d: A4 coated yarn

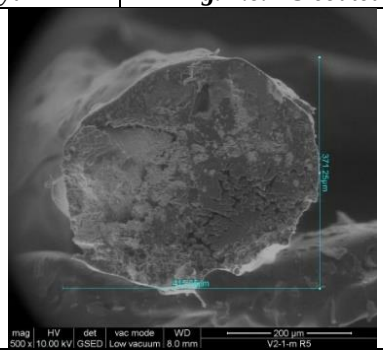

Fig. 2.e: *A5 coated yarn*

The size of barium ferrite magnetic inclusions was in the range 300 nm - 1.3 μm. From the SEM structural characterization we concluded that coating solutions with smaller amounts of magnetic powder penetrated more into the structure of the yarn, leading to a thinner layer, than solutions containing a higher percentage of the magnetic inclusions. In the latter case, the polymeric solutions become more viscous and thus penetration into the yarn structure is smaller which means a thicker layer at the surface of the yarns.

Table 2 shows that the apparent measured diameter of the coated yarns increases from 289,6 μm in A1 to 354,4 μm in A5. The increase is linear and directly proportional with the amount of magnetic inclusions in the coating solutions.

The degree of charging of these 5 coated yarns was also increasing by ~81% in the case of A1 and by more than 83,7 % in case of A5 which has a higher content of magnetic inclusions. The degree of charging was calculated using equation 1.

$$D_c = \frac{m_{Ai} - m_A}{m_A} \cdot 100(\%) \quad \textbf{(1)}$$

where:

- D_c degree of charging;
- m_{Ai} – coated yarn mass (i=1÷5), g/m;
- m_A – uncoated yarn mass, g/m.

The mechanical characteristics of both uncoated and coated support yarns were obtained with a Tinius Olsen H5KT tensile testing machine. The average values of the breaking strength and elongation at break, shown in Table 2, have been performed according to EN ISO 2062/2010.

Table 2: *Physical characteristics of uncoated support yarns and coated yarns*

Characteristics	Uncoated Yarn	Coated Yarn				
	A0	A1	A2	A3	A4	A5
Measured diameter (μm)	200.8	289.6	302.0	324.8	348.0	354.4
CV (%)	6.69	7.7	7.99	11.0	11.69	12.49
Degree of charging (%)	-	81.09	81.26	81.38	83.35	83.72
Breaking strength (N)	6.75	7.58	7.25	7.18	6.75	6.58
Elongation at break (%)	11.44	13.73	13.07	12.38	11.09	11.48

The breaking strength was higher for A1, A2 and A3 coated yarns than for the support yarn and increased slightly with the magnetic inclusion content (15wt%÷30wt% magnetic content). This is due to the fact that the thicker coating layer bonds stronger to the fiber components than the thinner one. For a higher magnetic inclusion content (>30 wt%), the strength decreased because the magnetic layer became stiffer. On the other hand, an increased coating layer thickness leads to a decreased elongation to brake of the yarns.

4.CONCLUSIONS

The design and development of the coated yarns with hard ferrimagnetic inclusions in polymeric matrix represents a new approach of functionalized textiles with potential applications in EMI shielding of electronic devices. In this research the support yarn was an artificial 100% viscose staple yarn with metric count 70/2 designed for woven fabrics.

Five coating solutions with various mass percentages of magnetic powder, varying in range from 15% to 45% wt, two polymers in liquid state and glycerine have been used to optimize the coating solutions. The binding polymers in the coating solutions showed a very good adherence to the viscose yarns due to high hygroscopicity and hairiness of the yarns. The solutions penetrated deep in the yarn structure without air gaps between fibers in coated layer.

From the physical characterization of the coated yarns we concluded that both the diameter and the degree of charging depend on the percentage of the magnetic inclusions in the coating solutions. Both properties exhibit a linear variation with the magnetic content.

The breaking strength of the coated yarns was higher up to a certain degree of charging value (< 82%) than the breaking strength of the support yarn and then decreased directly proportional with the increasing of magnetic content.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CREASING BEHAVIOR OF SOME WOVEN MATERIALS MADE FROM COMBED YARNS TYPE

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Abstract: *The paper analyses the behavior to creasing of some woven materials made from yarns type wool used for ready-made clothes. Factors like fibrous composition, properties of constituent fibers, wovens structure parameters, mechanical properties of warp and weft yarns and finishing treatments that influenced the recovery capacity from crease/folding were investigated experimentally through several tests which revealed their importance in the process.*
The creasing of woven materials made from combed yarns type wool used for ready-clothes is an undesired deformation effect with temporary or permanent character, which is caused by a composed strain of bending and compression during utilization, processing or maintenance. It is manifested by the appearance of wrinkles, folds or stripes on the surface of wovens materials, thus diminishing their qualitative appearance and also their practical value.
Creasing is the result of irreversible changes created through the reciprocal sliding of structural fiber components when exposed to a bending strain. Creasing is specific to oriented structures with high crystallinity (cellulosic fibers). The sliding appears because of hydrogen bond breaking which can, however, reform easy in other positions conferring a permanent character to creasing.Functional apparel will be subjected to a wide range of end uses such that a garment will be affected by intern (fibres, yarn fineness warp/weft, fabric density, thickness, fabric count) and external factors (external environment - exposure to sunlight, wind, rain, cold weather conditions, fabric/human body interaction). These factors affect the performance and behaviour of functional.

Key words: *recovery coefficient, fabric count, flotation, creasing, recovery angle after folding*

1. INTRODUCTION

Crease recovery behaviour is an important property of fabrics for apparel applications. Good agreement is observed between experimental data and theoretical predictions for wool/polyester blended and worsted fabrics [1-3]. Based on the semicircular form for a fabric bend, the model established by Chapman and Hearle is improved by considering that bending starts from a finite radius. The relationship between creasing behavior and deformation is deduced and solutions are given for a linearly elastic material with constant internal frictional constraint, and then the improved model is applied to the creasing of semicircular and looped specimens made of different fabrics [4-

6]. Two basic parameters are needed to characterise the fabric in the crease recovery model: the bending rigidity and bending hysteresis of the fabric; both are readily measured in a pure bending test [7]. Agreement between theoretical predictions and experimental results is very satisfactory.

Understanding and predicting the structure and properties of woven textiles is important for achieving specific performance characteristics in various woven applications. Woven textiles are used in a range of products such as apparel, technical and industrial textiles [8-10]. Woven textile structure: theory and applications provides comprehensive coverage of the structure, behaviour, modeling and design of woven fabrics and their relevance to the textile industry [10-13].

Textiles are usually subjected to a wide range of deformations such as bending, folding, creasing, and wrinkling, which may be added deliberately during manufacturing and care or produced by movement of the body during use. Adding wrinkles to a fabric can produce some desirable features as fashionable appearance, usefulness and minimum care. But unintentionally developed, short, irregular wrinkles are unsightly [13].

2. EXPERIMENTAL PART

2.1. Materials and methods

The experimental trials have been performed on a series of woven materials made of **45%Pes+52%Wool+3%Dorlastan,** codified **C1** to **C9**. Factors like fibrous composition, properties of constituent fibers, structural woven parameters, mechanical properties of warp and weft yarns and finishing treatments that influenced the recovery capacity from creasing/folding were investigated such as to assess their importance.

In order to reveal the influence of bonding on the surface characteristics of wovens we have expressed it through the mean flotation F_{warp} for warp yarns and mean flotation F_{weft} for weft yarns. The intersection between a warp yarn and weft yarn is called bonding point, thus the bonding contains all bonding points having a warp or weft effect along a longitudinal or transversal direction. One or more bonding points having the same effect and forming one bonding segment can exist in longitudinal or transversal direction. The bonding segments with the same effect are called flotation (F). They can be warp flotation (F_{warp}) when the warp yarn passes over the weft yarn and weft flotation (F_{weft}) when the weft yarns passes over the warp yarn. The flotation size, similar to the bonding segment, have the minimum value F=1. The following relations exist between the ration (R), number of passes (t) and mean flotation (F):

$$F_{warp} = \frac{R_{weft}}{t_{warp}}; F_{weft} = \frac{R_{warp}}{t_{weft}} \quad \textbf{(1)}$$

The measurements are done on woven samples having standard dimensions. These are folded at 180° and pressed along the direction of one of the constituent fiber systems by applying over a defined time interval folding forces which are dependent on the unit surface mass. After the removal of the folding forces, the sample is left to relax freely. The recovery angle is measured in the end of a determined time interval.

The following indicators are for estimating the capacity of textile materials to maintain their initial shape and dimensions during the wearing time:

- **the recovery angle after folding (α)** - the angle between the sample sides folded according to the SR EN 22313:1997 after the removal of the folding force;
- **recovery coefficient λ (%)** calculated according to relation (2):

$$\lambda = \frac{\alpha_1}{180^o} 100 \quad \textbf{(2)}$$

where the recovery coefficient λ can be determined:

-at t_1=1 minute after detension when either λ_1 (%) or the instantaneous recovery coefficient is determined;

-at t_2=10 minutes after detension when either λ_2 (%) or the slow recovery coefficient is determined. The latter is defined by relation (3):

$$\lambda_2 = \frac{\alpha_2 - \alpha_1}{180^o} 100 \quad \textbf{(3)}$$

The total coefficient of recovery after folding is calculated according to relation (4):

$$\lambda = \lambda_1 + \lambda_2 \quad \textbf{(4)}$$

2.2. Results and discussions

The recovery capacity from creasing depends on the fibrous composition and on the level of deformations. Additionally, also technological processing through mechanical, physical or chemical processes can influence positively or negatively the evolution of the indicator.

Several operations have been performed for each item from the woven materials considered in the study:

-evaluation of the recovery angle after folding (α) and of the recovery coefficient λ (%) along the direction of the two yarn systems, *i.e.* warp and weft. The experimental values are given in Table 1;

-Fig.1 and Fig. 2 are illustrating the plots of functions α and λ by considering the woven materials grouped based on their flotation size.

Following useful observations for the design of woven materials can be drawn based on the analysis of the values in Table 1 and on their graphical representation:

- the largest value of the recovery angle was recorded for the wovens having the average flotation F=2 trialed along the warp direction. These were followed by wovens with same flotation value but along the weft direction;

- by reducing the flotation the recovery angle decreases while the recovery coefficient increases;

- while the yarns diameter increases the recovery angle decreases;

-these types of materials have the highest value of recovery angle after the bending of the direction of the weft threads as they have in their composition the Dorlastan monofilament yarn.

For example, article C3 : α_{weft}=179,6º and α_{warp} =172,2º with Nm_{warp}=Nm_{weft}=52/2, P_{warp}>P_{weft}, with bonding $D\frac{2}{2}/$ so the average float is F=2. For the same article, it may be found that the differentiation on the technological axes, capacity to recover from the creasing on weft axis is larger than the resilience of the crease on the warp direction (axis). For example, article C2 α_{warp} =160,2º and α_{weft} =172,2º, with (Nm_{warp}=Nm_{weft}=60/2, P_{warp}>P_{weft}), canvas armure, so having the average float, F=1.

***Table 1**: Evaluation indicators for assessing the creasing behavior of the studied wovens*

Cod Art.	Bonding	Yarn count Nm		Flotation		Recovery angle from creasing, α		Recovery coefficient from creasing λ	
		Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
C1	D2/1	56/2	37/1	1.5	1.5	165	174.2	8.3	3.2
C2	pânza	60/2	60/2	1	1	160.2	175.2	11.0	2.7
C3	D2/2	52/2	52/2	2	2	172.2	179.6	4.3	0.2
C4	D2/1	52/2	52/1	1.5	1.5	164.2	174.5	8.8	3.1
C5	D2/1	56/2	37/1	1.5	1.5	164.1	176.4	8.8	2.0
C6	D2/2	56/2	37/1	2	2	174.6	173.2	3.0	3.8
C7	D2/1	60/2	60/2	1.5	1.5	164.3	174	8.7	3.3
C8	D2/1	60/2	60/2	1.5	1.5	165.2	174.6	8.2	3.0
C9	D2/1	37/1	37/1	1.5	1.5	166.2	171.8	7.7	4.6

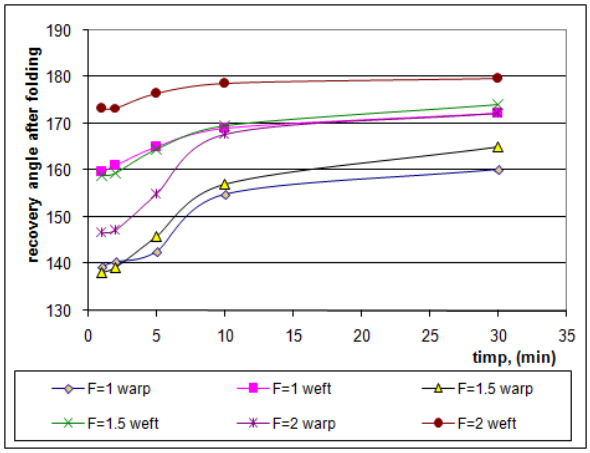

***Fig.1:** Variation of recovery angle after folding from creasing for the studied wovens*

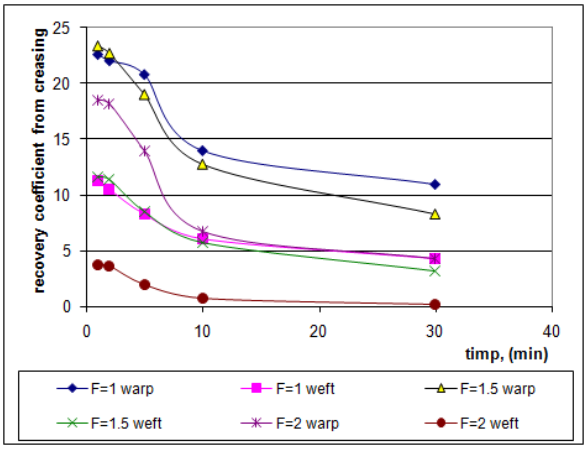

***Fig.2:** Variation of recovery coefficient from creasing for the studied wovens*

Based on the data presented above one can observe that under the standard conditions the recovery angle is higher along the weft yarns direction, which could be because of the following reasons:

- warp yarns fatigue during the weaving process;

- density difference of the two yarn systems;
- different respons of the two yarn systems;
- during the finishing process.

The lowest values of the coefficient of crease recovery were obtained at those sorts of fabric applied in the weft direction, for example: **article C3**, λ_{weft}=0,2, Nm_{warp} 52/2, Nm_{weft} 52/2, $P_{warp}>P_{weft}$, with bonding $D\frac{2}{2}/$.

3. CONCLUSIONS

The creasing of wovens is a complex process of deformation under the action of mechanical stretching, bending and compression strains.

1. Regarding the influence of fibrous composition and the constituent fiber characteristics on the recovery capacity from creasing

The behavior to creasing is determined by the deformability of the constituent fibers with respect to the creasing conditions.

The response at a certain strain level (strain speed, time alternation of application direction, compression or stretching level) is evaluated depending whether the creasing is under or over the elasticity limit of the mentioned strain.

The strain level through creasing determines the total deformation which in turn is determining the ratio between the elastic components of recovery and the remanent deformation value.

2. Regarding the influence of structural parameters on the recovery capacity from creasing

The yarns fineness, technological density and the type of bonding is signficantly influencing the creasing/folding behavior.

The yarns fineness is influencing, at constant structure parameters, the woven thickness. Thus increasing the thickness by increasing the linear density of the used yarns leads to a higher resistance to creasing.

The yarns density is influencing the creasing behavior because the decrease of this parameter leads, independent of the used bonding type, to lower creasing tendency.

The length of flotations has a positive influence on the recovery capacity from creasing.

The simultaneous decrease of yarns density and flotations length parameters leads to a lower fiber tension state of the two yarns systems. This is reflected in the values of the recovery angle. For instance: for yarns with same composition and structure: $Nm_{warp}=Nm_{weft}$=60/2, Item **C2** in Table 1, with P_{warp}=210 yarns/10cm, P_{weft}=205 yarns/10cm, α_{warp}=160,2°, α_{weft}=175,2° and λ_{warp}=11%, λ_{weft}=2,7% , plaine bonding ; Item **C7** in Table 1, with P_{warp}=230 yarns/10cm, P_{weft}=220 yarns/10cm, α_{warp}=164,3° α_{weft}=174° and λ_{warp}=8,7%, λ_{weft}=3,3% , diagonal bonding $D\frac{2}{2}/$.

The plaine bonding presents a low recovery capacity from creasing, thus the flotation increase for both of warp yarns and weft yarns is favorable for reducing the creasing. The effect is compensated because the density in the two yarn systems is different.

3. Regarding the influence of the mechanical properties of warp and weft yarns on the recovery capacity from creasing

Warp yarns are more strained and worn during processing than weft yarns. Thus, even if the two yarns have identical structures, the elasticity module of warp yarns is higher, *i.e*. they become more rigid. This is reflected in lower values of the recovery angle for samples orientated along the warp direction.

Creasing is influenced by increased stiffness during stretching, which is expressed through the elasticity module.

The higher the elasticity module value, the lower is the recovery angle and the higher the creasing recovery coefficient. The interdependence between elasticity module and creasing recovery capacity is illustrated by the experimental data recorded, for instance: Item **C4**, with $Nm_{warp} \neq Nm_{weft}$, $P_{weft}>P_{warp}$, α_{warp}=164,2º, α_{weft}=174,5º and λ_{warp}=8,8%, λ_{weft}=3,1% , having the diagonal bonding $D\frac{2}{2}/$, elasticity E_{warp}=45,75 N/tex, E_{weft}=28,58 N/tex; Item **C6**, with $Nm_{warp} \neq Nm_{weft}$, $P_{weft}>P_{warp}$, α_{warp}=174,6º, α_{weft}=173,2º şi λ_{warp}=3,0%, λ_{weft}=3,8%, having diagonal bonding $D\frac{2}{2}/$, elasticity module E_{warp}=25,62 N/tex, E_{weft}=25,31 N/tex.

The present study is also revealing the differentiation, in the frame of the same item, according to technological axis, the recovery angle from creasing along weft direction is higher than the recovery angle along warp direction. When the fineness $Nm_{warp} = Nm_{weft}$, the recovery angle is higher along warp direction and depends on the ration between technological densities and bonding type.

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ANNALS OF THE UNIVERSITY OF ORADEA
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IMPROVING KNITTED FABRICS BY A STATISTICAL CONTROL OF DIMENSIONAL CHANGES AFTER THE DYEING PROCESS

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Abstract: *One of the most important problems that cotton knitted fabrics present during the manufacturing process is their dimensional instability, which needs to be minimised. Some of the variables that intervene in fabric shrinkage are related with its structural characteristics, use of fiber when producing yarn, the yarn count used or the dyeing process employed. Conducted under real factory conditions, the present study attempted to model the behaviour of a fabric structure after a dyeing process by contributing several algorithms that calculate dyed fabric stability after the first wash cycle. Small-diameter circular machines are used to produce garments with no side seams. This is the reason why a list of machines that produce the same fabrics for different widths needs to be made available to produce all the sizes of a given garment. Two relaxation states were distingued for interlock fabric: dyed and dry relaxation, and dyed and wash relaxation. The linear density of the yarn employed to produce sample fabric was combed cotton Ne 30. The machines used for optic bleaching were Overflow. To obtain knitting structures with optimum dimensional stability, different statistical tools were used to help us to evaluate all the production process variables (raw material, machines and process) responsible for this variation. This allowed to guarantee product quality without creating costs and losses.*

Key words: *Dimensional stability, shrinkage, knitted fabric, prediction, relaxed fabrics.*

1. INTRODUCTION

The considerable interest in studying the dimensional stability of cotton fabrics is shown by the publications found on this theme. One of the most highlighted publications talks about predicting dimensional changes in circular knitted cotton fabrics [1]. Along these lines, Ulson de Souza, Cabral Cherem and Guelli U.Souza produced a database for the relaxation processes for knitted cotton products for all production phases. In parallel, a development system is required that simulates all the process variables. This study is based on the principle that each industry must determine its own ***K*** dimensional factor, calculated for each processing line. According to Munden [2], with their equations it is possible to check that the factors which represent fabric dimensions are related with courses, gauge and loop length. Later for plain weave knitted fabrics, Doyle [3] discovered that stitch density depended only on loop length, and is independent of yarn variables and knitted fabric. Another study

by Münden [4] showed that, in a minimum energy state, the dimensions of plain weave wool knitted fabrics depend only on the yarn length in each loop. Nutting [5] introduced another variable, yarn count, and proposed making a minor modification to the basic equation. Knapton [6] demonstrated that dimensional stability in plain weave knitted fabrics can be accomplished by mechanical means, relaxation techniques or chemical treatments. This work also showed that the stable loop geometry for wool and cotton in plain weave knitted fabrics is almost identical.

The "Starfish" Project [7] [8] is a research programme that attempts to provide a rigorous working method and a sufficiently complete database to predict shrinkage and weight per square metre of cotton knitted fabric based on knowing only some parameters (machine, yarn, knit density), the end process and the final nominal dimensions. This project defines a ***"reference relaxation state for fabric",*** like that obtained after a wash and dry cycle by centrifuging, followed by four rinse cycles and tumble drying. Then it builds a database that describes a wide range of structure qualities According to this database, it generates some equations by linking the finished fabric parameters to the dimensions of the aforementioned state.

Conducted under real factory conditions, the present study attempted to model the behaviour of a fabric structure after a dyeing process by contributing several algorithms that calculate dyed fabric stability after the first wash cycle. It also attempted to calculate weight, stitch density and fabric performance with two variables: variation in tubular fabric width between the first wash and its initial stage after dyeing ***(ΔA)*** and wales/cm.

2. MATERIALS AND METHODS

2.1 Description of the fabric manufacturing process

Small-diameter circular machines are used to produce garments with no side seams (vests, bed covers, underwear, etc.). This is the reason why a list of the machines that produce the same fabric for different widths needs to be made available to produce all the sizes of a given garment because this tube width corresponds to the garment's girth.

The linear density of the yarn employed to produce sample fabric A was combed cotton Ne 30**.** The present study focused on knitted weft fabrics with an interlock structure. The machine used to produce pieces was a E20 gauge "Mayer IHG II", 12 inch diameter, 20 feeders, and 756 x 2 needles. The working speed was 70 rpm. Twenty pieces produced on this machine, which corresponded to different batches, were selected. Once they had been identified, they were each included in their batch, which meant 20 batches with 25 pieces each.

Next batches were submitted to an exhaustion dyeing process. The machines used for optic bleaching were Overflow. After completing hydroextraction and then drying pieces, those to be analysed were identified by taking one sample of them and placing it in a conditioning atmosphere.

Two relaxation states were distinguished for interlock fabric sample A:

- ***Dyed and dry relaxation (DDR).*** The dyed fabric was placed in a conditioning atmosphere until a constant mass was obtained.
- ***Dyed and wash relaxation (DWR).*** The fabric was dyed and conditioned until a constant mass was obtained, and it was submitted to a dimensional stability analysis according to Standard UNE EN ISO 6330, of September 2012.

2.2 Description of the variables to be analysed

The variables analysed for each relaxation state were: wales/cm (***P***), courses/cm (***C***), stitch density/cm^2 (***DM***), weight (***G***), width (***A***), loop length (***LM***), performance (***R***), shrinkage length (***EL***) and shrinkage width (***EA***). The variables that corresponded to relaxation state ***dyed and dry relaxation (DDR)*** are shown with subscript ($_i$), while those that corresponded to relaxation state ***dyed and wash relaxation (DWR)*** are shown with subscript ($_f$).

Standard UNE-EN 14971 was followed to determine variables ***P***, ***C*** and ***DM***. ***G*** was calculated according to Standard UNE-EN 12127, and ***EL*** and ***EA*** according to Standard UNE EN ISO 6330.

Variable ***ΔA*** represented variation in the existing width between the width obtained after relaxation state ***DWR*** *(A_f)* and that obtained from relaxation state ***DDR*** *(A_i).*

3. RESULTS AND DISCUSSION

The average, standard deviation and 95% confidence interval of the results obtained in the analysis with the 20 pieces included from distinct batches for relaxation states ***DDR*** and ***DWR*** are shown in ***Table 1***.

Table 1: *The experimental results of each variable in relaxation states DDR and DWR.*

PROPERTIES		Relaxation							
		Dry (DDR)				Wash (DWR)			
		Variable	Result	S_i	95% Confidence interval	Variable	Result	S_i	95% Confidence interval
Wales/cm		P_i	26.0	2.8243	[24.6-27.4]	P_f	28.1	2.5362	[26.9-29.3]
Courses/cm		C_i	14.1	0,5487	[13.9-14.4]	C_f	13.9	0.7039	[13.5-14.2]
Stitch density/cm^2		DM_i	368.42	50,2365	[344.21-392.63]	DM_f	390.68	48.597	[367.26-414.11]
Weight, g/m^2		G_i	254.66	16.5123	[246.70-262.62]	G_f	267.79	18.0656	[259.08-276.50]
Width, cm		A_i	26.3	0.8932	[25.84-26.70]	A_f	26.7	1.0879	[26.2-27.3]
Loop length, mm		LM_i	3.44	0.2045	[3.34-3.53]	LM_f	3.40	0.2214	[3.29-3.51]
Performance, m/kg		R_i	7.501	0.3466	[7.334-7.668]	R_f	7.008	0.2506	[6.887-7.129]
DC %	Length		-	-	-	EL	-7.05	0.0242	[-8.22--5.89]
	Width		-	-	-	EA	+1.74	0.0182	[+0.86-+2.61]

Table 1 shows a marked variation between the performances of the two relaxation states, where R_f was greater than R_i, which implies that the fabric was submitted to stretchings during the dyeing process. The dimensional stability in the longitudinal sense ***(EL)*** confirmed that the fabric had relaxed after the first wash, had shrunk by -7.05% longitudinally, while wales (P_f) and weight had increased. Fabric width also increased and, consequently, so did the dimensional stability to width ***(EA)*** by +1.74%, while courses (C_f) were lost.

After analysing the variables in each relaxation state, the intention was to see the relationship that existed between them and to obtain models that can predict variables ***EL, EA***, G_i DM_i and R_i. The models obtained by linear regression are found in ***Table 2.*** For dimensional stability in the longitudinal sense ***(EL),*** the selected model showed a linear relationship with variation in the width between both relaxation states ***(ΔA)***, while ***EL*** shrank as ***ΔA*** increased. However, the relationship between ***ΔA*** and ***EA*** in the proposed model acted in the opposite way as ***EA*** increased as ***ΔA*** did. A model was proposed to predict variable G_i from the existing increasing relationship with variable ***Pi***, and G_i increased as P_i did. Variable DM_i presented an increasing linear relationship compared to G_i, while the relationship between R_i and G_i diminished in the models proposed in *Table 2*.

Table 2: *Models proposed by linear regression.*

DEPENDENT VARIABLE	INDEPENDENT VARIABLE	LINEAR RELATIONSHIP	R^2
EL	ΔA	***EL=-0.0444888-0.055558·ΔA***	87.9356%
EA	ΔA	***EA=-0.002208+0.0417924· ΔA***	87.8229%
G_i	P_i	***G_i=110.68+5.5375·P_i***	89.9707%
DM_i	G_i	***DM_i=-359.95+2.86017·G_i***	88.3814%
R_i	G_i	***R_i=12.1763-0.0183587·G_i***	76.4545%

Of the models proposed in ***Table 2,*** it can be stated that from knowledge about dependent variables ***ΔA*** and ***P_i,*** dependent variables ***EL***, ***EA***, ***G_i***, ***DM_i*** and ***R_i*** are predicted. ***Figures 1-6*** graphically represent the proposed models.

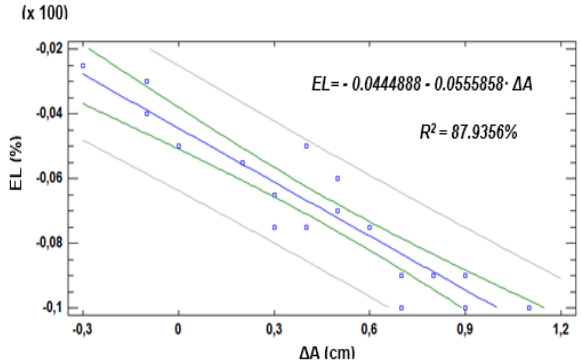

Fig.1: *Graph of the adjusted linear regression model that describes the relationship between longitudinal shrinkage* ***(EL)*** *and the width differential* ***(ΔA).***

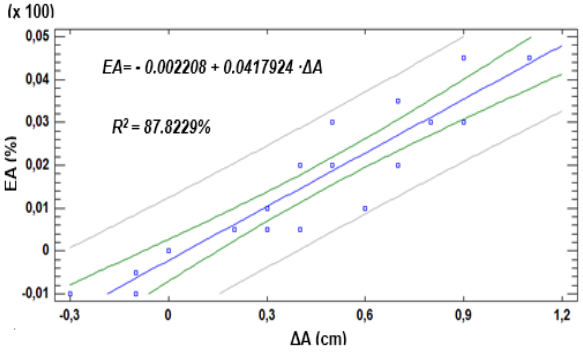

Fig.2: *Graph of the adjusted linear regression model that describes the relationship between shrinkage at width* ***(EA)*** *and the width differential* ***(ΔA)****.*

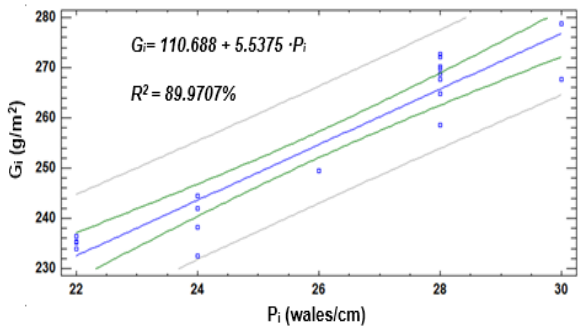

Fig.3: *Graph of the adjusted linear regression model that describes the relationship between variables weight* ***(G_i)*** *and wales/cm* ***(P_i).***

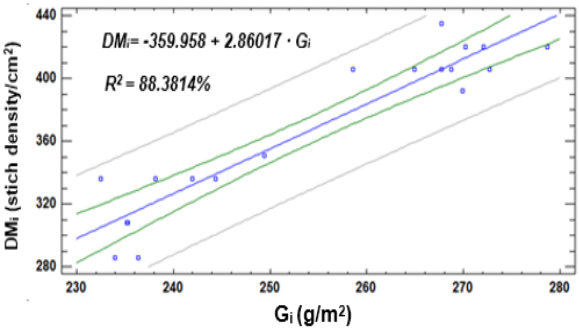

Fig.4: *Graph of the adjusted linear regression model that describes the relationship between variables stitch density/cm^2* ***(DM_i)*** *and weight* ***(G_i).***

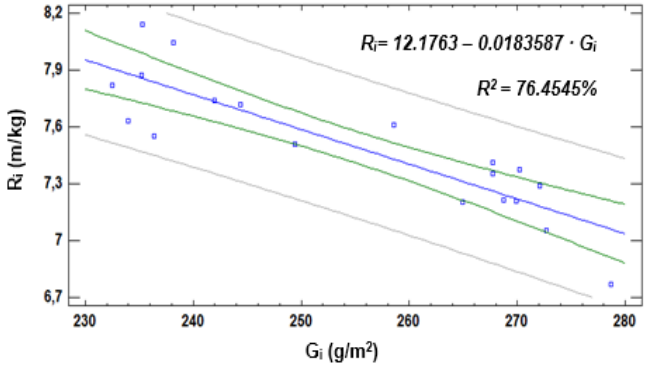

Fig.5: *Graph of the adjusted linear regression model that describes the relationship between variables performance* ***(Ri)*** *and weight* ***(Gi).***

Figures 1-5 represent the models proposed for variables ***EL***, ***EA***, ***Gi***, ***DMi*** and ***Ri***. They all had a high R^2, which would explain the very good variability from the linearity that existed with independent variables ***ΔA*** (in the models about dimensional stability)**,** ***Pi*** (in the dependent model of ***Gi***) and ***Gi*** (in the models dependent on ***DMi*** and ***Ri***).

4. CONCLUSIONS

This study has modelled the dimensional properties of the interlock fabric under study by linear regression models. Therefore, these models help us to predict the variability of the fabric's dimensional stability in a longitudinal sense and width-wise (***EL*** and ***EA)*** from the variation in the width of the tubular structure obtained after the first wash cycle (***Dyed and Wash Relaxation)*** and its initial state (***Dyed and Dry Relaxation)***. Despite having to run a wash test to know variation in fabric width with these proposed models, there is no need to run the sample marking and measuring process to determine dimensional variations, which evidently optimises the analysis process.

In parallel, by knowing the fabric's wales/cm values in relaxation state ***Dyed and Dry Relaxation,*** weight can be estimated without having to necessarily run an analysis in the laboratory as only a balance and sample cutter are required. Indeed simply using a thread counter suffices. Once this variable is known, it is possible to predict stitch density/cm^2 and fabric performance in parallel. By knowing fabric performance, we can deduce if a fabric has been considerably stretched or not, and can decide if it is re-operated to obtain the desired performance before running further analyses.

Improving the variability obtained in the different analysed results from each batch is proposed to optimise the dyeing process to, thus, avoid as much as possible any stretching that might take place during this process and overfeeding fabric in the drying place so it better recovers.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

OPTIMIZATION OF DYEING PARAMETERS TO DYE COTTON WITH CARROT EXTRACTION

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***Abstract**: Natural dyes derived from flora and fauna are believed to be safe because of non-toxic, non-carcinogenic and biodegradable nature. Furthermore, natural dyes do not cause pollution and waste water problems. Natural dyes as well as synthetic dyes need the optimum parameters to get a good dyeing. On some occasions, It is necessary the use of mordants to increase the affinity between cellulose fiber and natural dye, but there are other conditions to optimize in the dyeing process, like time, temperature, auxiliary porducts, etc. In addition, the optimum conditions are different depends on the type of dye and the fiber nature. The aim of this work is the use of carrot extract to dye cotton fabric by exhaustion at diverse dyeing conditions. Diffferent dyeing processes were carried out to study the effect of pH condition and the temperature, using 7, 6 and 4 pH values and 95 ºC and 130ºC for an hour. As a result some images of dyed samples are shown. Moreover, to evaluate the colour of each sample CIELAB parameters are analysed obtained by reflexion spectrophotometre. The results showed that the temperature used has an important influence on the colour of the dyed sample.*

***Key words:** Natural dyes, pH, temperature, carrot, cotton*

1. INTRODUCTION

In the last century, the development of synthetic dyes reduced the use of natural dyes [1], [3] due to their cheap price and the fact that these dyes are generally easy to dye and have good fastness properties. But there are drawbacks about synthetic dyes, mainly toxicity and environmental pollution caused by the wastewater expelled from dye-houses [4].

Recently, the use of natural dyes has risen mainly due to the increased demand for these dyes by the food, pharmaceutical, cosmetic and the textile colouration industry [5]. They are considered to have several advantages such as non-toxic functions, biodegradability, eco-friendliness and the safety of most of the natural dyes, which can even have curative effects, like curcumin which has antibacterial properties [6], [7].

Some research has been done to study the influence of the conditions used during the dyeing process using natural dyes.

In this work, the effect of the pH used in the dyed bath and the temperature reached during the dyeing process were studied, using carrot extract as the dye material for cotton fabric. To evaluate the differences obtained, samples were analized by refletion spectrophotometer.

2. EXPERIMENTAL

2.1 Materials

The fabric used was a 100% cotton twill fabric with 210 g/m^2, which had been chemically bleached through an industrial process. A commercial dye of carrot extraction was used as natural dye, supplied by Irisem. Acetic acid and sodium hydroxide were used to get different pH of the dye bath, 7, 6 and 4.

2.2 Methods

Dyeing experiments were performed using M:L (material to liquor) ratio of 1:40 and 5% owf dye concentration. To study the influence of the dye bath temperature two different exhaustion dyeing systems were used, opened system to use 90 – 95 ºC and closed system to avoid the bath evaporation reaching 130ºC. In both cases, dye processes were carried out for 1 hour. In table 1 the different conditions followed in each sample are shown:

Table 1: *Dyeing conditions*

Reference sample	pH	Temperature (ºC)
Carrot-7-95	7	95
Carrot-6-95	6	
Carrot-4-95	4	
Carrot-7-130	7	130
Carrot-6-130	6	
Carrot-4-130	4	

Dyed samples were prepared for colour measurement, which was carried out by following a standard procedure. Colour values were evaluated in terms of CIELAB values (L*, a*, b*, c*, h).

3. RESULTS

To compare the effect of using different pH in the dye bath and temperature in the dyeing process of cotton with carrot dye, images of dyed samples are shown in figure 1.

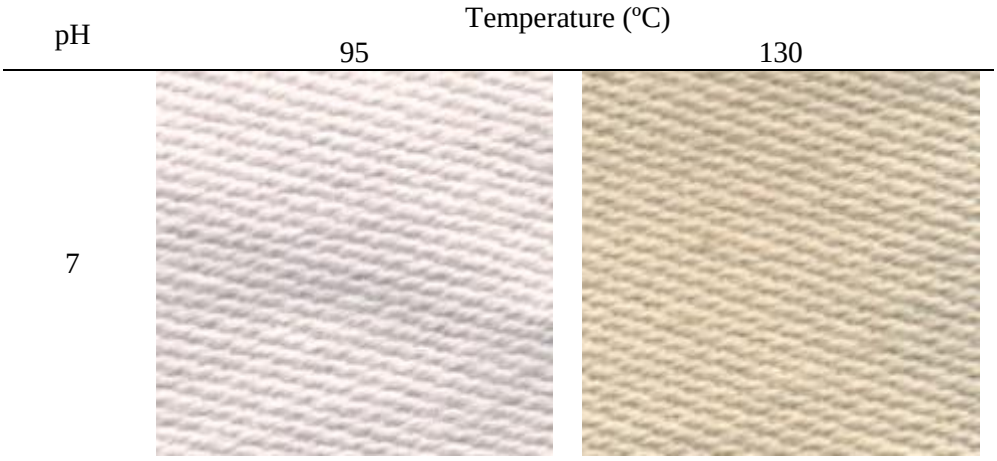

***Fig. 1**: Dyed samples images*

Dyed samples using lower or higher temperatures show different colours, seeing that dyed samples at 95ºC are pinker, however if the dye process is performed at 130ºC, then colour samples are yellower. Moreover, there are some differences about the colour intensity of dyed samples using different pH in the process. To verify this fact, the spectofotometer results are analyzed.

Table 2 shows the effects of pH and temperature used on the characteristics values of colour, CIELab and CIELch, of cotton fabrics dyed with carrot dye.

***Table 2:** Dyeing conditions*

	L*	a*	b*	C*	h
Undyed sample	90,4663	-0,296	1,6882	1,714	99,9454
Carrot-7-95	87,8897	0,4255	4,8189	4,8377	84,9539
Carrot-6-95	79,1773	8,5203	-0,5646	8,539	356,209
Carrot-4-95	79,2859	10,0819	-1,7894	10,2394	349,9358
Carrot-7-130	80,8252	2,5797	8,3814	8,7694	72,8922
Carrot-6-130	80,2854	2,9793	8,8312	9,3202	71,3579
Carrot-4-130	77,5515	3,8953	9,4787	10,2479	67,6596

The results demonstrate the important effect on colorimetric properties as marginal changes were observed in L*, a*, b*, c* and h values of samples dyed at 95 ºC in comparison to samples dyed at 130ºC, as seen in the images of the dyed samples (fig. 1). L* values refer to light-dark values from 100 to 0 representing white to black, a* values range from negative (green) to positive (red) and b* values range from negative (blue) to positive (yellow), samples dyed at 95ºC show a* higher

value indicating the red colour and samples dyed at 130ºC get b* higher value showing yellow colour.

5. CONCLUSIONS

In this work, carrot extraction to dye cotton fabric has been used getting good results. Conditions, like pH and temperature in the dyeing process were studied, and we conclude that the temperature used has an important influence on the colour obtained in the cotton sample. If the dyeing process is carried out at 90-95ºC, then colour of the dyed sample is pinker, however, if it is perfomed at 130ºC then the colour obtained is yellow.

The bath pH used has an important effect on the dyeing results too, because it has been seen that using acid pH, the intensity of the colour is higher in both cases.

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ANNALS OF THE UNIVERSITY OF ORADEA
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ANALYSIS OF THE TENSILE STRENGTH OF 100% WOOL YARN FROM DIFFERENT CLIMATIC AREAS

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Abstract: *One of the basic conditions required of yarns is to have enough tensile strength to allow them to be turned into textiles and also to give the final product durability. During processing, threads are subjected to various unavoidable forms of mechanical stress, simple or compounded, but the amount of stress can be kept under control by adjusting the corresponding operating parameters (speed, gauges, push force on the cylinders of the rolling train etc.). The values of the operating parameters of the spinning operation are set so as to obtain uniform products in large scale production, but also to ensure the preservation of the properties of the fibers and yarns, for further processing. To this end we analyzed the tensile strength of three batches of 100% wool yarn meant for knitting, from three different geo-climatic areas. These are fine woolen yarn of 25 tex and torque of 620 twists/meter. The study of the tensile strength was carried out using a Uster R Tensojet 4 (UTj4) tension meter, analyzing ten samples of 500 m from each batch. The statistical and mathematical processing of the data obtained after analyzing the samples indicated that the yarns from South Africa have better tensile strength and a lower mechanical impedance variation coefficient than yarns from Asia and England.*

Key words: *yarns, tension meter, tensile strength, variation coefficient, fineness*

1. INTRODUCTION

The most frequent type of stress that the yarn endures during processing and during use of the finished products is traction. Tensile stress always causes a deformation along the stress line [1].

Basically, the traction forces to which yarn is subjected during processing or use are most often lower than shear stress, however they can cause pronounced, irreversible deformation. Such deformations occur even after the first application of stress, or more visible after exposure to repeated stress. In both cases their size depends on the duration of the stress [2].

Each type of yarn is characterized by a specific behavior when subjected to traction, a behavior which needs to be studied and understood very well, to avoid partial or total destruction of the yarn before it is used in the finished product [3]. Also, knowledge of all aspects of yarn behavior when subjected to tensile stress allows for determining the most appropriate fiber mixture, to provide the finished product the properties required by the intended use of the product [1].

Although there is no generally valid correlation between tensile strength and other characteristics that measure the behavior of yarn under tensile stress, strength and elongation at break are and will remain key indicators for assessing the quality of yarns [4].

The tensile strength is measured by the size of the shearing force, or by specific indicators, and by specific resistance, toughness and breaking length, and mechanical work of shear [1]. For yarns of the same type and the same structure, the size of the shear force is dependent on the thickness of the yarns analyzed, so their use makes it possible to compare the tensile strength of yarns of different thickness. Any body under the action of sufficiently great tensile forces, will deform by increasing size in the direction of the force. This phenomenon is known as elongation.

2. CONTENT

The wool fibers, as all other types of hair, are multicellular fibers which, from morphological point of view, are made up of three main structural parts, or three cell layers, distinct from each other: the cuticular layer, the cortical layer which is the part that forms the core of the wool fiber (about 85% of the fiber's volume), and the medullary layer which is inside the fiber and only in thick wool.

Wool, as an organic material, belongs to the class of proteins, the keratin family being characterized by a high physico-mechanical, chemical and biochemical strength.

From an elasticity point of view, fleece ranks second after polyamide fibers. In wool's case, its elasticity gives the products made of it softness and wear resistance during use. Tensional properties of wool are determined by the morphological structure of the fiber, the quality of the wool and the test conditions.

The tensile strength of the wool yarn is its property to endure certain levels of external stress. Tensile strength is expressed in cN and depends on the diameter of the yarn from a physical point of view, and on the temperature in terms of the heat treatments to which it is subjected (bleaching, dyeing, etc.).

Tenacity is the ratio betweeen the breaking strength and the length density, or denier, expressed in tex (T_{tex} or T_{den}). Although the tenacity of wool yarns is generally low, the resistance to wear of wool clothing products is much higher than that of some products made of fibers with higher tensile strength, due to a good structural stability and a good resistance to repeated stress.

Elongation at shear point varies depending on the fineness of the constituent fibers. The shear force and tensile strength do not fully reflect the behavior of yarns (or fibers) to tensile stresses. For a more complete characterization, stress-elongation diagrams are used. During stress, variation in force depending on deformation can be represented graphically, as a curve, using for this purpose dynamometers equipped with recording devices (the Tensojet 4 Uster dynamometer). Charts thus obtained are called stress-elongation diagrams.

The shearing mechanical work is the mechanical work required to deform the yarn (or fiber) to the point of shearing and is equivalent to the area delimited by the curve, the abscissa and the parallel to the ordinate starting from the shearing point, and is measured in cN·cm.

The shearing mechanical work L(WorK) is obtained from the relationship[5]:

$$L = f \cdot F_r \cdot \Delta l_r \ (cN \cdot cm) \quad \textbf{(1)}$$

Where: f – is the shearing factor;
F_r – is the shearing force (cN);
Δl_r – is the elongation at shearing (cm).

The shearing mechanical work factor is a dimensionless value that indicates the capacity for deformation of a thread.

Tensile strength is one of the basic features of the yarn, because it influences the behavior of yarns in processing (weaving preparation, weaving or knitting), determining the technological

parameters of the equipments and their productivity. Also, yarn tensile strength is a qualitative characteristic, because the yarn's quality and the quality of the product made from it depend on its value. [6]

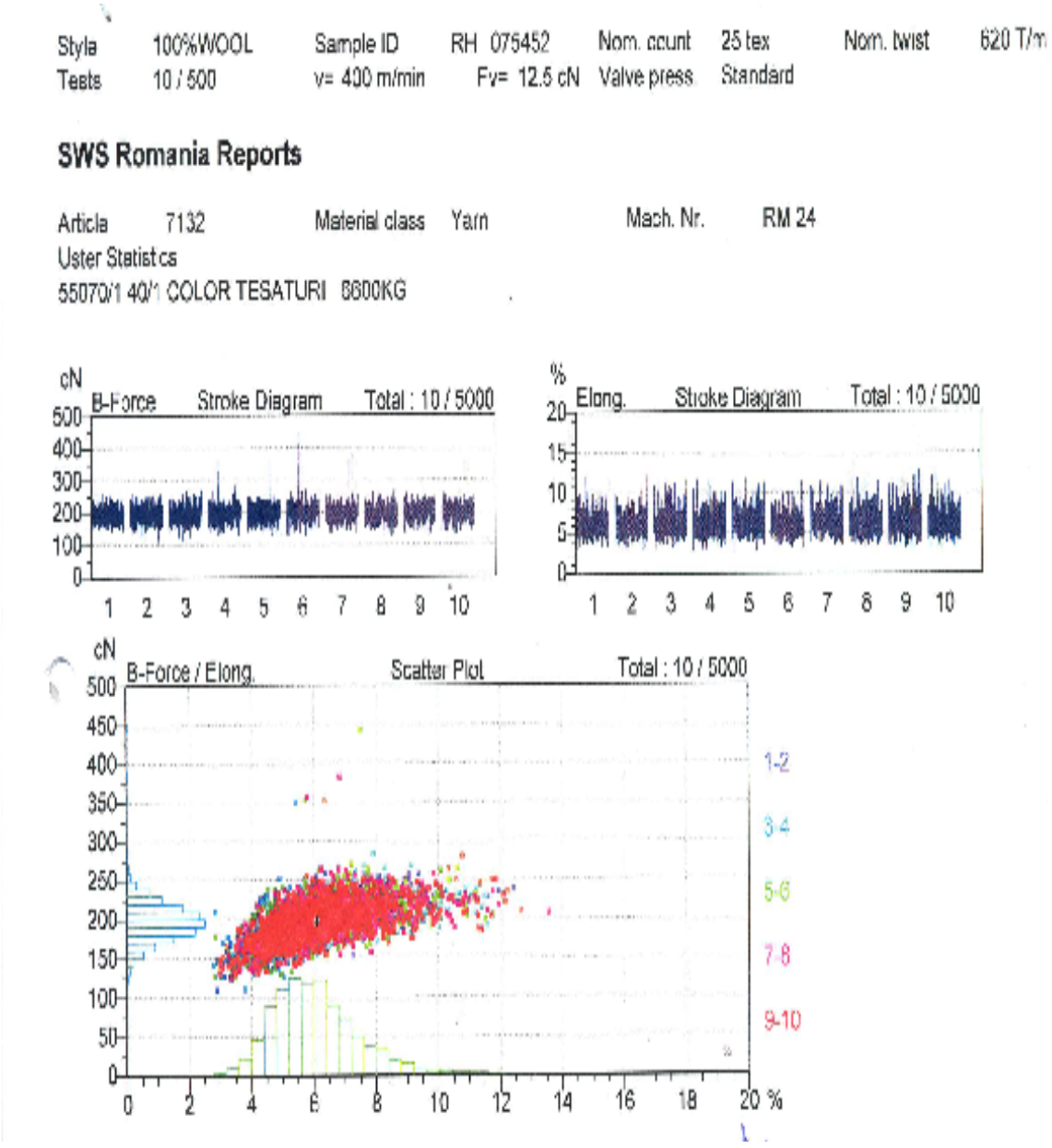

***Fig. 1**: The stress-elongation diagrams for Batch I originating from Asia*

For these reasons, the parameters analyzed were those which assess tear resistance, using the Tensojet 4 Uster R (UTj4) machine, obtaining the shearing force, the shearing mechanical work,

shearing elongation and tenacity. The study was performed on three batches of 100% wool yarn from three different geo-climatic areas.
Batch I (55070) – originating from Asia
Batch II (55330) – originating from South Africa
Batch III (55621) – originating from England
These yarns, meant for knitting, have a fineness of 25 tex and torque of 620 twists/ meter. Testing was carried out on 10 samples of 500 m from each yarn batch.
Analysis and the machine F_2

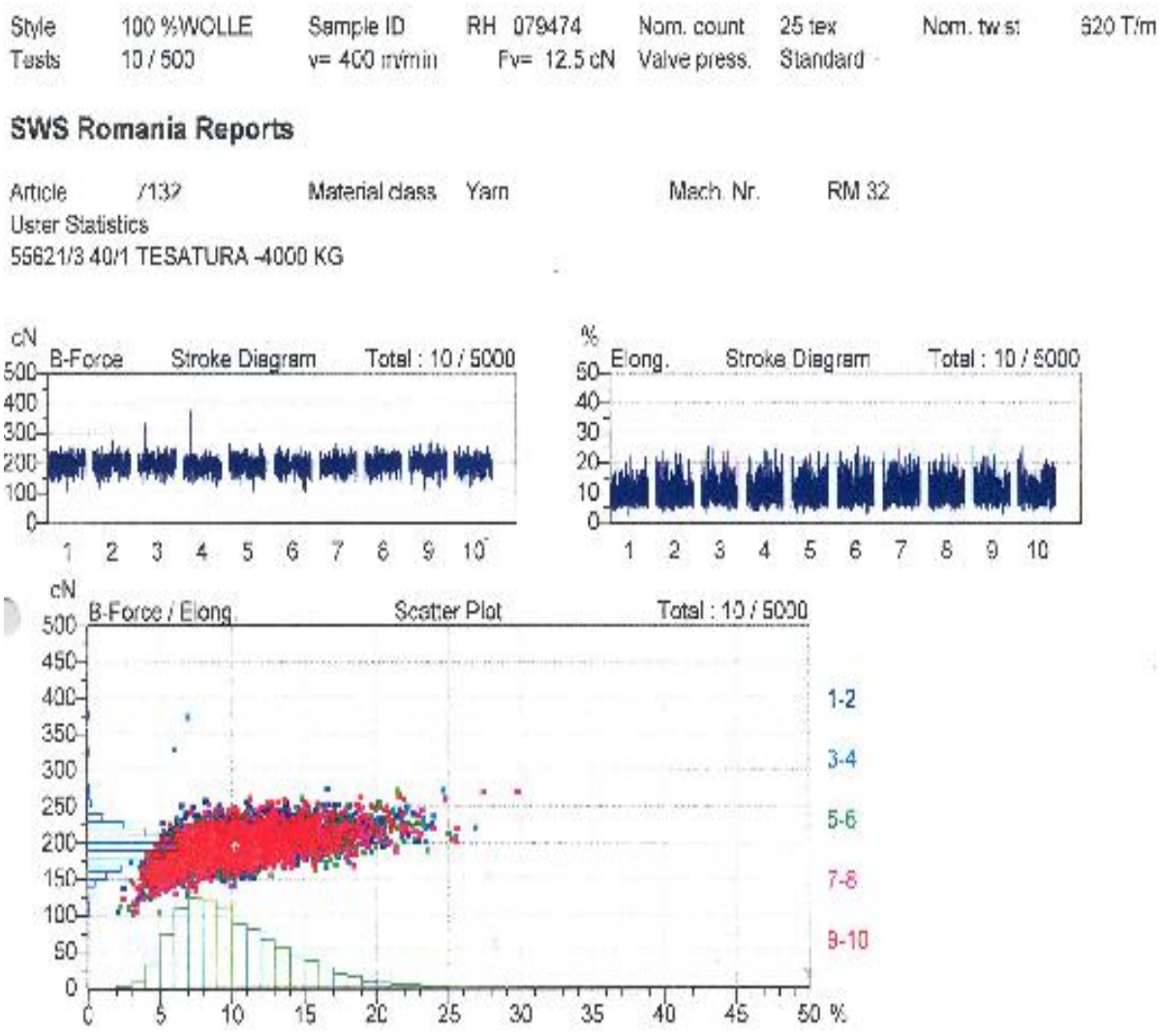

***Fig. 2**: The stress-elongation diagrams for Batch II originating from South Africa*

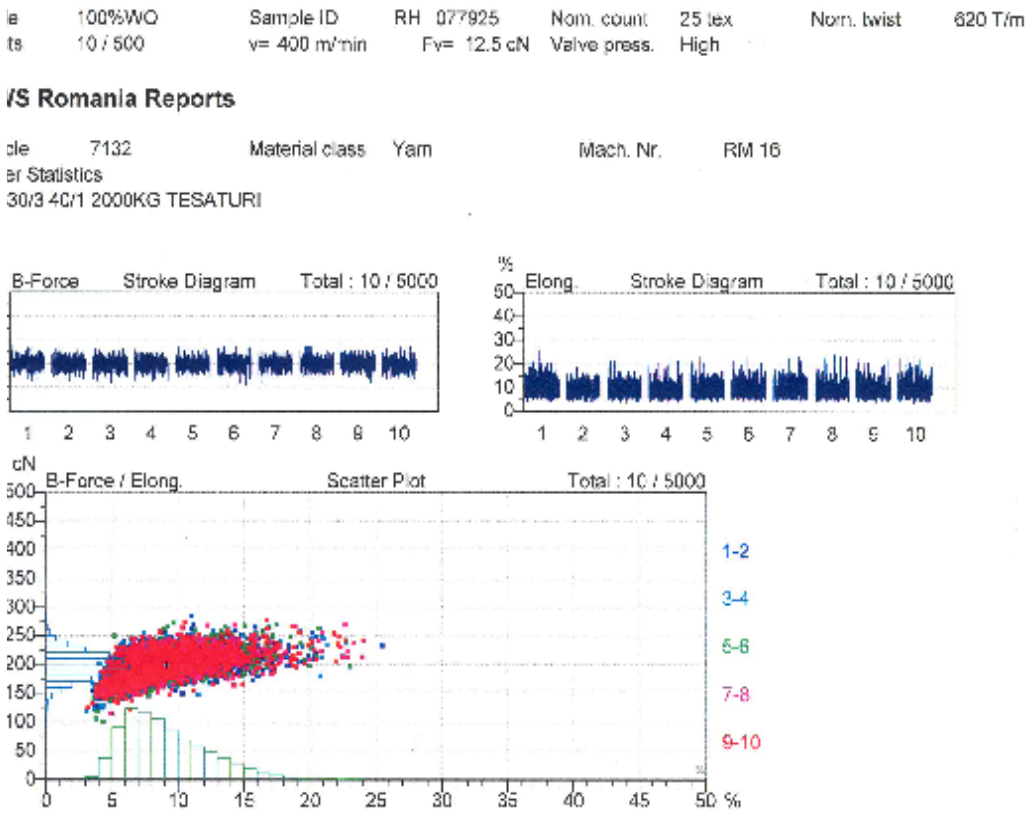

***Fig. 3**: The stress-elongation diagrams for BatchIII originating from England*

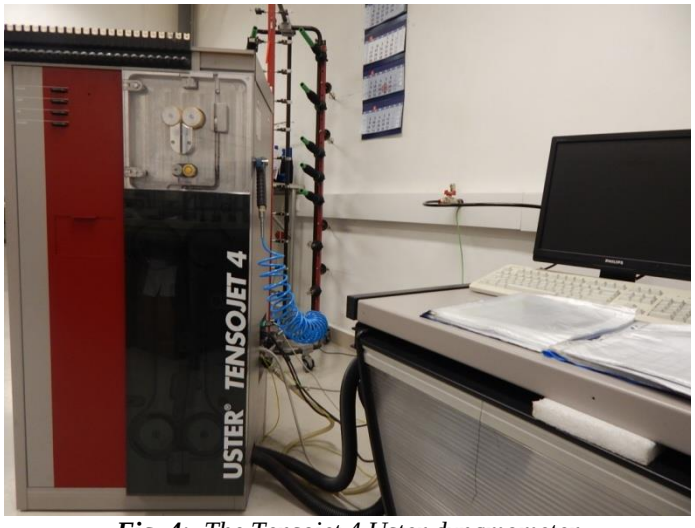

***Fig. 4:** The Tensojet 4 Uster dynamometer*

3. CONCLUSIONS

Based on the study conducted on three batches of wool yarn and the processing of the statistical and mathematical data produced by the Uster R Tensojet 4 machine, we found that woolen yarn from South Africa are high quality, with a better tensile strength and lower mechanical strength variation coefficient than yarns from Asia and England.
Tensional properties of the wool yarns are determined by the morphological structure of the fiber and wool quality, which are influenced by geo-climatic conditions, which also influence the degree of unevenness in terms of tensile strength.

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DETERMINING THE NEED FOR ZERO SERIES EXECUTION IN MANUFACTURING PROCESSES IN THE TEXTILE GARMENT INDUSTRY

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Abstract: *Because the industrial production requires the application of some transformation procedures on the material resources, so that a clothing product comes out with optimal use value in terms of maximum economic efficiency, one of the main influencial factors is the quality of the products. To make manufacturing processes more efficient, it is necessary to carry out the zero series in order to ensure the quality of the technological processes, as well as to prevent some design deficiencies. Among the main operations undertaken to ensure the quality of the zero series, we mention: creating the conditions for launch, tracking and finalizing the accompanying production documents under similar series production conditions; zero-series producers are usually the same workers who make up the series production line; equipping with the appropriate equipment and providing with necessary devices in order to create the technical conditions for the execution of the zero series; providing technical assistance in relation to manufacturing and control documentation for eliminating the design deficiencies. This paper presents the architecture of the zero series execution in manufacturing processes in the textile garment industry. The information obtained from the zero-series analysis is directed to the technical support, for possible corrections of the patterns according to which the products were manufactured.*

Key words: *zero series, technical documentation, design, quality, fold, inside fold, defects.*

1. INTRODUCTION

The zero series consists of a small number of copies of the prototype for a certain dimensional scale, in order to track the materialization in the technical and constructive documentation of the product design features, observing the technical and economic indicators from the standards. Following the implementation of the zero series, the deficiencies noted will be reported in a minutes report and the corresponding changes will be made in the constructive and technological documentation, so that the final technological process is as elaborate as possible.

The switch to serial production will be done only when the technological process is considered to be in line with current standards, internal norms and material specifications.[1]

2. CONTENT

2.1. Checking the zero series.

The systematic review of the products quality that make up the zero series is analyzed by successive samples on the standard body or on the mannequin. The defects noticed on the dressed body in orthostatic position, and those that are highlighted as priority, are the ones of assembly make up of layers of a product, as well as those of the constructive design. The defects resulting from inappropriate technology will only be tracked if they lead to major disruptions in the product acquisition process. If these deficiencies are identified, it will be possible to make adjustments or corrections to the technological process[2].

The defects of structural composition of the layers assembly of a product are characterized by the tendency of rolling the end edges and the small reference marks, some loose or fixed folds may apper with different orientation, on layers, inside or outside, which is due to the inconsistency of the component layers characteristics of a product, or due to incorrect dimensioning of thickness additions.

The constructive defects when dressing are manifested by changing the body position in dynamics, identifying them as follows[3,4]:

- the appearance of folds or plaits, creases with different orientation;
- the change in the state of equilibrium of the final product or some component parts and making it difficult to carry out some natural moves.

From the practical point of view, for zero series the following issues are analyzed:

- positioning the product on the body;
- base material;
- constructive - decorative lines.

Following these analyses we compare the concordance between the copies and the standard model (prototype).

1. The folds are a result of over-dimensioning some constructive reference marks. This inconvenience can easily be rectified by recutting the reference mark. Fixed folds occur after under-dimensioning the respective reference mark. The fixed folds are oriented on the same direction as the undersized segment that caused them to appear. The folds usually indicate problems of inappropriate layout of the reference parts on the body. The horizontal folds typically occur if the product is too adjusted, above or below a protrusion.

The skirt is a classic example that is stretched in the underbottom area, showing horizontal folds above the hips towards the waist. In the case of some materials, the fixed horizontal folds lead to the destruction of the joint line by slipping the fabric.

In the case of shoulder-support products, the appearance of the fixed back folds is due to the under-dimensioning of the back width or the diameter of the sleeve cut at the back reference mark. This type of defect can be rectified by modifying the rear reference mark as shown in Figure 1.

For undersized reference marks in the transverse direction on the back of the garment, there appear loose vertical folds. This deficiency occurs very often at the back of the jackets, dresses, but they also appear on skirts, trousers or sleeves. Such a flaw is shown in Figure 2.

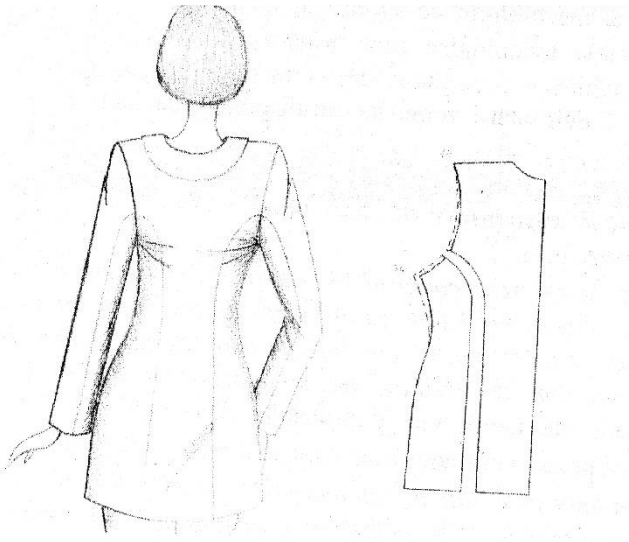

Fig. 1 *Example of fixed horisontal folds*

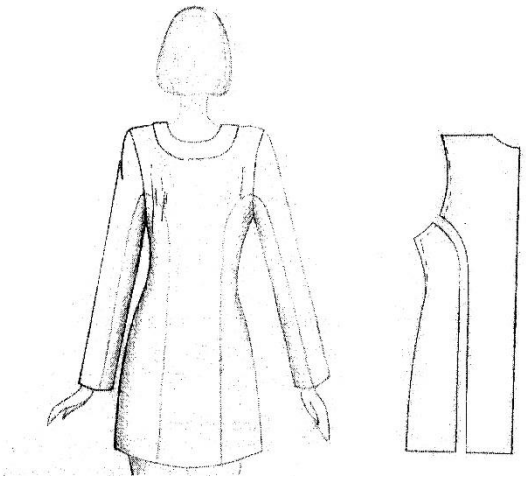

Fig. 2 *Example of vertical folds*

The oblique folds appear when placing the product on the body, and in order to rectify this deficiency it is necessary to increase the cut of the sleeve in front or at the back and increase the length of the shoulder line as in figure 3.

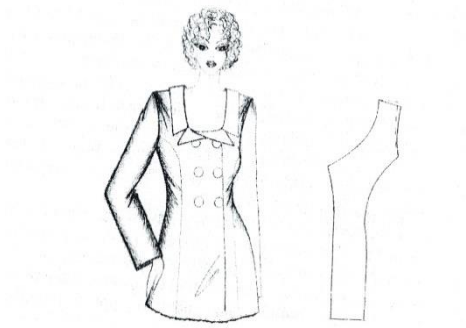

Fig. 3 *Example of oblique folds*

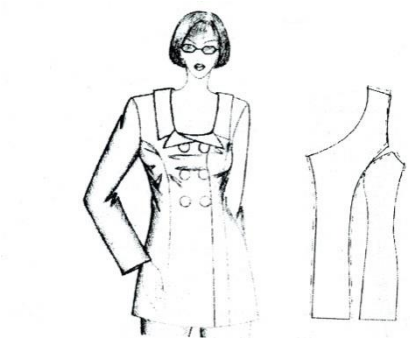

Fig. 4 *Example of radial folds*

If the design was incorrectly executed in the case of inside folds of constructive modeling in the areas of the nipple, abdominal, buttocks or shoulder prominencies, the tensioning forces concentrate on the protruding area forming radial folds. Correction of this deficiency is done as shown in Figure 4. In the case of waist-type products, this type of folds appear around the limb joints when the textile material is less elastic and the cross-sectional dimensions of the reference marks are relatively reduced.[5]

2. The equilibrium of the product represents the perfect match of the product with the body, as well as the influence on the arrangement of the product on the body. The product must be arranged in the same way on the symmetrical elements of the product. The equilibrium defects are characterized by the tendency of the product to twisting towards the front or back. These defects are manifested by overlapping or removing the product opening lines in front, lifting or semi-lowering the front end or back end line, deflection of the lateral stitch line to the front or back of the product and moving the shoulder line to the front or back. This defect is rectified by redesigning the back or front patters as appropriate.

3. The proper positioning of the product on the body is characterized by the absence of folds (creases) placed diagonally in the direction of the warp or weft.

4. The influence of the textile material is highlighted in the case of inappropriate choice of the material inconsistent with the chosen model, as well as by defects caused by not considering the sense of positioning the patterns on the material. For refrence marks that have to keep the direction of the warp, its non-compliance either due to printing errors or due to special design effects, result in bent reference marks that eventually manifest by changing the finish of the product, through curls or wrinkles, defects that are accentuating after first uses and washes of the product. For almost all the reference marks for the main perimetesr of the body, the position of the woof should be parallel to the horizontal plan. Failure to follow the weft direction for the main perimeter causes the product to be tightened on the symmetry lines, which can be seen by the appearance of fixed folds on the horizontal direction.

5. The influence of the constructive-decorative lines can be highlighted as follows: in order for the product to correspond to the spatial form of the human body, it is necessary to obtain certain lines made by joining with a structural or/and decorative role, through pleats or inside folds forming the silhouette of the product.

Most of the times the joints on the symmetry line of the back, from the middle of the front, on the side seams of the trousers, are positioned in the direction of maximum dimensional stability, respectively in the direction of the warp. For a product with shoulder support, the shoulder stitch is positioned just above it, and the inside folds are oriented towards the area that shapes it. Failure to observe the position of the shoulder by oversizing the back height leads to the appearance of loose

horizontal folds in the upper part of the back (see Figure 5). Also in the case of this type of defect that occurs on the front part of the product it should solved in the same way.

If the product does not fit properly on the support area, if the product pressure is uneven, there are tensions leading to oblique folds. For example, for shoulder-based products, these folds may appear in the support area if the shoulder line inclination is too large or too small - Figure 6.[6]

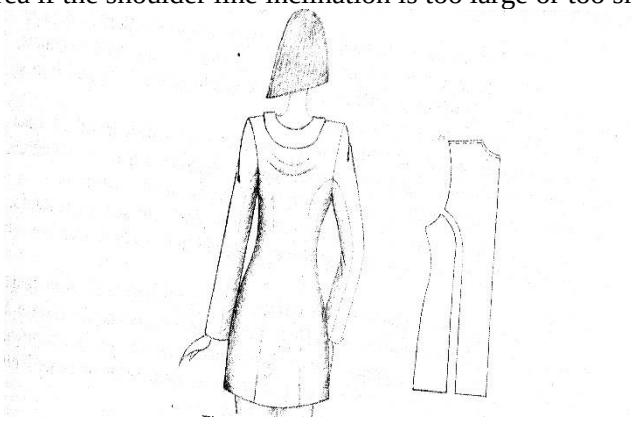

Fig. 5 *Example of horizontal folds in the upper part of the back*

Fig. 6 *Example of shoulder line inclination*

The following defects may occur on the neckline cut [7]:

- loose folds when the neckline cut is under-dimensioned and its rectification consists in raising the neckline contour to the front and back pattern with the necessary value;
- the radial folds from the neckline cut to the outside indicate that the neckline is too fixed to the perimeter of the neck, and its correction consists in lowering the contour of the neckline to the front and back pattern with the necessary value;
- the folds diagonally oriented when the collar is placed on the body, it requires to rectify the size of the neckline cut in the back and to increase the shoulder line dimensions with the same value.

The terminal line of products, which must be positioned at equal distances from a horizontal plan, can be modified due to problems of product placement on the body, uncorrelation between product dimension and product size, non-compliance with the positioning direction of the patterns on the fabric, as well as due to the poor construction of the patterns. In the case of vertical folds or pleats,

the strict non-observance of the nominal direction leads to the appearance of some changes in the modeling lines, materialized by rolling of the endings towards the front or back of the product.

3. CONCLUSIONS

The information obtained from the zero-series analysis is directed to the technical support, for possible corrections of the patterns according to which the products were manufactured.

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ANNALS OF THE UNIVERSITY OF ORADEA
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OPTICAL WHITENING OF 50/50% PES/WOOL FABRICS

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Abstract: *If a high level of whiteness is required for wool and wool blends, it is normal to carry out a combined oxidative/reductive bleaching treatments. A higher whiteness can be achieved by the use of optical whitening agents. The aim of this experimental work was to whiten 50/50% PES/Wo woven fabrics. 50/50% PES/Wool fabrics were first bleached in acidic conditions by hydrogen peroxide, and then, the reduction washing processes were carried out by sodium hydrosulphite (Merck), thiourea dioxide (Merck) or sodium borohydride (DyStar). The optical whitening agents, Hostalux ETB Liq. and Leucophor BSB Liq. were later applied at four different concentrations either in a single bath or in two separate baths to the fabrics treated with one of these three chemicals. The processes were repeated twice to check the repeatability of the results. The optical whitening processes were carried out in a laboratory type HT machine (Roaches). The colour measurements were carried out by Datacolor SF600+ spectrophotometer. The Whiteness Indexes of the optically whitened samples were evaluated in accordance with CIE Whiteness Index. The optical whitening agent used for wool gave better results, and also the best results were obtained in single-bath treatments. The best whiteness value was obtained with hydrogen peroxide bleached and washed with sodium hydrosulphide samples which were later optically whitened with 0.8% Hostalux ETB Liq. and 2% Leucophor BSB Liq. at 95°C treatment.*

Key words: *optically whitening, 50/50% polyester/wool blends, reductive washing*

1. INTRODUCTION

The whitening of 50/50% PES/wool blends is a difficult task[1-3]. Oxidative (based on stabilised hydrogen peroxide), reductive (based on thiourea dioxide or hydrosulphite) or combined oxidative/reductive are commonly used in exhaust bleaching processes for wool. Where a high level of whiteness is required, it is normal to carry out combined oxidative/reductive bleaching treatments[4-7]. In this work, 50/50% PES/Wo woven fabrics was optically whitened using different methods. 50/50% PES/Wo fabrics were first bleached in acidic conditions by hydrogen peroxide, and then, the reduction washing processes were carried out by sodium hydrosulphite (Merck), thiourea dioxide (Merck) or sodium borohydride (DyStar). The optical whitening agents, Hostalux ETB Liq. [8] and Leucophor BSB Liq. [9] were later applied at four different concentrations either in a single bath or in two separate baths to the fabrics treated with one of these three chemicals. The colour measurements were carried out by Datacolor SF600+ spectrophotometer. The Whiteness Indexes of the optically whitened samples were evaluated in accordance with CIE Whiteness Index.

2. EXPERIMENTAL

50/50% PES/Wool (293 g/m^2) woven fabric was used throughout this experimental work. In the processes, hydrogen peroxide (Merck), Peristal EJP (Dr. Petry), Imerol JW TR Liq. (Clariant), hydrosulphite (Merck), thiourea dioxide (Merck), Sera Con C-BOR (DyStar), Sera Con C-RAP (DyStar), Hostalux ETB Liq. (Clariant), Leucophor BSB Liq. (Clariant), Dilatin POE (Clariant) and acetic acid were used. Roaches HT Sample Dyeing Machine was used in the treatments. The spectral measurements of the samples were carried out by Datacolor SF600+ spectrophotometer, and the CIE WI values were calculated using Datamatch software with 10° Standard Observer and D65 illuminant.

In the bleaching treatment, 40 mL/L H_2O_2 (%35), 2 mL/L Peristal EPJ and 1 mL/L Imerol JW TR were used. The liquor ratio was 20:1. The process was carried out at pH 5.5-6.5 and at a temperature of 60-80°C for 1 hour. Then, a hot and a cold rinses were given to the material. The process conditions of the reductive washings were given in Table 1. The fabrics were eventually rinsed by hot and cold water.

Table 1: *Process conditions of the reductive washings of the materials.*

Chemicals Used	**Amount Used**		
	Reductive washing by sodium hydrosulphite	**Reductive washing by thiourea dioxide**	**Reductive washing by sodium borohydride**
Hydrosulphite	4 g/L	-	-
Thiourea dioxide	-	0.5 g/L	-
Sera Con C-BOR	-	-	3 g/L
Sera Con C-RAP	-	-	30 g/L
Imerol JW TR	1 g/L	-	1 g/L
pH	-	5- 5.5	-
Temperature (°C)	50	80	85
Time (min.)	40	10	20

The conditions of the optical whitening processes were given in Table 2. After each process, the fabric was given a hot and cold rinses, respectively.

Table 2: *Optical whitening processes.*

Chemicals Used & Process Conditions	**The process in which PES and Wool optically whitened in a single bath**	**The process in which PES and Wo optically whitened in two separate baths**	
	Amount used	**Amount used**	
		Step 1: Optically whitening of PES	**Step 2: Optically whitening of Wool**
Hostalux ETB Liq.	0.2%, 0.4%, 0.6% and 0.8%	0.2%, 0.4%, 0.6% and 0.8%	-
Leucophor BSB Liq.	0.5%, 1%, 1.5% and 2%	-	0.5%, 1%, 1.5% and 2%
Dilatin POE	2%	2%	-
Hydrosulphite	-	-	3 g/L
Imerol JW TR	-	-	0.5 mL/L
pH	4.5- 5.5	4.5- 5.5	4.5-5.5
Temperature (°C)	95 or 110	110	70
Time (min.)	30	40	60
Liquor Ratio	1:10	1:10	1:10

3. RESULTS AND DISCUSSIONS

The CIE Whiteness Indexes of the untreated and the reductive washed samples were given in Table 3. As seen in Table 3, the CIE Whiteness Index of the untreated sample is very low, CIE WI 14.6. After bleaching the fabric with hydrogen peroxide, and later reductive washing the samples with sodium hydrosulphite, sodium thiourea dioxide or sodium borohydride slightly changed the whiteness values only.

***Table 3**: The Whiteness Indexes of the oxidative bleached and later reductive washed samples.*

Sample	CIE Whiteness				
	WI	**T_w**	**x**	**y**	**Y**
Untreated	14.6	-4.8	0.34	0.35	68.7
Bleached and reductive washed with sodium hydrosulphite	48.1	-0.1	0.32	0.34	73.0
Bleached and reductive washed with sodium thiourea dioxide	34.0	-4.5	0.33	0.35	73.4
Bleached and reductive washed with sodium borohydride	30.9	-6.1	0.33	0.35	70.1

The Whiteness Indexes of the samples which were bleached, treated with reductive clearing agents and also with optically whitening agents were given in Table 4 and Table 5.

***Table 4:** The Whiteness Indexes of the samples which were bleached, treated with reductive clearing agents and also with optically whitening agents.*

Reductive washing	Process	Applied concentration	CIE Whiteness				
			WI	**T_w**	**x**	**y**	**Y**
Reductive washed with hydrosulphite	Processed with optically whitening agent for PES	% 0.2 H	65.5	-2.1	0.32	0.33	69.2
		% 0.4 H	76.2	-2.8	0.31	0.33	68.9
		% 0.6 H	82.8	-2.4	0.31	0.32	69.6
		% 0.8 H	**85.2**	-1.1	0.31	0.32	70.1
	Processed with optically whitening agent for Wo	% 0.5 L	76.1	-1.0	0.32	0.33	80.2
		% 1 L	81.2	-0.2	0.31	0.33	77.5
		% 1.5 L	81.6	0.5	0.31	0.33	75.6
		% 2 L	81.1	0.4	0.31	0.33	78.0
Reductive washed with thiourea dioxide	Processed with optically whitening agent for PES	% 0.2 H	56.4	-5.4	0.32	0.34	71.4
		% 0.4 H	62.5	-5.6	0.32	0.33	70.5
		% 0.6 H	64.1	-5.2	0.32	0.33	70.0
		% 0.8 H	72.5	-5.2	0.32	0.33	70.7
	Processed with optically whitening agent for Wo	% 0.5 L	60.6	-2.1	0.32	0.34	77.7
		% 1 L	51.0	-2.7	0.32	0.34	75.9
		% 1.5 L	54.8	-3.0	0.32	0.34	76.1
		% 2 L	63.6	-1.9	0.32	0.34	78.5
Reductive washed with sodium borohydride	Processed with optically whitening agent for PES	% 0.2 H	67.1	-3.5	0.32	0.33	69.8
		% 0.4 H	71.2	-3.6	0.32	0.33	67.9
		% 0.6 H	76.5	-3.2	0.31	0.33	69.4
		% 0.8 H	75.5	-3.2	0.31	0.33	68.3
	Processed with optically whitening agent for Wo	% 0.5 L	67.4	-0.7	0.32	0.33	73.8
		% 1 L	77.6	-0.7	0.31	0.33	73.9
		% 1.5 L	**86.2**	-0.4	0.31	0.33	73.4
		% 2 L	80.6	-1.0	0.31	0.33	74.3

** **H:** Hostalux ETB Liq.; Optical whitening agent for PES, **L:** Leucophor BSB Liq.; Optical whitening agent for Wo*

If one of the components in the blend is optically whitened, the WI value increases dramatically, even at low concentrations of the optical whitening agents used. The best results for the samples, of which one of the components in the blend was optically whitened only, were obtained with sodium hydrosulphite washed and 0.8% Hostalux treated fabric, and also sodium borohydride washed and 1.5% Leucophor treated samples (WI = 85.2 and 86.2, respectively). Table 5 summarizes the results of the single-step and two-step processed samples, of which each of the components in the blend was optically whitened with suitable optical whitening agents.

Table 5: *The Whiteness Indexes of the samples which were bleached, treated with reductive clearing agents and also with optically whitened in the single-step or in the two-step processes.*

Reductive washing	**Optically Whitening Process**	**Applied concentration**	**CIE Whiteness**				
			WI	**T_w**	**x**	**y**	**Y**
Reductive washed with hydrosulphite	Two-step process; PES and Wo optically whitened	% 0.2 H- % 0.5 L	70.7	-2.2	0.32	0.33	76.9
		% 0.4 H- % 1 L	80.9	-0.1	0.31	0.33	72.4
		% 0.6 H- % 1.5 L	78.2	-0.7	0.31	0.33	73.8
		% 0.8 H- % 2 L	81.4	-0.7	0.31	0.33	75.7
	Single-step process; PES and Wo optically whitened at 110 °C	% 0.2 H- % 0.5 L	65.5	-5.4	0.31	0.32	72.3
		% 0.4 H- % 1 L	**98.6**	-0.5	0.30	0.32	68.7
		% 0.6 H- % 1.5 L	**99.9**	-0.2	0.30	0.32	67.6
		% 0.8 H- % 2 L	**100.6**	-0.1	0.30	0.32	68.6
	Single-step process; PES and Wo optically whitened at 95°C	**% 0.2 H- % 0.5 L**	**92.7**	-0.5	0.31	0.32	70.4
		% 0.4 H- % 1 L	**97.2**	-0.1	0.30	0.32	67.4
		% 0.6 H- % 1.5 L	**97.3**	0.0	0.31	0.32	68.7
		% 0.8 H- % 2 L	**106.7**	1.3	0.30	0.32	68.4
Reductive washed with thiourea dioxide	Two-step process; PES and Wo optically whitened	% 0.2 H- % 0.5 L	70.2	-3.0	0.31	0.33	76.9
		% 0.4 H- % 1 L	67.0	-3.0	0.31	0.33	75.6
		% 0.6 H- % 1.5 L	78.2	-0.7	0.32	0.33	75.6
		% 0.8 H- % 2 L	76.3	-2.0	0.32	0.33	76.4
	Single-step process; PES and Wo optically whitened at 110 °C	% 0.2 H- % 0.5 L	65.5	5.4	0.32	0.33	72.3
		% 0.4 H- % 1 L	81.0	-1.3	0.32	0.33	74.7
		% 0.6 H- % 1.5 L	83.1	-4.0	0.31	0.33	75.1
		% 0.8 H- % 2 L	84.1	-3.6	0.31	0.33	75.2
	Single-step process; PES and Wo optically whitened at 95°C	% 0.2 H- % 0.5 L	79.7	-3.8	0.31	0.33	74.3
		% 0.4 H- % 1 L	82.4	-3.6	0.32	0.33	74.1
		% 0.6 H- % 1.5 L	83.6	-3.2	0.31	0.33	73.8
		% 0.8 H- % 2 L	**92.6**	-2.2	0.31	0.32	78.3
Reductive washed with sodium borohydride	Two-step process; PES and Wo optically whitened	% 0.2 H- % 0.5 L	84.9	-1.0	0.31	0.33	74.9
		% 0.4 H- % 1 L	81.2	-2.0	0.31	0.33	69.2
		% 0.6 H- % 1.5 L	82.6	-1.2	0.31	0.33	70.3
		% 0.8 H- % 2 L	84.1	-1.4	0.31	0.32	69.2
	Single-step process; PES and Wo optically whitened at 110 °C	% 0.2 H- % 0.5 L	71.5	-3.6	0.32	0.33	70.7
		% 0.4 H- % 1 L	80.7	-3.8	0.31	0.32	70.2
		% 0.6 H- % 1.5 L	82.4	-3.5	0.31	0.32	68.3
		% 0.8 H- % 2 L	86.0	-2.9	0.31	0.32	69.2
	Single-step process; PES and Wo optically whitened at 95°C	% 0.2 H- % 0.5 L	70.2	-3.1	0.32	0.33	71.0
		% 0.4 H- % 1 L	70.8	-3.5	0.32	0.33	71.8
		% 0.6 H- % 1.5 L	88.4	-2.5	0.31	0.32	68.6
		% 0.8 H- % 2 L	88.4	-2.3	0.31	0.32	74.1

* ***H:*** *Hostalux ETB Liq.; Optical whitening agent for PES,* ***L:*** *Leucophor BSB Liq.; Optical whitening agent for Wo*

The best results obtained in the experimental work are printed in bold in Table 5. The application with 0.8% Hostalux and 2% Leucophor on 50/50% PES/Wo in a single-step process gave the best result. In Figure 1, the results with these concentrations are also compared in respect to the reductive washing agent.

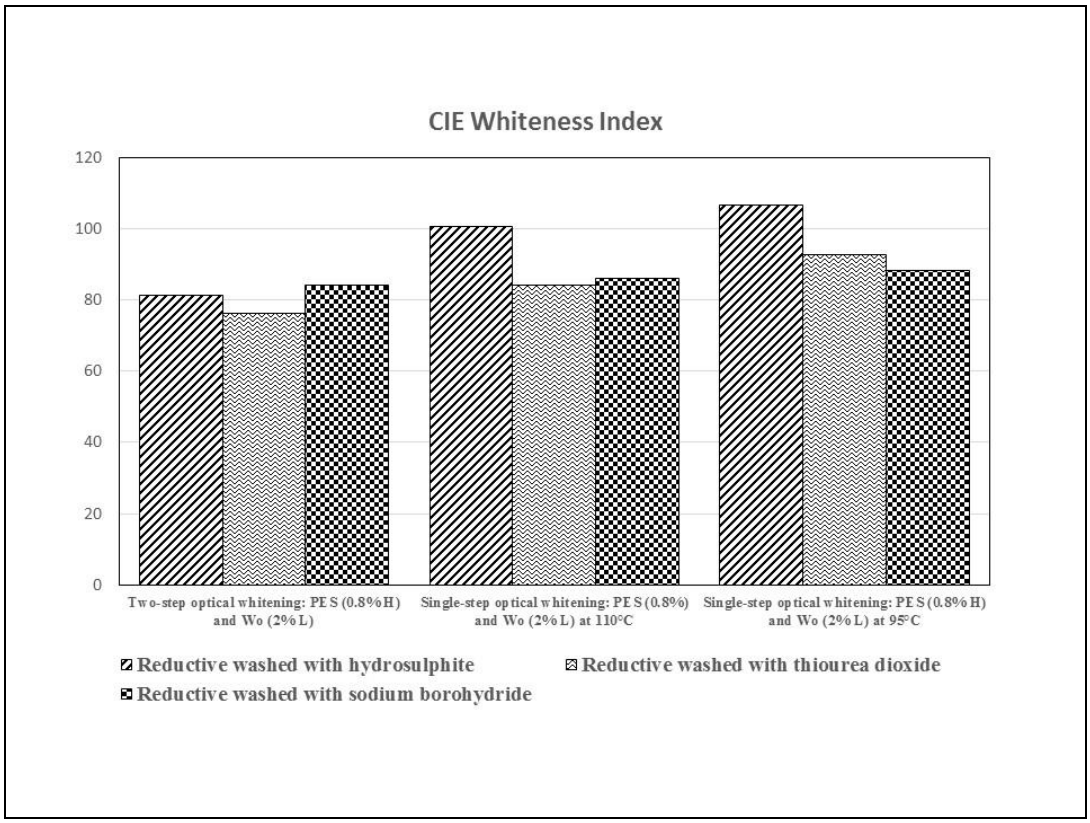

Fig. 1: *CIE Whiteness Index values of the samples which were bleached, reductive washed and optically whitened (Optical whitening agents used: "H": Hostalux ETB Liq. for PES and "L": Leucophor BSB Liq. for wool).*

The CIELab values of some of the untreated and treated samples with a CIE WI value having above 90 are given in Table 6 and Table 7, respectively.

Table 6: *The CIELab values of the untreated sample and "the bleached and reductive washed" samples.*

Sample	**CIELab Values**				
	L*	**a***	**b***	**C***	**h°**
Untreated	86.35	0.13	10.99	10.99	89.32
Bleached and reductive washed with sodium hydrosulphite	88.45	-1.13	5.12	5.25	102.46
Bleached and reductive washed with sodium thiourea dioxide	88.65	0.65	8.20	8.23	85.49
Bleached and reductive washed with sodium borohydride	88.65	0.65	8.20	8.23	85.49

Table 7: *The CIELab values of the treated samples with CIE WI > 90.*

Sample / Process(*)	Applied Optic Concentration	CIELab Values				
		L*	a*	b*	C*	h°
HS, SS, 110°C	% 0.4 H- % 1 L	86.32	1.83	-6.37	6.62	286.03
HS, SS, 110°C	% 0.6 H- % 1.5 L	85.81	1.77	-6.84	7.06	284.54
HS, SS, 110°C	% 0.8 H- % 2 L	86.28	1.59	-6.82	7.0	283.10
HS, SS, 95°C	% 0.2 H- % 0.5 L	85.71	1.55	-5.33	5.55	286.21
HS, SS, 95°C	% 0.4 H- % 1 L	86.36	1.65	-6.47	6.67	284.30
HS, SS, 95°C	% 0.6 H- % 1.5 L	86.19	1.61	-6.57	6.76	283.80
HS, SS, 95°C	% 0.8 H- % 2 L	86.00	2.31	-6.24	6.65	290.36
TUD, SS, 95°C	% 0.8 H- % 2 L	88.94	2.27	-1.98	3.01	318.96

* ***HS****: Sodium hydrosulphite;* ***TUD****: Sodium thiourea dioxide;* ***SS****: Single-step process;* ***H:*** *Hostalux ETB Liq.;* ***L:*** *Leucophor BSB Liq.*

Table 7 summarizes the CIELab values of the samples which have WI > 90 only. As seen in Table 7, the treated samples have very close L* values to that of the untreated sample, but b* values are negative (blueish) and also T_w values are very close to zero. The values of T_w (Tinting value) when positive, indicate a greenish hue; when negative, indicate a reddish hue; and when zero, indicate a bluish hue with a dominant wavelength of 466 nm.

4. CONCLUSIONS

The optical whitening agent used for wool gave better results, and also the best results were obtained in single-bath treatments. The best whiteness value was obtained with hydrogen peroxide bleached and washed with sodium hydrosulphite samples which were later optically whitened with 0.8% Hostalux ETB Liq. and 2% Leucophor BSB Liq. at 95°C treatment. The tensile strength of the treated samples remained almost unchanged. The reductive washings were found to be effective in order to get a whitened fabric, and the most effective reducing agent was sodium hydrosulphite.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FUNCTIONALIZATION OF TEXTILE FABRICS WITH MICROENCAPSULATED VITAMIN E

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Abstract: *In this study the experimental deposition of vitamin E microcapsules by padding technique on the textile support made of 50% cotton and 50% polyamide high tenacity Nm 50/1 were performed. The preliminary preparation of textile materials has been made in four consecutive sequences: hot alkaline treatment in absence of NaOH, bleaching, drying and curing. In the pretreatment of textile materials the crosslinking agent Itobinder AG is used, which is an anionic emulsion based on the acrylic copolimer, being followed by the application of a dispersion with content of vitamin E microcapsules. In the present raport the evaluation of obtained performances was made through SEM, GC and FTIR-ATR analysis. By SEM has been determined the wash durability of deposition of vitamin E microcapsules before and after one washing cycle. Following qualitative analysis by Gas-Chromatography coupled with Mass Spectrometry and Fourier Transform Infrared Spectroscopy with Attenuated Total Reflection absorption the related compoundes presents on the surface of the textile materials were identified. After retention time the vitamin E acetate is found with preponderance in all chromatograms at 15, 70 min with aproximation. Also by FTIR-ATR the presence of vitamin E acetate is confirmed by the apparition of a new peak at 1731 cm^{-1} and changes of intensity of various peaks, especially in the fingerprint region of the spectra of the functionalized fabrics.*

Key words: *textiles, microcapsules, vitamin E acetate, FTIR-ATR, SEM, GC-MS*

1. INTRODUCTION

The study of vitamin E is relatively complex because it can be found in many forms. These forms are jointly called tocols and are classified in tocopherols and tocotrienols [1]. An alternative of using vitamin E is the vitamin E acetate which hydrolyze when meets the H_2O molecules on the human skin being converted to free vitamin E. Also, vitamin E can be absorbed through all the skin layers to the cell membrane offering healthy glow to the skin and speeding up regeneration [2], [3]. The vitamin E acetate is less prone to oxidative stress and more stable during the light and heat exposure, than free tocols [1]. It is known that the vitamin E is the most common lipophilic antioxidant meet into the structure of the human skin layers, reacting with the reactive oxygen

species to protect the skin [4], [5], [6]. Once with the degradation of the epidermal structure by the UV exposure, the concentration of the vitamin E decreases [2], [7], [8]. So one of the most met way to protect the skin from UV exposure is to wear protective clothes, clothes functionalised with vitamin E. In this study the deposition of vitamin E microcapsules by padding technique on the textile materials made of 50% cotton and 50% polyamide high tenacity Nm 50/1 were performed.

2. EXPERIMENTAL PART

2.1 Materials

Deposition of suspension with vitamin E microcapsules content (LJ Specialities, UK) was performed on fabrics with fiber composition of 50% cotton/50% polyamide high tenacity, Nm 50/1. Textile fabrics were pretreated with Itobinder AG, a crosslinking agent supplied from LJ Specialities (UK). Itosilicone LJ88 has been used as non-ionic agent (LJ Specialities, UK).

2.2. Preliminary preparation of textile materials

For ensuring a good hydrophilicity of the textile materials, these were preliminary prepared by hot alkaline treatment at 95ºC temperature, for 90 minutes, in absence of NaOH to avoid the unwanted deffects on the polyamide component from the mixture. After hot alkaline treatment, the fabrics were washed repeatedly at 80ºC, 60ºC, 40ºC and at room temperature for 10 minutes.

2.3. Pretreatment of textile materials with crosslinking agent

For fabrics pretreatment Itobinder AG has been used as a crosslinking agent, applied by padding technique. Itobinder AG is an anionic emulsion based on the acrylic copolimer with good properties of adhesion and lasting effect in the treatments of washing and chemical cleaning. The textile materials were padded with different concentration of Itobinder AG, dried at 120 ºC for 2 minutes, followed by curing at a temperature of 150 ºC for 1 minute.

2.4. Treatment of textile materials with vitamin E

For deposition and for fixation of vitamin E microcapsules on the surface of the pretreated textiles the next technological steps has been followed: impregnation, drying and curing. The pretreated textile materials were impregnated with the suspension which contains vitamin E microcapsules under the following conditions: 2 passes and 2 bar squeezing pressure, followed by drying of the impregnated material at a temperature of 120^{0}C for 2 minutes and curing of of 150 ºC for 1 minute. In the drying and curing proceses the drying/curing/heat-setting/vaporization**,** model TFO/S 500 mm (ROACHES, UK) was used.

Table 1*: Codification of experimental variants in order to deposit and fix Vitamin E microcapsules*

Variant Code	Bath composition of treatment by padding method	Drying		Curing	
		Time (min)	Temperature (ºC)	Time (min)	Temperature (ºC)
V_{3a}	Itofinish Vitamin E = 30 g/L Itobinder AG = 50 g/L	2	120	1	150
V_{3b}	Itofinish Vitamin E = 30 g/L Itobinder AG = 60 g/L	2	120	1	150
V_{3c}	Itofinish Vitamin E = 30 g/L Itobinder AG = 80 g/L	2	120	1	150
V_{3d}	Itofinish Vitamin E = 30 g/L Itobinder AG = 80 g/L Itosilicone LJ88 = 20 g/L	2	120	1	150

The codification of experimental variants carried out in order to deposit and to fix the vitamin E microcapsules on the textile materials is shown in the Table 1.

2.5. Methods

2.5.1. FT-IR Spectroscopy – Attenuated Total Reflection

FT-IR measurements were performed using Bruker Vertex 70 spectrophotometer and OPUS software. The ATR spectra were measured in the wave number interval 400 – 4000 cm^{-1}, using 64 scans and 4 cm^{-1} resolution.

2.5.2. Gas-Chromatography (GC)

For the identification of vitamin E derivative compound, GC was carried out with an Agilent 6890N Gas-Chromatograph coupled with 5973N Mass Spectrometer. The column was a DB-35MS J&W Scientific (35m x 0.25 mm i.d., 0.25 µm film thickness). As carrier helium gas has been used with a flow rate of 1.2 mL / min constant volume and a column headpressure of 17.83 psi.

The sample of 2 g of textile material was immersed in 100 mL hexane, stirred using VWR Mini-Shaker device. After stirring, the solution was filtered using PTFE 0.45 µm and injected using the autosampler. The injection volume was 1.0 µL. Injection temperature was 290 °C, the oven temperature was started from 180 °C with an increase of 15°C/min to 280°C ending with a 10 min of isothermal at 280°C and the auxiliar temperature was 300°C.

The identification was made using NIST RESEARCH LIBRARY. The detector was a Mass Spectrometer. MS parameters were: 70 eV with a scan interval in the 30-500 mass units. The temperature for MS Source was 230 °C and for the MS Quadrupole was 150°C.

2.5.3. Scanning Electron Microscopy

For study the distribution of Vitamin E microcapsules on the fabrics surface the Quanta 200 (FEI, Netherlands) electron microscope with X-EDS module integrated was used.

3. RESULTS AND DISCUSSIONS

3.1. FT-IR Spectroscopy – Attenuated Total Reflection

ATR spectra of the fabrics before and after functionalization treatment are shown in the Figure 1. Typical cellulose and amide bands are easily identified at 1029, 1106 and 1632 cm^{-1} respectively [9, 10]. A new band at 1731 cm^{-1} and several changes of peaks intensity in the fingerprint region are observed after functionalisation, confirming the presence of vitamin E microcapsules.

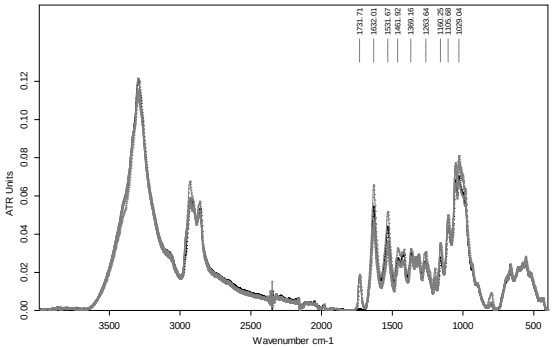

Fig. 1: *ATR spectra of reference (with black) and functionalized (with gray) fabrics*

3.2. Gas-Chromatography coupled with Mass Spectrometry

GC analysis of textile hexane extract of vitamin E is shown in the Figure 2 and Figure 3.

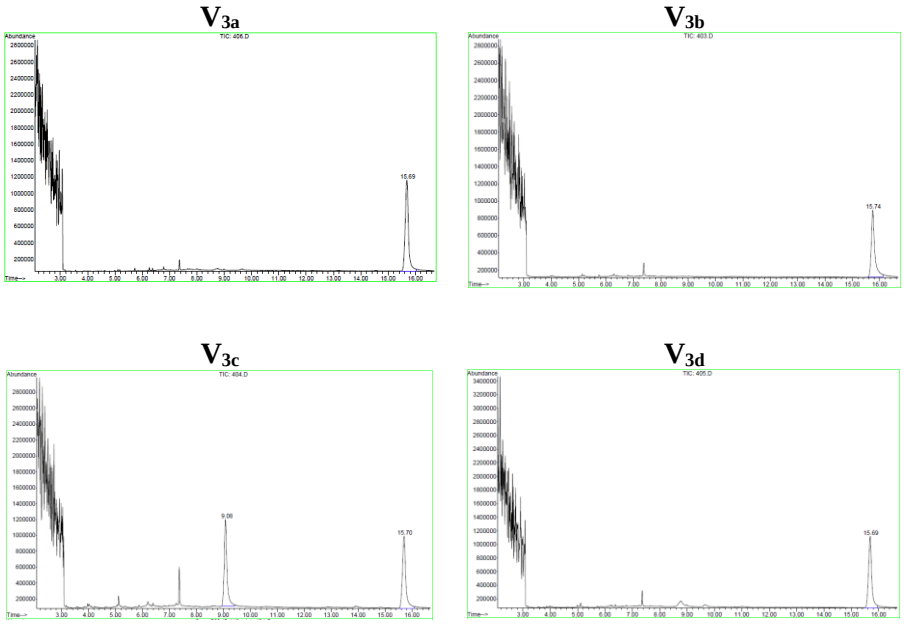

***Fig. 2**: GC-MS chromatogram for hexane extract of vitamin E*

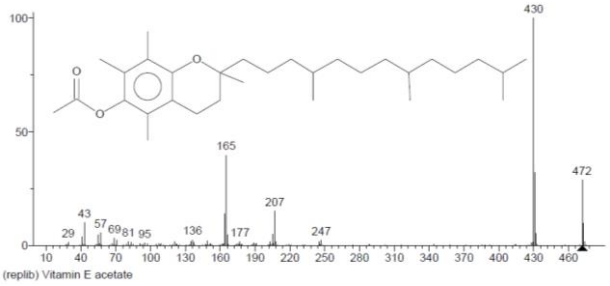

***Fig. 3**: Characteristic mass spectrum of vitamin E acetate*

In all chromatograms, at the beginning peak is attributed to the hexane solvent. Peak allure is given by the detector saturation with solvent. The appereance of several peaks is attributed to isomers existence of vitamin E like vitamin E acetate. According to the method used, vitamin E acetate has been identified at an approximate retention time of 15,70 min.

***Table 2**: Result based on MS and NIST identification*

Sample no.	Chemical constituents	RT	Peak area	MW	MF
V_{3a}	Vitamin E acetate	15,69 min	9374335	472,74	$C_{31}H_{52}O_3$
V_{3b}	Vitamin E acetate	15,74 min	6848088	472,74	$C_{31}H_{52}O_3$
V_{3c}	Vitamin E acetate	9,08 min	7844820	472,74	$C_{31}H_{52}O_3$
	Vitamin E acetate	15,70 min	7819407	472,74	$C_{31}H_{52}O_3$
V_{3d}	Vitamin E acetate	15,69 min	8427270	472,74	$C_{31}H_{52}O_3$

3.3. Scanning Electron Microscopy

In the Figure 4 is presented the distribution of vitamin E microcapsules on the surface of textile materials before and after washing process, the images were obtained at a magnification of x 4000. Electronic images recorded for textile materials treated with vitamin E reveal a predominant interfibrillar distribution of microcapsules. These are presenting spherical shape of different sizes and the majority are found in unbroken forme after the curing step, which demonstrate that the shell of the microcapsule is resistent at high temperature values. In the case of treatment variants with a higher concentration of binder (80 g/L) it is observed a deposition of some smaller microcapsules. After one washing cycle the number of vitamin E microcapsules from textiles surface is diminished.

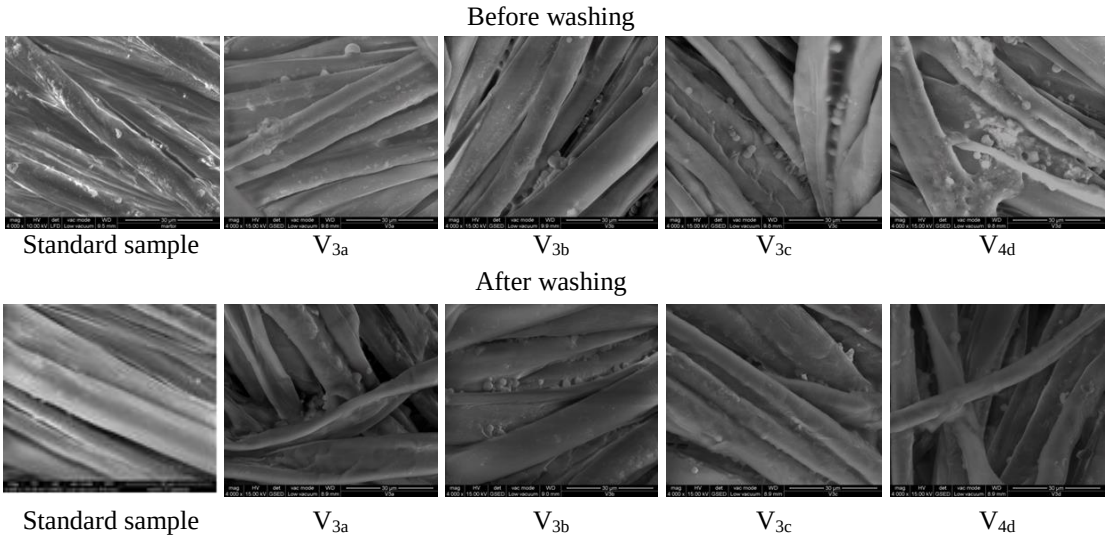

Fig. 4*: SEM images before and after one washing cycle of the textile materials*

4. CONCLUSIONS

Using GC-MS analysis has been evidencied the presence of vitamin E acetate, confirming the presence of vitamin E deposited on the textile materials for each experimental variant. A new band at 1731 cm^{-1} and several changes of peaks intensity in the fingerprint region were observed after functionalization treatment of textile materials, confirming the presence of vitamin E microcapsules. Electronic images recorded for textile materials treated with vitamin E microcapsules reveal a preponderant interfibrillar distribution of vitamin E microcapsules that were predominantly intact on the textile support, having smaller or larger sizes with spherical shapes. After one washing cycle, the number of vitamin E microcapsules from the surface has been reduced.

ACKNOWLEDGEMENT

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

SUITABLE MORDANTS FOR DYEING POSIDONIA OCEANICA FIBERS

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***Abstract**: Posidonia oceanica is the most extended sea grass in the Mediterranean Sea. Important quantities of this alga are accumulated on coasts making necessary the cleaninness of those beaches where it can be found. For this reason, many authors are developmenting new products made by this raw material, like green composites or are studing this material to be used as biomass, for example. The aim of this study is to dye the Posidonia Oceanica fiber using commercial natural dye to change their appearance to get a material more attractive for different areas. To achieve this aim, fibers were scoured and bleached in order to remove the brown colour of the Posidonia Oceanica fibers. Scoured and bleached processes were followed by the treatment done for cellulosic fibers, because some researches indicate that P. Oceanica is composed of high quantity of cellulose. Different types of biomordants were use in the pre-treatment of the fiber to improve the affinity between the fiber and the dye used.*
To compare the results, we evaluate the colour of each sample using CIELAB parameters and colour differences (ΔE), which are obtained by reflexion spectrophotometre. The results showed that medium molecular weight chitosan, which was used as biomordant, gets the highest intensity of colour*

***Key words:** Posidonia Oceanica, scouring, bleaching, biomordant, dyeing*

1. INTRODUCTION

Posidonia is an endemic marine plant at the Mediterranean Basin forming wide grasslands playing an important ecological role in the Mediterranean system [1], which are involved in the oxygenation of seawaters, fauna protection and littoral erosion prevention [2]. The P. oceanica dead leaves in the form of called “Neptune balls” are accumulated in a large scale on the beaches. These residues represent a great environmental, economical, social and hygienic problem in all coastal zones of Mediterranean and the high costs for their removal and disposal to landfill. For this reason there are many authors, which have reported different alternatives to reuse Posidonia Oceanica (PO) residues [2], [3].

These fibers show a brown colour consequently, the number of applications to develop new products are limited because of their appearance.

In order to remove the colour from Posidonia fibers the same treatment for prepearing cellulosic fibers, scouring and bleaching processes were carried out. Moreover, to get a new appearance more attractive bleached fibers were dyed using a natural dye. However, those dyes do not show deep intensities in colour and a mordant is requested to improve the colour yeld. Mordants

which should be eco-frendly in order to maintain the process as an environmentally friendly one [4],[5], [6].

2. EXPERIMENTAL

2.1 Materials

The balls of Posidonia Oceanica were collected from Valencia beach (Spain). First of all, these balls were shred in order to get individual fibers and washed with water to remove the sand (figure 1).

Fig. 1: *Images of balls of Posidonia Oceanica and these srhed.*

To remove the brown colour of the fibers, scouring and bleaching processes were carried out using NaOH, Leophen (suministrated by Basf) as moistening agent and Kieralon (suministrated by Basf) as surfactant for scouring process and H_2O_2 and a stabilizer for bleaching process. Red natural dye was supplied by Irisem. Chitosan with different molecular weight, low and medium, and alum were used in a pre-treatment of bleached fibers as mordants, using the same concentration of each one (5 g/L).

2.2 Methods

In table 1 conditions followed for scouring, bleaching and dyeing processes are shown.

Table 1*: Scouring, bleaching and dyeing conditions*

Scouring		**Bleaching**		**Dyeing**	
R/b	1/40	R/b	1/40	R/b	1/40
NaOH (g/L)	8	H_2O_2 (g/L)	25	Dye concentration	2% spf
Moistening (g/L)	1	Moistening (g/L)	1	Temperature (ºC)	90-95
Surafactant (g/L)	1	NaOH (g/L)	1	Time (min)	60
Temperature (ºC)	90-100	Surfactant (g/L)	0,5		
Time (min)	120	Stabilizer (%)	1		
		Temperature (ºC)	80-90		
		Time (min)	120		

Scoured, scoured and beached and scoured, beached and dyed samples were prepared for colour measurement. To investigate the effect of biomordant used on the dyed samples, the reflectance spectra were measured before and after treatments using an Minolta CM-3600d. CIELAB color coordinates (L*, a*, b*) were calculated from the reflectance data for 10° observer

and illuminant D65. The shift of the coordinates of the color in the colour spaces L*, a*, and b*, based on the theory that color is perceived by black-white (L), red-green (a), and yellow-blue (b), was summarized by the ΔE* value. The value of ΔE* represents the overall color difference between each treated sample and the standard (untreated sample).

3. RESULTS

To compare the effect of using different mordants and evaluate dyed fibers, CIELAB and ΔE* values of each sample are shown in table 2.

***Table 2**: CIELAB parameters and ΔE**

Posidonia sample	L*	a*	b*	ΔE*
Untreated	50,9557	3,8666	10,7047	
Scoured	50,1729	4,1665	10,61	0,8436
Bleached	62,3764	3,7052	16,8276	12,9595
Chitosan Low + dyed	54,0729	6,0683	12,2579	4,1203
Chitosan Medium + dyed	44,7564	15,5356	7,5954	13,5745
Alum + dyed	57,6869	9,6967	15,7451	10,2325

First of all, it has been observedthat there are no significant differences when fibers are only descrudadas, however we can appreciate the big difference of L* and ΔE* values when the Posidonia fibers are descrudadas and bleached. L* values refer to light-dark values from 100 to 0 representing white to black, then these results verify the loss of brown colour of untreated Posidonia fibers, because L is higher than the untreated and descrudada sample.

Regarding dyed samples, if we compare the different mordant used in the pre-treatment, before the dyeing process, it is observed that chitosan with medium molecular weight shows the highest ΔE*.

Furthermore, if we focus our attention on a* value, whose positive values indicate red colour, all dyed samples using different mordants show higher values than untreated, descrudado and bleached samples. In figure 2 we compare the results of a* value of each sample.

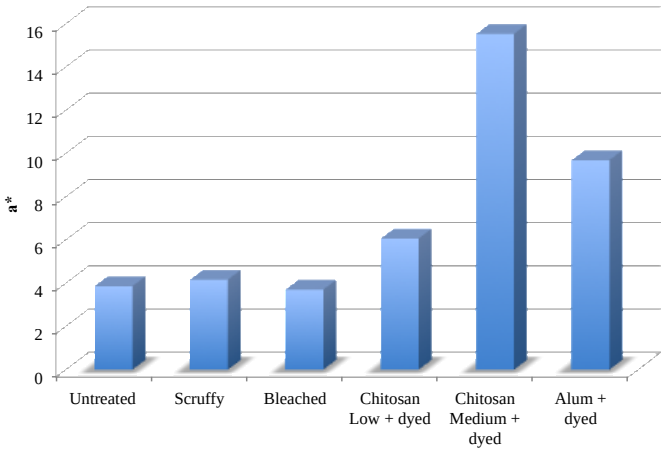

***Fig. 2:** Graphic of a* value of each sample*

It is clearly observed that pre-tretated sample with medium molecular weight chitosan show the highest result, being pretreated fibers with alum the second best result.

5. CONCLUSIONS

We can conclude that scouring and bleaching processes used to treat cellulose fibers are effective to treat Posidonea Oceanica fibers, as the bleached fibers show highest L* value which indicates the sample is whiter than untreated and scoured samples. On the other hand, when bleached fibers are dyed, using different types of mordant, all dye samples show higher a* value, this value indicates the red color. Pretreated samples with medium molecular weight show the highest a* value, being the best result.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECT OF UV IRRADIATION ON THE DYEING OF COTTON FABRIC WITH REACTIVE BLUE 204

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Abstract: *Reactive dyes are synthetic organic compounds used on a wide scale in textile industry, for painting materials of different types and compositions (e.g. 100% cotton, wool, natural satin, viscose, synthetic fibres). Reactive dyes are solid compounds (powders) completely water soluble at normal temperature and pressure conditions. Their structures contain chromophore groups, which generate colour, and auxochrome groups, which determine the compounds water solubility and the capacity to fix to the textile fiber. Such organic compounds absorb UV-Vis radiations at specific wavelengths, corresponding to maximum absorbtion peaks, in both solution and dyed fiber. The human organism, through the dyed clothing, comes in direct contact with those dyes which can undergo modifications once exposed to UV radiations, having the posibility to reach the organism via cutanated transport. As it is known, the provoked negative effects are stronger during summer when UV radiations are more intense and in order to reduce their intensity dark coloured clothing is avoided. Dyes can be transformed in compounds which are easily absorbed into the skin. Some of these metabolites can be less toxic than the original corresponding dye, whilst others, such as free radicals, are potentially cancerous. Knowledge of the biological effects of the organic dyes, reactive dyes in particular, correlated with their structural and physical characteristics, permanently consists an issue of high scientific and practical interest and its solution may contribute in the diminishing of risk factors and improving of population health. UV radiation influence on the structural and colour modifications of textile materials were studied. Colour modifications are due to structural changes in aromatic and carbonil groups. In most cases photo-oxidative processes were identified in the dye structure. Dyeing was performed using non-irradiated and irradiated cotton painted with reactive blue dye 204.*

Key words: *Cotton fabric, Ultraviolet protection, Reactive Blue 204, Photodegradation, Cellulose*

1. INTRODUCTION

Reactive dyes are organic synthesis compounds used on a wide scale in the textile industry, for painting materials of different types and composition (e.g. 100% cotton, wool, natural satin, viscose, synthetic fibres) [1], [2], [3], [4]. Their multiple applications are due to the covalent binding and good attachement to the fiber, features which endow the painted material with strong lasting colour and good resistance to washing and rubbing [5], [6].

The dye's complex structure and high resistance to degradation under weathering factors, make them environmentally hazardous. The high quantities of reactive dyes in residual waters are ecologically harmful, due to their colour and especially to toxicity of the decomposition products, and are cancerous for wildlife and humans.

Knowing the reactive dyes biological effects, correlated with physical and structural characteristics has become a permanent issue of high scientific and practical interest and its solution may contribute in the diminishing of risk factors and improving of population health. The need of such research has risen from the fact that textiles dyed with the Reactive Blue 204 dye undergo significant and important colour and structural modifications at the dye-substrate interface.

2. EXPERIMENTAL

2.1. Materials and methods

A fabric, manufactured mainly of alkaline cleaned and bleached cotton fibers was obtained from a commercial source (IASITEX S.A. Iasi, Romania). Fabric dyeing was achieved by fleet depletion technique in alkaline media (pH 9-10) with computerized plant Mathias Polycolor Uniprogramer 2002 type (Werner Mathias AG, Switzerland). Aqueos solutions containig 5% dye Reactive Blue 204 ($C_{42}H_{28}O_{20}N_{14}S_6Cl_2F_2Na_6$, M_n = 1487.97 g/mol) was used to paint the fabric [5].

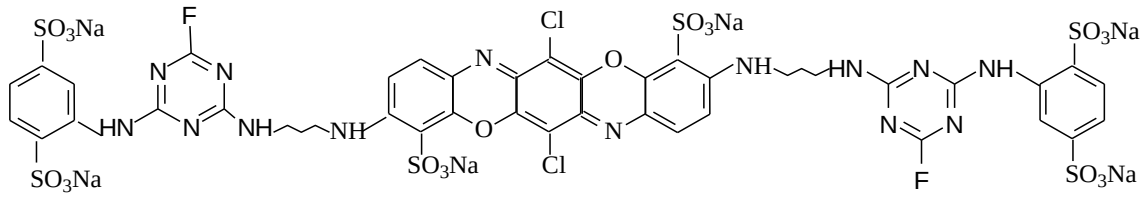

Fig. 1: *Reactive Blue 204 (Cibacron Blue F-GFN) [5]*

The temperature in the dyeing bath increased from 21 to 80 °C with a heating rate of 5 °C min^{-1}. Rinsing with hot water, cold water and finally with distilled water was used to remove the traces of unreacted dye. The Reactive Blue 204 has an absorbtion maximum in the visible domain at 636 nm for solutions of concentrations c = 8 μg/mL = 0,008 g‰, at neutral pH (Fig. 2).

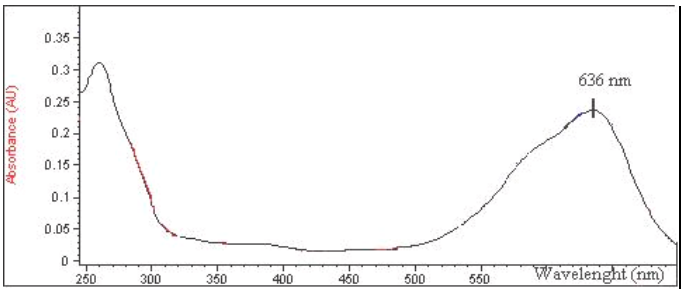

Fig. 2: *UV–Vis absorbtion spectrum of Reactive Blue 204 dye*

One may observe a decrease in colour intensity with irradiation time, due to dye decomposition, hence the increase in discoloration degree. The sample died with 3 % solution of Reactive Blue 204 and irradiated 25 hours was the least affected by irradiation (discoloration degree of 12.736 %).

Table 1. *Colour intensity, discoloration degree and dye quantitiy of samples dyed with 1, 3 and 5 % solution of Reactive Blue 204 dye and UV irradiated*

Reactive Blue 204 dye	Irradiation time (hours)	Discoloration degree (%)	µg dye after irradiation
(1%)	0	0	5140
	25	23.661	3924
	50	29.464	3626
	75	41.518	3006
(3%)	0	0	24489
	25	12.736	21370
	50	19.575	19695
	75	31.840	16692
(5%)	0	0	39892
	25	16.008	33506
	50	17.326	32980
	75	28.060	28698

2.2. Equipment

The 1, 3 and 5 % dyed samples were irradiated in air at periods of 25, 50, 75 and 100 hours in a rotating device of accelerated aging, equipped with a UVA lamp which has a polychrome emission spectrum, with a maximum wavelength $\lambda = 365$ nm. The aging studies were conducted by exposing the leather surface samples (70x40x0.5 mm) to UV radiation up to 100 hours in air. The samples were irradiated with UV filtred light emitted by the medium intensity mercury vapor lamp (model B-100AP, manufactured by Analytik Jena Company, with emission maximum located at 365 nm. A PMA 2100 radiometer manufactured by Solar Light Company equipped with PMA 2110 detector with response in the spectral region 320-400 nm was used to measure the irradiance and the irradiation dose during photochemical aging. The irradiance values were 23.3 Wm^{-2}. This value was measured in irradiation chamber at the level of sample holder.

Colour modifications during irradiation on the sample surfaces were followed with a Lovibond LC 100, RM 200 model apparatus manufactured by Tintometer Ltd., UK, using a white pellet from $BaSO_4$ as standard. The standard DIN 6174 (Farbmetrische 15 Bestimmung von Farbabständen bei Körperfarben nach der CIELAB-Formel, 1979) has been used for colour evaluation using D65 illuminant and the results have been expressed in CIELAB ($L^*a^*b^*$) system. In CIELAB ($L^*a^*b^*$) the colours are described by parameters L^* which is lightness, a^* which denotes the red/green value and b^* for yellow/blue value. The colour differences between the irradiated and non-irradiated samples were calculated with Eq. 1, where with ΔL^*, Δa^* and Δb^* are the differences between each parameter after and before irradiation.

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad \textbf{(1)}$$

3. RESULTS AND DISCUSSIONS

Colour modification studies during UV irradiation of Reactive Blue 204 dyed cotton samples (1, 3 and 5 %)

After 25 hours irradiation time L^* values increase for samples painted with 1 % and 3 % dye, while decreasing for the one painted with 5 % dye. L^* values witness a slow ascending tendency for all three dyed samples in the irradiation time range 25–50 hours, followed by a pronounced

decrease for samples painted with 1 % and 3 % dye and a slow decrease for the one painted with 5 % dye in the range 50–75 hours (Table 2).

Table 2: *Variation of chromatic parameters with UV irradiation time*

Irradiation (h)	**L***			**a***			**b***		
	1%	3%	5%	1%	3%	5%	1%	3%	5%
0	34.46	23.29	19.65	14.44	17.62	16.60	-33.22	-34.15	-32.87
25	37.04	26.81	18.37	12.72	14.33	14.06	-30.81	-31.19	-28.72
50	37.27	27.02	18.97	11.06	13.93	10.84	-27.47	-29.93	-29.75
75	35.05	24.58	17.90	8.27	13.00	8.88	-24.37	-28.67	-27.83
100	35.86	23.66	16.76	7.61	13.72	8.35	-21.00	-25.35	-27.06

L^* values decrease for all dyed samples in the irradiation time range 50–100 hours. A pronounced decrease for samples painted with 1 % and 3 % dye and a slow decrease for the one painted with 5 % dye occurs in the range 50–75 hours. Samples dyed with 1 and 3 % dye discoloured in the ranges 0–25 hours and 25–50 hours, while the sample painted with 1 % dye also discoloured within the range 75–100 hours, being the most affected by UV irradiation. The sample dyed with 5 % darkens during UV irradiation. The variation of a^* and b^* chromatic coefficients indicates accumulation of green and yellow chromophores due to photo-oxidation processes.

4. CONCLUSIONS

Sample painted with 1 % was the most affected by UV irradiation. The sample dyed with 5 % darkens during UV irradiation. Samples behaved as if they accumulated green and yellow chromophores due to photo-oxidation processes.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE RELATIONSHIP BETWEEN WORDS, TEXTS, CLOTHES AND TEXTILES

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Abstract: *In this paper we will speculate the possible relationships between "word," "text," "textile," and "clothing". Many of the terms we use to describe our interactions with words are derived from the common linguistic root and numerous other expressions associated with reading and writing are drawn from the rich vocabulary of cloth. Textiles are one of the most ubiquitous components of material culture and they are also integral to the material history of texts. The intersection between texts and textiles locates the relationship between language and dress, as together they structure the fashion scene over the century. We compare these texts and storytelling with the process of making clothes, they go from fibers that are spun and then create the fabric or the material out of which the clothes are made. Besides the similitude of the words "text" and "textile" that have four similar letters there is also the resemblance in the way they transmit a message. While texts are meant to transmit something to the reader, to enchant and to create emotions in so various ways, just in the same way clothes are also meant to transmit emotions and feelings to the wearer or to the people watching them.*

Key words: *language, interconnection, words, fabrics, clothing, interpretations*

1. INTRODUCTION

How do the fabrics of language intersect with the languages of fabric? The *text/textile* interface has often surfaced as an explicit preoccupation in literature. Many have explored the structural similarities between ancient Greek textual analysis and techniques of weaving, with particular attention to the relationship between the 'starting border' of a cloth and the *creation* of a text such as Hesiod's *Theogony*. Text is not necessarily linguistic, even though we think of text as words— think of text as filled with signs that sometimes consist of something other than graphemes, words or language.

Apart from pockets of thinking that consider the crafts theoretically impenetrable because of their foundation in tactile rather than intellectual knowledge, interdisciplinary research is paying increasing attention to the comparative opportunities textiles offer. In particular, analysis of the similarities between texts and textiles is one of the many areas expanding under this broadened field of vision. Writing and woven textiles, in particular, lend themselves to comparison on many levels,

from the linguistic roots the two words share, to the structural similarities found in networks of words and threads.[1]

"Textile" – 1620s, from Latin *textilis* "a web, canvas, woven fabric, cloth, something woven," noun use of *textilis* "woven, wrought," from *texere* "to weave," from PIE root **teks-* "to make."[2] "Cloth" is fabric which is made by weaving or knitting a substance such as cotton, wool, silk, or nylon. Cloth is used especially for making clothes.[3]

2. GENERAL INFORMATION

The shared origin of *text* and *textiles* in Latin *texere- to weave* is very interesting and offers many ways to interpret them. Textiles are one of the most ubiquitous components of material culture and they are also integral to the material history of texts. Paper was originally made from cotton rags and in many different cultural and historical settings, texts come wrapped, covered, bound or decorated with textiles. Across the domestic, public, religious and political spheres textiles are often the material forms in which texts are produced, consumed and circulated.

The similitude of printed paper and printed fabric is looked by essayist Amber Shaw as a kind of conflation of the represented thing and the thing itself; in other words with fashion magazines and rag newspaper, the production of the fabric became the very book or magazine, the weave of the page coexistent with the dress fabric, the text with the textile.[4]

India is a land of textiles. Traditionally Indian people are wearing fabrics rather than clothes. Even today lots of Indian women wear sarees on a daily base. So we can say there is a very tight connection between the material i.e. the textile and the clothes themselves.

3. DIFFERENT APPROACHES TO TEXTILES

3.1. Wearing texts on textiles

Words and cloth have drawn inspiration and meaning from each other for centuries, continuing into the present. The incorporation of the written word into textiles appears in two distinct forms: either words are rendered in a legible manner or they are intentionally illegible. From this difference, one can discern two vastly different forms of motivation for the textile artist. On one hand, the written word is employed to communicate an accessible message. On the other, it is a response to the beauty of mark-making.[5]

From this separation comes a further distinction, the technical rendering of the word itself. Words are sewn, woven, or screen printed onto the surface of fabric or transferred with methods that tend to be associated with the printed word such as Xerox or laser printing. Textual transcription onto cloth brings new techniques to textile design, while methods such as embroidery and weaving often have historical associations. Although these delineations may seem simple, the ways in which textile artists have combined these sources of inspiration are surprisingly broad.

Clothing is one of the most eloquent forms in which we encounter textiles. Ben Cartwright (Cambridge) discussed the way that clothing 'regestures' the body, and emphasized the need to wear rather than merely to look at clothing from the past in order to understand its histories. Cartwright's research explores the ways in which the crafts of spinning and weaving, as 'learnt bodily histories' (performing the task requires the learning of certain repetitive body movements and behaviours), contribute to community and individual identity. He is interested in how these crafts shape the means by which people behave and present themselves to themselves and others - not least in the clothes they wore. Clothing is one of the ways in which people, or groups of people, make themselves distinctive. This is likely to have been as true a thousand or so years ago as it is today. When people take on different roles, new clothes give them new ways of behaving. The tailoring,

material, and weave of the cloth restrict or emphasise certain movements that made up a social system of manners.[6]

3.2. Texts versus Textiles

In his *In Search of Lost Time,* the French writer Marcel Proust makes a comparison between writing a book and making a dress. His narrator, who is just about to embark on writing a novel, says that instead of building it "ambitiously like a cathedral" he is going to craft it "quite simply like a dress".[7] The book-as-a-dress comparison is ingenious in numerous ways. For one, it lends us a way of looking at a novel as so much more than simply its plot or the basic story. While the plot is something that might give an overall shape to a book, like a certain model to a dress, there is a lot more we judge it by than the basic shape — the colour and feel of the material, and how the invisible seams hidden from sight hold it together.

In order to make a quality dress, you need quality material. The fabric needs to be woven with thought and feeling — in the book's case, *of* thought and feeling. For example in Proust's own *Search*, despite its colossal scale of over three thousand pages, very little happens. Or rather, very little happens in terms of action, while the stuff you might often gloss over in life becomes hugely important. The crux of Proust, one might say, is that the ordinary becomes extraordinary when it happens to *you*.

Another brilliant aspect of Proust's 'not-cathedral-but-a-dress' imagery is that if writing a book is like making a dress, then reading a book can be thought of as wearing one. It breaks down the subject-object opposition between reader and text: a novel is not a holy shrine with limited access. Instead of visiting a 'cathedral,' going in and coming out again, the reader can put the text on and *wear* it out in the world. While someone else has crafted it, the dress subsequently becomes a part of its wearer.

Clothes do not make a man: a garment can never transform us completely, and neither does a book lose its autonomy as a work of art when it is read by thousands or millions of readers and interpreted in different ways. But surely for most of us, what we put on does affect the way we feel, look and behave, and in this sense, what we wear does become a part of who we are. In the same way as with a dress — we can't just know by looking whether it will fit us — with a book, it is not just what the book is *about* that affects us when we read: where, when and how we read condition our experience too.

If we think of our favourite clothes, those perhaps already a bit worn out, the ones that are so comfortable and incredibly difficult to throw out. It is similar to have a favourite book: when we first 'put it on' it seems to shape us and sometimes even change us, but the longer we wear it, the more it becomes moulded to our shape. Indeed, perhaps this is what Proust's narrator means when he says he wants his readers to be not *his* readers, but "the readers of their own selves". A book we fall in love with can reveal us a lot about ourselves, for if we love it, we will end up walking around wearing it and embracing life through its textile.

3.3. Textiles and fashion

There has always been a tight connection between textiles and fashion. They have forever been central to life and were a means of communication. The wearing of clothing is exclusively a human characteristic and is a feature of most human societies. It is not known when humans began wearing clothes but anthropologists believe that animal skins and vegetation were adapted into coverings as protection from cold, heat and rain, especially as humans migrated to new climates. Clothing and textiles have been important in human history and reflect the materials available to a civilization as well as the technologies that had been mastered. The social significance of the finished product reflects their culture.

Textiles can be felt or spun fibers made into yarn and subsequently netted, looped, knit or woven to make fabrics, which appeared in the Middle East. From the ancient times to the present day, methods of textile production have continually evolved, and the choices of textiles available have influenced how people carried their possessions, clothed themselves, and decorated their surroundings.

Textiles and fashion can be regarded as a visual language reflecting the spirit of the time, coupled to materials, craft and tradition. Finding a personal balance between textiles and fashion is essential. Textiles and fashion industries are important in economic and social terms, in the short-run by providing incomes, jobs, especially for women, and foreign currency receipts and in the longrun by providing countries the opportunity for sustained economic development in those countries with appropriate policies and institutions to enhance the dynamic effects of textiles and clothing. The potential of the textile and fashion industries to contribute to long-run growth and development will depend not only on the attributes of the investors, but also on the quality and effectiveness of government policies and institutions in developing countries to build on this investment.[8]

4. CONCLUSIONS

We started from a word and tried to show the possible connections the word "text" might have with the word "textile". "Text" relates to "texture" and "textile" and traces back to "*texo"* – "to weave", referring to the way words and sentences are "woven" together. We speak of "weaving" a tale or "spinning a yarn." A "subtle" idea is a "finely spun" one.

There are many possible interpretations to this correlation, but as we could see just like the way words are made up of morphemes, syllables, the textiles are spun up, knitted and then made into clothes. There is a whole process that the morphemes, syllables and words go through when in the end they make up texts that build the stories which have so many connotations and meanings. We can compare these texts and storytelling with the process of making clothes, they go through fibers that are spun and then create the fabric or the material out of which the clothes are made. Finally the clothes industry leads to the fashion industry which is one of the most important industries in the world in the moment.

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ANNALS OF THE UNIVERSITY OF ORADEA
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MAINTENANCE PLANNING OF THE SEWING NEEDLES OF SIMPLE SEWING MACHINES

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Abstract: *The effectiveness of simple sewing machines can be increased through the planning of predictive maintenance activities. The monitoring of the technical condition of the sewing needles of simple sewing machines was based on the measurement of their noise level. For this purpose a Center 322 sonometer was used, while the data obtained during the monitoring process was analyzed through the E322 software. The working speed of the simple sewing machine that was used for obtaining the experimental results varied from 200 stitches/minute to 4000 stitches/minute. The noise levels of a new needle at the working speed of 200 stitches/minute and 4000 stitches/minute were measured. The noise levels for a fault needle at the same working speed of 200 stitches/minute, respectively 4000 stitches/minute were also measured.*
Using Fuzzy Logic Toolbox ™ module of Matlab®, a decision-making system for determining when replacement of the sewing needles of simple sewing machines should be performed was developed. A case study illustrates the employment of the decision-making system based on fuzzy logic for a simple sewing machine. By replacing the sewing needles of simple sewing machines at the time specified through the decision-making system based on fuzzy logic, the occurrence of the failure can be prevented and the quality of textile products can be improved.

Key words: *Maintenance, fuzzy, wear, Matlab, sewing machines.*

1. INTRODUCTION

In the case of simple sewing machines, vibrations [1-5] and temperature [6] are among the main factors that negatively influence the function of such equipment. The wear is a phenomenon that appears in the case of moving components, while the abrasive wear influences the technical condition of the components of textile equipment [7].

The wear of sewing needles of simple sewing machines is manifested through the changing of the needles dimensions and their bending. The wear of sewing needles conducts to a nonconforming stitch, which influences the quality of products manufactured with simple sewing machines. The wear of sewing needles also increases the noise level during the technological process of sewing textile products.

In practice, depending on the characteristics of sewing material an optimum operating regime of the simple sewing machines is required. Optimal regime of the simple sewing machines is

determined so that the productivity of the sewing technological process is increased, but at the same time the quality of manufactured products is assured.

2. THE EXPERIMENTAL PART

For a simple sewing machine the maximum level of noise of the sewing needles during the sewing process was measured using a Center 322 sonometer (Figure 1).

Fig. 1: *The measurement of the level of noise of sewing needles for a simple sewing machine*

The sonometer was calibrated before performing the sound measurement, while for the analysis and graphical representation of data the E322 software was used. The sewing material was denim and the needles Nm 100/16 were used. The sewing machine operating mode was from 200 stitches/minute up to 4000 stitches/minute. For the working speed of a simple sewing machine of 200 stitches/minute, measurements were performed for a fault needle (Figure 2) and for a new needle (Figure 3).

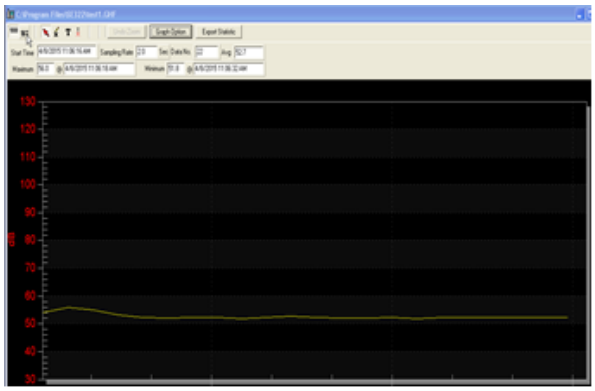

Fig. 2: *The maximum level of noise of a fault needle of simple sewing machine (working speed of 200 stitches/minute)*

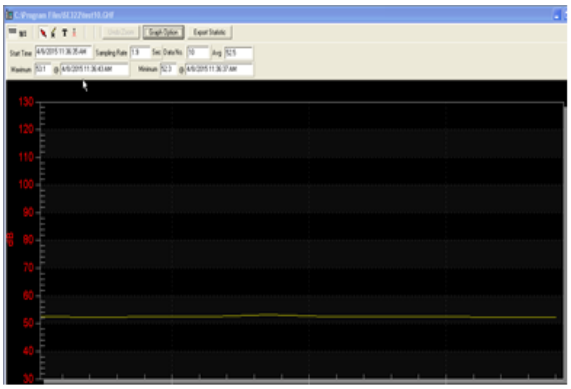

Fig. 3: *The maximum level of noise of a new needle of simple sewing machine (working speed of 200 stitches/minute)*

For the working speed of a simple sewing machine of 4000 stitches/minute, measurements

were also performed for a fault needle (Figure 4) and for a new needle (Figure 5).

In the case of a fault needle the noise levels was obtained between 56-82.5 db, while for a new needle the noise levels resulted between 53.1-81.5 dB. The Fuzzy Logic Toolbox ™ module of MATLAB was employed to develop a decision-making system to determine the time of replacement the sewing needles of simple sewing machines.

The inference rules of the decision-making system based on fuzzy logic for determining when replacement of the sewing needles of simple sewing machines should be performed are shown in (Figure 6).

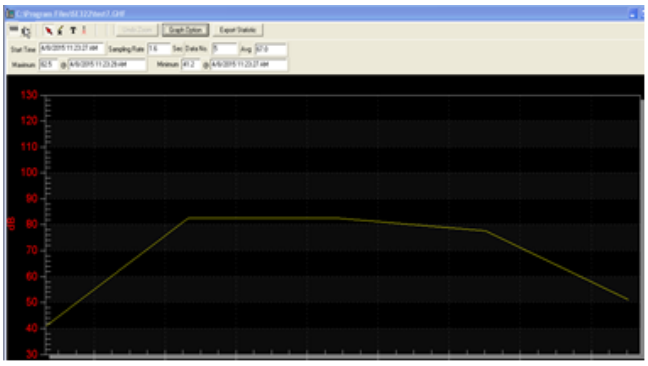

Fig. 4: *The maximum level of noise of a fault needle of simple sewing machine (working speed of 4000 stitches/minute)*

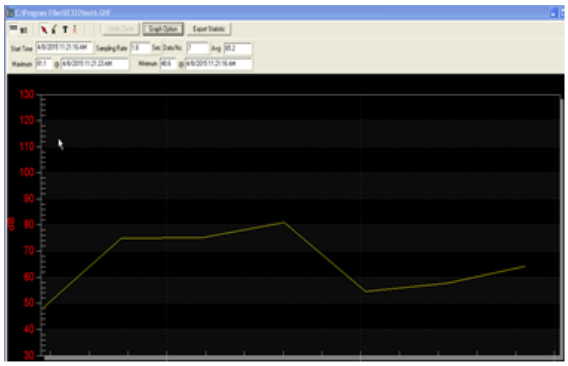

Fig.5: *The maximum level of noise of a new needle of simple sewing machine (working speed of 4000 stitches/minute)*

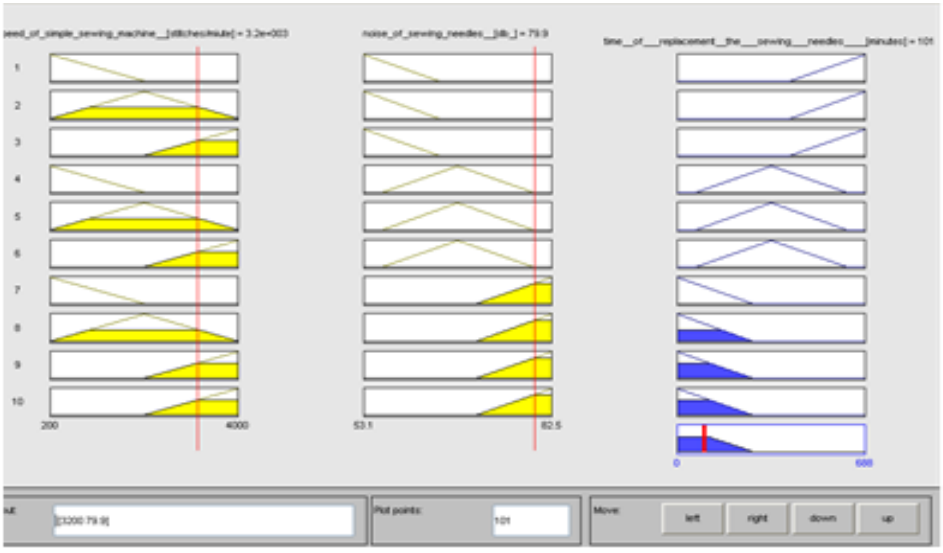

Fig. 6: *The inference rules of the fuzzy decision making based on a fuzzy logic approach to determine when replacement of the sewing needles of simple sewing machines should be performed*

3. INTERPRETATION OF RESULTS

If the working speed of simple sewing machine is = 3200 stitches/minute and the noise of sewing needles of sewing is=79,9 db, then from figure 6 the time of replacement the sewing needles of simple sewing machine results equal to 101 minutes. Therefore, the replacement of the sewing

needles of simple sewing machine should be carried out after 101 minutes.

4. CONCLUSIONS

In this work, a decision-making system based on fuzzy logic for determining when replacement of the sewing needles of simple sewing machines should be performed it was developed, depending on the operating speed of the sewing machine and the noise of sewing needles. The Fuzzy Logic Toolbox™ module of MATLAB was used to develop the decision-making system and its effectiveness was shown through an example.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE BEHAVIOUR OF THE 2:2 RIB STRUCTURES MADE OF 100% COTTON YARNS, NM 40/1, AFTER KNITTING PROCESS

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Abstract: *Researches made on the 2:2 rib structures have demonstrated that for obtaining knits with maximum dimensional stability it is necessary that in their structure to be introduced tensions with the lowest values, structures to balance dimensionaly from the relaxation phase after knitting, and the dimensional modifications on the stitch course direction and stich course in vertical direction to be minimum. It is well-known that the 2:2 rib structures are relatively unstable form dimensional point of view due to the rib platinum loop, in a different plan from the two plans of the knit, and also due to the small number of thread-thread contact points with consequences on the relatively high sliding of the yarns in the structure. The influence of the technological knitting process is imposed by the correlation of the processed yarn characteristics, together with the technical characteristics of the knitting machines, with the technological parameters of knitting operation and with the structural parameters of knitted fabrics which are to be obtained.*
The study concerns the dimensional changes of the 2:2 rib structures during relaxation after knitting. The dimensional changes are analyzed in their complexity, both on the stich course direction and also on the stich courses in vertical direction, proposing a mathematical model for the study of these changes.

Key words: *2:2 rib structure, dimensional stability, relaxation of the knits, technological parameters of the knitting operation*

1. INTRODUCTION

The issue of the dimensional stability of knitted fabrics is a complex one. In order to obtain knitted fabrics wish a good dimensional stability, and due to the fact that the dimensional changes are within ±2%, it is necessary the involvement of several factors, starting with the yarns form which the knitted fabrics are produced and finishing with the relaxation processes, where can actually be found the data related to the dimensional stability [1]..

The influences of the quality yarns on the dimensional stability of the knitted fabrics is given by the obtaining process of these and by the quality of the fibres from which the yarns are spin [2,3].

The influence of the technological knitting process is imposed by the correlation of the processed yarn characteristics [4], together with the technical characteristics of the knitting machines, with the technological parameters of knitting operation and with the structural parameters of knitted fabrics which are to be obtained [5,6,7].

2. MATERIALS AND METHODS

2:2 Rib knitted fabrics made of yarns with 40/1 metric count of yarns made of 100% cotton yarns were made on circular knitting machines with large diameter MAYER & CIE TIP FV-20. The technical characteristics can be found in table 1.

Table 1. *Technical characteristics of the knitting machine MAYER & CIE TIP FV-20*

Crt. no.	Type of knitting machines	**Technical characteristics of the knitting machines**				Yarn type	Metric count of yarn [Nm]	Fabric structure
		Needle bar diameter ["]	Finenss [E]	Number of systems	Number of needles			
3	MAYER & CIE TIP FV-20	20"	16E	42	2x1008	100% cotton	40/1	rib 2:2

The structures undergoing researtch were detailed analyzed, and the rezults of the practical determination were statistically processed. For the statistical processing of the results, for all the knitting structures, was proposed am experimental program with two variables x1 and x2, which represent the entry data (x1 – represents the wale density on the knitting machine[stitches/cm], and x2 – represents the turn of the needle bar [rotations/minutes]).

There were determined the coefficients of regression ecuation, the ecuations were writtens and the response surface was graphically represented for each case, as well the sections through the response surface. After knitting process, the 2:2 rib structures were put in folded position for relaxation 24 hours in standard condition.

There have been studied the dimensional changes which have appeared after the relaxation process. To determine the influence of the knitting parameters on the dimensional change, it was established a mathematical model of correlation between contraction during relaxation which is considered as a dependence variable (response) and the wale density and the turn of the needle bar, which are considered independent. The proposed program is a central mathematical rotatable model composed by two variables. The meaning of the coefficients was tested with test T, and the adequacy of the coefficients with test Student.

In table no.2 are represented the encoded and real values for the independent variables, and also the responses for the 2:2 rib structure made of 100% cotton yarns, with metric count of yarn 40/1.

Table 2. *Real and coded values of variables*

Crt. No.	x_1 enclosed	x_2 enclosed	Wale density [stitches/cm] (x1 real)] (x_1 real)	Turn of needle bar [rot/min] (x_2 real)	Dimensional changes during relaxation on stitch course direction [%]	Dimensional changes during relaxation on stitch course in vertical direction [%]
1	-1	-1	8,79	22,92	-5,30	-5,10
2	1	-1	10,20	22,92	-3,20	-3,50
3	-1	1	8,79	37,07	-5,80	-5,60
4	1	1	10,20	37,07	-3,50	-3,60
5	-1,414	0	8,50	30,00	-6,90	-6,50
6	1,414	0	10,50	30,00	-2,90	-3,90
7	-1	-1,414	9,50	20,00	-4,40	-4,50
8	1	1,414	9,50	40,00	-5,30	-4,90
9	0	0	9,50	30,00	-5,10	-4,20
10	0	0	9,50	30,00	-4,75	-4,50
11	0	0	9,50	30,00	-4,60	-4,80
12	0	0	9,50	30,00	-4,50	-4,70
13	0	0	9,50	30,00	-5,20	-4,30

Study on the dimensional changes on stitch course direction during relaxation in raw condition for the 2:2 rib structures made of 100% cotton with metric count 40/1.

The regression equation which describes the relaxation process of 2:2 rib structure made of 100% cotton with metric count 40/1, on stitch course direction is given by the following relation:

$$f(x,y) := -4.83 + 1.257\cdot x + 0.071\cdot y - 0.259\cdot x^2 + 0.096\cdot y^2 + 0.05\cdot x\cdot y \quad \textbf{(1)}$$

In fig. 1. there are presented sections through response surface, which represents the dependence y= f(x1, x2), for the relaxation shrinkage on stitch course direction for 2:2 rib knitted fabrics studied.

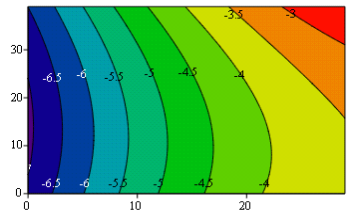

***Fig. 1**: Sections through response surface in the relaxation shrinkage, on stitch course direction, for the 2:2 rib structures made of 100% cotton yarns, Nm 40/1*

From the graphic representation from fig.2, results that: the level curves represent parts of hyperbolas; while the wale density increases, the relaxation shrinkage decreases; the structures have different behavior in the area of higher desity compared to the ares of lower desity; in the areas of lower densities, the level curves represent a maximum point of contraction, while in the area of higher densities the relaxation shrinkage is descending.

In fig. 2 is represented the dependence of y=f(x1) for x2=constant.

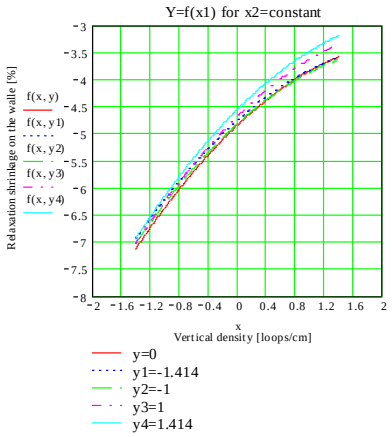

***Fig.2**: Variation of $y=f(x_1)$ pentru x_2 constant in case of dimensional changes after relaxation, on stitch course direction, for the 2:2 rib structures, made of 100% cotton yarns Nm 40/1*

From the graphic analyze from fig.2 results that: together with the increase of wale density, the shrinkage relaxation decreases; the decrease of the shrinkage relaxation is more intense in the area of high densities than in the area of low densities; the switch from one level to another is made easier in the area of high densities than in the area of low densities;

In fig. 3 is represented the dependence $y=f(x_2)$ for (x_2) constant.

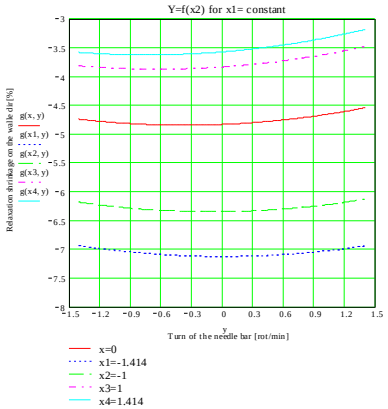

Fig. 3: *Variation $y=f(x_2)$ pentru x1 in case of dimensional changes during relaxation, in the direction of vertical stitches courses, for 2:2 rib strucutres made of 100% cotton yarns, Nm 40/1*

From the graphic analyze from fig.3, results the following:

- The relaxation shrinkage on the stich course direction for the studied structure, varies in lower limits together with the turn of the needle bar;
- For the higher turns of the needle bar, the shrinkage relaxation modifies within [0-0.5%];
- Due to the variation of the turn of the needle bar, there are obtained variations of the shrinkage relaxation, which are lower than through wale density variation across the field.

Dimensional changes study on stitch course in vertical direction, during relaxation in raw condition, for the 2:2 rib structures, made of 100% cotton yarns, Nm 40/1

The regression ecuation which describes the relaxation process of the 2:2 rib knitted fabrics made of 100% cotton, 40/1 metric count of yarn, on stich course in vertical direction is given by the following relation(2):

$$f(x,y) := -4.5 + 0.91\cdot x - 0.225\cdot y - 0.146\cdot x^2 + 0.025\cdot y^2 + 0.1\ x\cdot y \qquad \textbf{(2)}$$

In fig. 4 are represented the sections through response surface, which is the dependence $y=f(x_1, x_2)$, in the shrinkage relaxation situation, on stitch course in vertical direction for the 2:2 rib knitted fabrics studied.

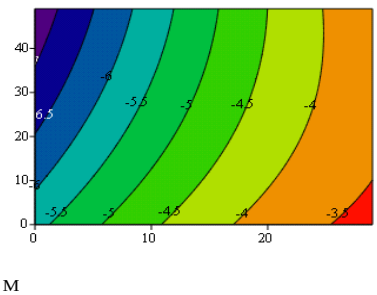

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Fig.4*: Sections through response surface in shrinkage relaxation situation, on stitch course in vertical direction, for 2;2 rib structures structures, made of 100% cotton, 50/1 metric count of yarn*

From the graphic representation of sections through surface response from fig. 5, results that: together with the increase of wale density, the shrinkage relaxation on stich course in vertical direction decreases; the level curves present the same evolution on the entire variation files of the wale density; on entre variation field of wale density, it can be observed that shrinkage relaxation appear on the stich course in vertical direction, and in no situation is with elongation.

In fig.5 is represented the dependence $y=f(x_1)$ for x_2=constant.

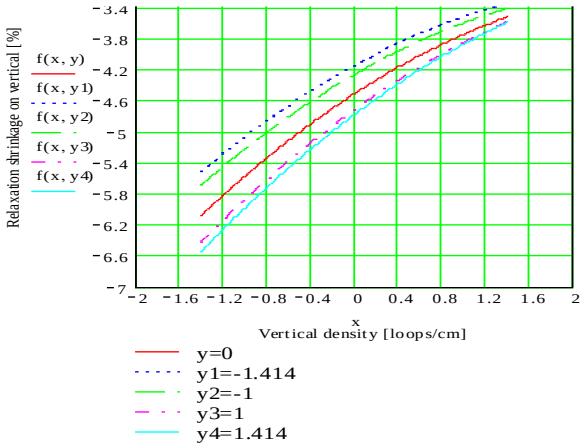

***Fig.5**: Variation Z=f(y) for x=constant in case of dimensional changes during relaxation, on stitch course in vertical direction, for the 2:2 rib structures, made of 100% cotton yarns, Nm 40/1*

From the graphic representation form fig. 6 results the following: the wale density has a determinant influence on the relaxation shrinkage in the stich course in vertical direction, for the 2:2 rib structures studied; together with the increase of the wale density, the shrinkage relaxation decreases with real values of –6,6% to –3,4%; the influence of the wale density is higher in the lower density area and decrecreases in the high density areas.

In fig. 6 is represented the dependence $y=f(x_2)$ pentru x_1=constant

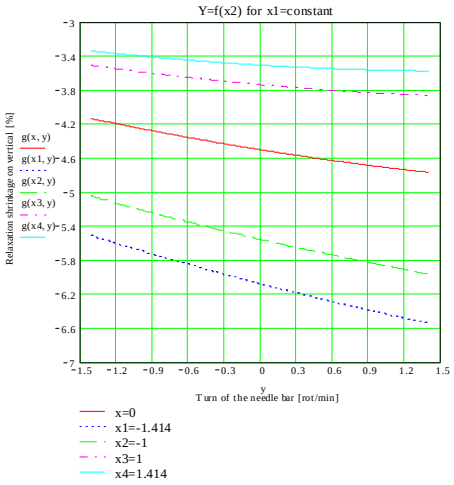

***Fig.6**: Variation $y=f(x_2)$ pentru x_1 in case of dimensional changes during relaxation on stitch course in vertical direction, for 2:2 rib structures made of 100% cotton, 40/1 metric count of yarn*

From the graphic anlayze from fig.6 results that: the turn of the needle bar influences in a lower manner the shrinkage relaxation of 2:2 rib structures; the shrinkage relaxation on the stich course in vertical direction for the 2:2 rib knitted fabrics studied, increases together with the increase of the turn of the needle bar, which is a big disadvantage; the influence of the turn of the needle bar on the shrinkage relaxation is stronger in the sections with lower turns and decreases together with the decrease of this.

3. CONCLUSIONS

1. After the relaxation of the knitted fabrics, after the knitting procces, there can be observed, mostly elongations on the stitch course direction and cotractions on the stitch course in vertical direction.
2. All processes within a technological process must be conducted with minimum stress finishing of knitted fabrics because any tension inserted can relax only partially after each stage of the process flow.
3. The program is designed such in a matter, that the dimensional changes after knitting, finshing and knitting relaxing can be foreseen, depending in the wale density values and turn of the needle bar, for the kntting machines on which the structures were made.
4. The originality of the porposed program consists in the fact that can be obtained knits with the same dimensional stability, by modifing the wale density on the knitting machine, or the turn of the needle bar.
5. The results have practical effects, because knowing the technical characteristics of the knitting machine, the turn of the needle bar, the finess of the 100% cotton yarns, the wale density on the knitting machine, there can be determined the dimensional changes of the knits after knitting process.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE PSYCHOLOGICAL IMPACT OF PERSONALISED TEPESTRY INSIDE PUBLIC MEANS OF CONVEYANCE ON PASSENGER – STUDY CASE

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Abstract: *The present paper wishes to present the effects of the personalisation of tapestry inside public means of conveyance on the passengers' psychology. Thus, a study case is presented, regarding a project from May 2016. The project regarded a certain theme personalisation of the seat tapestry inside a tram in Iasi following the diminishment of vandalising acts on means of conveyance involved in the cultural project Iasi – The City of Painted Trams, initiated TRAMCLUB IAȘI NGO. Beyond its cultural role, the project aimed at growing the quality of the travel experience, both at a physical level, as well as a psychological one, by carefully choosing the fabrics, the colours and the graphic personalisation of the tapestry. Also, the project wanted to discourage the acts of vandalism by involving the members of the civil society. The participation of the students of the Faculty of Visual Arts and Design in the project of interior personalisation of the public mean of transport led to a sense of respect and belonging among the passengers. On a long term the project has as objective the change of the negative perception regarding urban public transport and discouraging the use of the personal vehicle in the urban areas.*

Key words: *personalised tapestry, public mean of conveyance, anti vandalism, passenger's psychology, travel quality, social cohesion.*

1. INTRODUCTION

A common presence in big cities worldwide, public means of conveyance represents, from the 17th century, a testimony of demographic, economic and political development of urban settlements. During the contemporary period, the urbanisation represents one of the most important processes in the evolution of society worldwide through the enrichment of the individual's life quality and through the access to a superior form of education, aspects which encourage the emigration and the establishment of people from the rural areas into urban areas. The expansion of cities in industrial and commercial areas and in neighbourhoods is directly proportional to the expansion of public transport networks, generating an evolving dynamic system [1]. Obviously, the public transport aspects are very important, the citizens' need of moving being a compulsory one.

Despite the growing number of personal cars, public transport remains one of the most important and stable component of urban dynamics.

2. GENERAL INFORMATION

Nowadays, public transport has various forms, result of climatic, topographic, political, social, cultural and economic influences. During the last couple of decades, in Romania's difficult economic context, the public transport networks from the big cities had to come up with a compromise solution in order to improve the transport conditions – acquiring second hand means of transport from the West-European countries. This measure was a positive alternative for a medium period of time on the safety and quality of local public transport [2]. Despite all of these, the passengers felt this decision in a very negative manner, fact which led, in time, to a hostile attitude towards public transport throughout the country. Thus, the citizens of big cities started investing in personal vehicles and gradually stopped using the public transport network. Some of the most visible effects of this hostility are the destructive acts of vandalising the exterior and interior of public means of conveyance as a form of protest.

Beginning with 2013, TRAMCLUB IASI NGO started various unconventional projects with the purpose of rehabilitating the public perception towards public transport. One of the most important projects is *Iasi – The City of Painted Trams* [3], project which was initiated and coordinated by Silviu Teodor-Stanciu (TRAMCLUB IASI NGO). The project refers to the graphic personalisation of the trams from Iasi in order to promote local and national cultural values, encouraging young artists, students or faculty graduates to actively get involved in designing the urban aesthetics of Iasi and on the other hand, encouraging the use of public transport and not the personal car. During four years, seven trams were personalised in this project, with the help of CTP Iasi [4], of the "George Enescu" National University of Arts Iasi and of the National Paints Factory. The personalised trams were noticed by the citizens of Iasi and by the local press, the passengers being respectful towards the entire work and the public means of transport. Unlike the usual trams, the seven personalised ones were not vandalised, fact which started a whole new project – the personalisation of seat tapestry. The Education Tram, the most recent project (May 2016), surprised the public with its theme personalised tapestry.

In full concordance with the style and colour of the exterior elements, the seat tapestry was personalised in the Department of Design, Section of Textile Design of the Faculty of Visual Arts and Design. The composition shows through a graphic language the importance of the educational process in order to achieve progress, everything being imprinted on a turquoise background, colour which represents the idea of support, depth and sensibility. In order to personalise the seats, the technique of thermal imprinting was used. The graphic elements were previously chosen by the students of the department, under the guidance of an interdisciplinary team made of professors. The films were applied on a textile fabric called duck (thick cotton fabric, used in making summer clothes, overalls, tarpaulins) [5], in a turquoise shade. For this project, there were used 81 different patterns, from which 22 were chosen, imprinted and distributed on the 45 back of seats from the Education Tram, **Fig. 1**.

Fig. 1: *The Education Tram - steps of the tapestry's personalisation -*
- FIE DESIGN exhibition (2016)

The tram was presented in public on Sunday, the 22nd of May 2016, in the opening of the International Festival of Education. During the festival, the tram was the host of the unconventional design exhibition called "FIE DESIGN", made of projects belonging to students and graduates of the

Design Department. After that, the vehicle started being used in a normal way, on various routes throughout the city. Until now the tapestry was verified and, except certain normal wear marks, no acts of vandalism were registered, unlike the normal trams of the Public Transport Company. The exterior and interior personalisation of public means of transport has created among passengers a sense of belonging and respect, fact which changed the perception on the vehicles [6]. The Education Tram's interior became the subject of various newspapers and online articles, thus making the citizens of Iasi and the turists eager for going on a trip with this personalised tram. The enlargement of the concept could lead in the future to the growing of the number of citizens who choose to use public transport, to a surplus of physical and psychological confort during the travel period and to improve the traffic flow.

PROJECT RESOURCES:

INITIATION / DESIGN: TRAMCLUB NGO Iasi
EDUCATIONAL: "George Enescu" National University of Arts, Iasi
ECONOMIC: National Paints Romania

3. CONCLUSIONS

In this case, the seat tapestry personalisation project went beyond the cultural feature, influencing in a positive manner the passenger's psychology. During the monitoring process, various commentaries and positive reactions were received from the passengers regarding the clean and unconventional look of the seats. Choosing a natural fabric, soft and resistant such as duck, represented an important surplus in achieving the goal. The involvement of local community members who come up with innovative and original ideas is a fact which leads to cohesion and respect among the citizens, discouraging the acts of vandalism.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

MILITARY TEXTILE MATERIALS FOR EXTREME WEATHER CONDITIONS

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Abstract: *Despite the leaps in technology in warfare and modern weaponry, the human soldier remains the most important aspect of a competitive army. Military textile materials are an essential, yet often neglected, factor that protect the soldier and enable his or her actions in varying fields around the globe. The participation of most countries in larger military or peacekeeping organisations like the NATO and the UN involves the extension of the geographical areas of activity in environments varying greatly from the soldiers' country of origin. Protection from the varying weather conditions and comfort are important factors for the optimal operational ability of a person in humanitarian actions or at combat field. Research in performance textiles has given rise to various forms of multilayered clothing and functional membranes with several commercial tradenames. These performance textiles aim at specialized sports and recreational activities as mountain climbing, hiking and cycling, among others. Additional advancements involve even more specialized function like the incorporation of microelectronics monitoring of vital signals of the human body or for the control of equipment.*
The incorporation of such technological advancements is a current challenge for the national and international military forces that inherit a set of strict procedures. These procedures involve standardization, detailed technical descriptions, cost and of course customs particular to each force. On the other hand, the advancements cannot be neglected and the numbers of soldiers involved are significant to enable the need for change. Current paper is concentrated on the clothing and fabric developments relating to the protection of the soldiers from extreme weather conditions.

Key words: *Military textiles, multi-layered clothing, body insulation, membranes, waterproof fabrics, shell fabrics.*

1. INTRODUCTION

Despite the leaps in technology in warfare and modern weaponry, the human soldier remains the most important aspect of a competitive army. Military textile materials are an essential, yet often neglected, factor that protect the soldier and enable his actions in varying fields around the globe. Protection and comfort are important factors for a soldier that delivers its best. In this article, current developments in military textiles are examined. These developments enable soldiers to perform in varying weather conditions.

2. HISTORICAL PERSPECTIVE

The weather conditions and seasons of the year have always been considerable factors in warfare strategic planning. Often, they proved to be critical or even fatal for the outcome of important missions. For instance:

- In 1812 when Napoleon withdrew from Prussia, 250.000 of his soldiers died due to cold weather.
- In WWI, the British army suffered 115.000 injuries related to cold.
- In WWII, the German losses in the East Front were around 100.000.

Each age and time has its relative clothing systems that affect and are affected from the rules of combat. Additionally, they are naturally influence by the available technology of each period. Terrorist attacks and actions of modern era, and missions in Iraq and Afghanistan, lead to the development of novel clothing systems especially suited for urban combat [1].

3. SHOLDIER PHYSIOLOGY FOR PRESENT – DAY CLOTHING SYSTEMS

Soldiers' bodies often face extremely varied weather conditions that consequently affect the body temperature balance. Additionally, soldiers in the field operate in conditions producing high metabolic rates, therefore generating additional heat that often must be quickly dissipated. These are challenges for the development of military textiles that are currently designed taking into consideration a complex system consisting of the human body, the textile material and the weather conditions [2].

The clothing system should be designed in such a way that it will maintain the body temperature in the natural state of 37˚C. The underlying concept in hot weather conditions is that moisture levels of the system should remain minimal while excess heat produced by the body should be quickly and efficiently dissipated to the environment. The moisture dissipation is a key factor since it helps sweat evaporation from skin which is the mechanism used by the human body to cool.

On the other hand, in cold weather conditions heat is normally transferred from the human body to the environment, which is undesirable. In this case the textile system should provide insulation but simultaneously let the moisture produced leave the body. If moisture is trapped between skin and the material, it tends to form concentrates and reduce comfort, therefore soldier performance. Additionally, moisture concentrates reduce the insulation level that is also undesirable.

Military clothing systems nowadays are brilliantly designed to be part of the complex system body, material and environment.

4. MULTILAYERED CLOTHING SYSTEMS FOR COLD WEATHER

Most contemporary military clothing systems, for cold weather, used in the field are multilayered variants. They consist of a series of compatible clothes that are used in layers according to specific needs. The multilayered clothing has significant advantages over the conventional approach where one material provides the desired functionality in a monolithic way. They permit the soldier to individually adjust the level of performance and insulation by wearing more layers or by removing excess ones according to environmental and physiological conditions. Additionally, each individual layer is designed in such a way so that it fits the body more comfortably than a single thick cloth [3].

A basic structure of a multilayered military outfit consists of 3 layers namely [4]:

1. **Underwear layer**: It is the layer that has as a main function the removal of sweat from skin surface. This takes place via a strong wicking effect and by the function of breathability. Currently, this layer has also antimicrobial properties allowing the suppression of odour and resulting in increased comfort and hygiene. The underwear layer is designed to have optimal fitness on the body allowing comfort and enabling easy addition of the other layers.
2. **Middle layer**: this layer's function is wicking, breathability but mostly insulation. Insulation is mainly obtained by fibrous structures trapping a relatively high volume of air.
3. **Outer layer**: this layer is subjected to the environmental conditions and it is probably the one that faces most challenges. Its functions vary widely. In terms of weather protection usually it must be *waterproof*, yet *breathable*. It should also be *windproof*. The other functions may be *camouflage*, *bullet proofing* and *chemical protection*, among others.

Fig.1: *A three – layer system for cold environment (©Polartec)*

Insulation is not only necessary for the main body of the soldier. It is important to insulate the ending parts like hands, feet and head. This is of course obtained with gloves, footwear and head covers among other materials. Since the whole soldier uniform is regarded as a system, the additional materials should remain compatible with the system so that altogether they perform optimally. For example, the sleeves of the jacket may be compatible with the gloves so that when the soldier uses the latter the connection between the materials will be without gaps that will allow air flow and decrease of performance.

Modern military textile materials designed for cold weather are based on the multilayer approach usually have the 3 layers described above, but they are enhanced with other layers of specific function. This ability for customization allows the soldier to operate in cold conditions ranging from -40°C to +4°C. For example, the third generation *3G* or *GEN III Extended Climate Warfighter Clothing System* used by the US military consists of 7 layers and 12 components.

5. MEMBRANES

Membranes are polymeric materials that have hundreds of millions of pores on their surface. They are placed on the top of the textile materials and act together as a system. On one hand the textile material supports the membrane and on the other hand the membrane gives to the fabric waterproof and windproof properties [5].

The porosity of the membrane allows it to be breathable, therefore permitting the body moisture to dissipate into the environment improving comfort. The pores should have an adequate diameter for this to happen. This diameter however should be small enough to resist its penetration by water, like rain for instance, from the outside of the system. The size of the pores is therefore optimized under these two constraints. Membrane technology used in outer clothing in past decades is often referred to as hard shell because it makes the fabric harder to the touch. This was a side – effect most often undesirable.

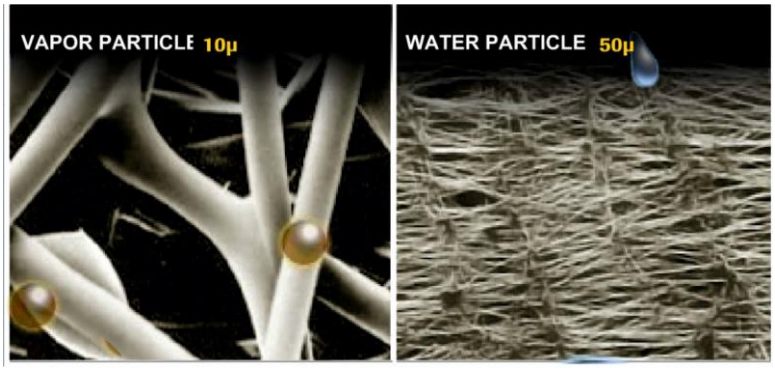

Fig. 2: *The porous system of a membrane (© Gore-tex)*

Technologies are developed a technology where the membrane film is more flexible therefore giving it the description as *soft – shell.* The *soft – shell* technology is so flexible that can be used in the middle layers of the clothing system. This technology combines a weatherproof outer surface with a fleece inner therefore producing fabrics with a combination of properties including insulation, water resistance and breathability, among others. The water resistance specifically in *soft – shell* is lower to that in the *hard –shell* alternatives yet it can be improved by additional finishing processes on the outer surface. The most important element in the *soft – shell* technology is the flexibility and the resulting comfort of the fabrics produced via this technology. Often the consumer and user of such materials is pleasantly surprised upon their utilization because traditionally he perceives that protection is combined with a *hard – shell* fabric. The *soft – shell* fabrics fit well and their use is very much widespread in modern military clothing.

6. SMART MATERIALS

Smart materials belong to a whole family of modern textiles with a wide array of characteristics. They do range from materials with unconventional properties to fabrics that include electronic sensors. *Smart* materials for adaptation to extreme weather conditions are those that have some sort of interaction with the environment adjusting to changes of temperature and moisture [6]. Due to such properties, smart materials can often be

considered as heating elements since due to their chemistry and physical structure, when temperature drops they provide some heat and better insulation than otherwise. This occurs automatically, without the soldier's intervention. *Smart* materials, for the particular application, are:

- *Shape memory* materials
- *Phase changing* materials

The *shape memory materials (SMM)* can change their shape according to the environment, i.e. they react to changes of temperature or moisture, for example. Their main categories are *polymer SMM* and *gel SMM*. The *polymer SMM* can store heat in the warm environment and give it back when the environment gets cold. Additionally, in the warm environment they allow moisture transfer whereas in the cold environment they reduce moisture transfer imparting good insulation. The *gel SMM* are an even more advanced technology where they react to temperature, pressure and moisture, among others, changing their whole volume by capturing and releasing water molecules. *Gel SMM* can change their volume 1000 times more when swollen to their un-swollen condition and this process is reversible. The *gel SMM* are readily applied over textiles.

Phase changing materials (PCM) have also the ability to store and release heat in larger quantities than the *polymer SMM*. The material is changing from solid to liquid or gel when it absorbs heat and recovers to its solid state when it releases heat. These materials are usually in the form of microencapsulates and in this form, they are embedded in the textile material.

7. THE MULTI-CLIMATE PROTECTION SYSTEM

The *multi – climate protection system* for military applications was developed in the US Navy and has the components mentioned:

1. **Inner layer**: it consists of the underwear that are made in such a way as to be light wear and absorbent, allowing moisture dissipation from skin via the wicking effect. Currently, it is often required to have flame retarding properties.
2. **Moderate insulating layer**: this is used over the underwear in moderate environmental conditions. It has insulating properties, flame retardancy, moisture transfer and wind proofing.
3. **Heavy insulation**: it consists of the top, pants and the full – body outfit. Has similar properties to the second layer, mentioned above, yet it focuses on more extreme conditions therefore its insulation properties are more advanced.
4. **Jacket and fleece vest**: they are treated to have 2 times the air resistance of conventional materials while maintaining moisture transfer ability and flame resistance.
5. ***Hard – shell* jacket and pants**: they are used as additional outer layers providing heavy waterproof protection and flame retardancy.
6. **Face mask**.

8. CONCLUSIONS

The human component of a modern army remains a significant asset in most combat situations. The unfortunate evolution of terrorist acts and the resulting transfer of military actions in urban environments lead to the development of novel clothing systems for all armed and police forces. These clothing systems provide protection against several kinds of attack and a wide range of environmental conditions. Present article focused upon the protection relating to the climate conditions where the materials used provide protection and comfort simultaneously and it is part of an onward research by specialized comittees of the military forces, working on the technical descriptions of advanced uniforms. Novel uniforms will enable the optimal performance of soldiers, while protecting them in extreme cold conditions, that have proved to be fatal for a battle outcome but also on peacekeeping missions, where soldiers offer invaluable protection of civil population or provide vital service in natural disasters.

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ANNALS OF THE UNIVERSITY OF ORADEA
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TEXTILE IMPACT PLATES FOR NANOPARTICLES

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Abstract: *The paper presents textile materials with destination impact plates, having different surface architectures and active treatments for functionalization, with influence upon the aging process of nano-Ag and nano-CeO2. The woven and knitted samples from 100% cotton, cotton/PES blend and 100% PES were treated by impregnation on the laboratory padding machine, drying and condensing on the machine for drying-condensing-heat setting, with the following recipes: 50g/l RUCOSTAR EEE6+20 ml 5% nano-Ag dispersion, or 10% nano-CeO2 in ethylene glycol, respectively water and 0,5ml acetic acid 60% for products from 100% cotton and PES/cotton and 50g/l NUVA N 2114 liquid with the same percent of nanoparticles but with 1 ml/l acetic acid 60%, in case of 100% PES samples. The samples were treated in 2 steps – hydrophobic/ oleo phobic in the first stage and hydrophobic/ oleo phobic/ functionalization with nano-Ag and nano-CeO2 in the second stage.*
The complex characterization of both type of materials : hydrophobic and oleo phobic properties, color change, whitening degree, DCS, FT-IR, SEM and microbiology, evidenced through the obtained results the justness of the selection for: the raw materials (100% cotton, cotton/PES, 100% PES), the weave (plain, twill, rib, pique), the fabric tightness and fabric cover etc. These data allowed the elaboration of textile material's specifications for impact plates.

Key words: *nanoparticle, woven fabric, knitted fabric, hydrofobization, oleofobization, functionalization*

1. INTRODUCTION

The emergence of MMM (Metallic Monodisperse Nanoparticles) is getting more frequent, occurring in everyday applications with effect upon consumers and generally upon humans [1]. Nano-Ag and nano-CeO2 are the most common types of MMM, having relevance for the absorption by inhalation [2]. They are relatively cost-effective and they are produced in much larger quantities than other exotic nanomaterials such as fullerenes and quantum dots. There is an increasingly number of research studies regarding these materials (Demokritou et al. 2013, Molina et al. 2014). Inhalation is the most relevant modality for MMM absorption. During exposure, MMM get on specific chemical media. Generally speaking, the aerosolized MMM do not penetrate the organism barriers in pure state. Nevertheless, the general effects of MMM aerosols and their potential absorption are a subject of research at the moment [3-4].

2. EXPERIMENTAL WORK

2.1 Raw materials characterization

The following variants of woven and knitted fabrics were designed in order to define textile impact plates: 100% cotton, cotton / polyester and 100% polyester, with plain and twill weave for woven fabrics and rib and pique weave for knitted fabrics. The fabric cover of the warp yarns ($\mathbf{e}_u$), of the weft yarns ($\mathbf{e}_b$) and of the woven fabric ($\mathbf{e}_t$) were computed. This parameter had values in the range of 0,54-0,65 for the woven fabrics with plain weave and values in the range of 0,54-0,79 for twill weave. The tightness degree had values in the range of 54,73-70,05 for the woven fabrics with plain weave and 73,93-76,32 for twill weave.

Rib and pique weaves were used in order to design the knitted structures, by computing: the superficial fabric cover coefficient.This parameter had values in the range of 13,6-15,2 for the rib weave and in the range of 30-35 for the pique weave. The linear fabric cover coefficient δ_l, had values in the range of 0,97-1,23 for the rib weave and 1,55-5,69 for the pique weave.

2.2 Characterization of the nano-Ag and nano-CeO_2 dispersion

The UV-VIS analysis was performed on the laboratory equipment: Spectrophotometer UV-VIS-NIR Lambda 950, Perkin Elmer. The UV-VIS diagram for the nano-Ag dispersion at 800-1400 nm is presented in figure 1, while the diagram at 200-800 nm is presented in figure 2.

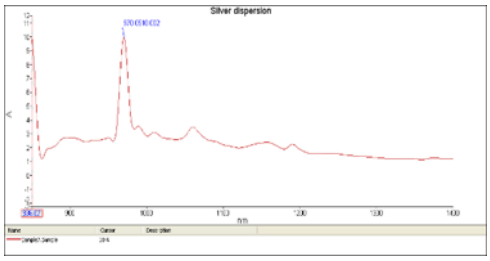

Fig.1: *NIR spectrum nano-Ag at 800-1400 nm*

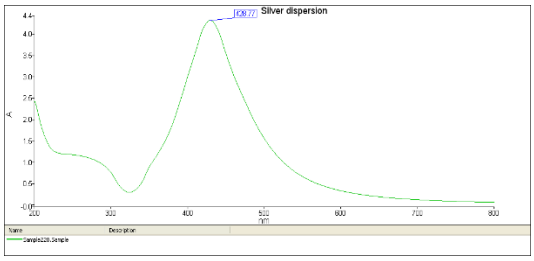

Fig 2: *UV-VIS spectrum nano-Ag at 200 -800 nm*

The NIR absorption spectrum shows a maximum absorption at the wavelength of 970 nm, a specific value for nano-Ag and of 450 nm, a specific value for nano-CeO2. The UV-VIS absorption spectrum shows a maximum absorption at the wavelength of 470 nm for nano-Ag and 2700 nm for nano-CeO2, confirming the purity of dispersions.

The IR spectrum for the nano-Ag dispersion proves the presence of specific functional groups: alkyne, alkanes, aldehyde, cumulenes, alkene etc. at the specific wave number. FT-IR nano-CeO2 analysis proves specific functional groups for nano-CeO2 dispersion: isothiocyanates, alkyne, amide, nitro etc. (figure 3 and table 1).

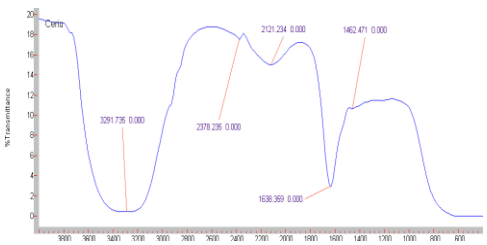

Fig.3: *FT-IR spectrum*

Table 1: Specific functional groups

Wave number (cm^{-1})	Specific functional group
3291.7	-OH(alcohol)
2378.2	O=C=O
2121.2	N=C=S(isothiocyanates), -C≡C(alkyne)
1638.4	C=O(amide)
1462.5	N=O(nitro)

2.2 SEM and TEM analysis of nano-Ag and nano CeO_2

The electronic transmission microscope images were obtained with the electronic microscope Titan Themis 200, which performs analyses at low temperatures – in the modus (HR)TEM, STEM, EFTEM, SAED, CBED and 3D tomography in the modus TEM and STEM [5]. The SEM image of the nano-Ag sample is presented in figure 4 and the TEM image of the same sample in bright light is presented in figure 5.

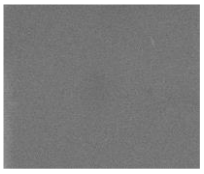

Fig.4: *SEM image*

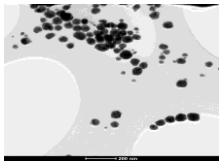

Fig.5: *TEM image-nano-Ag*

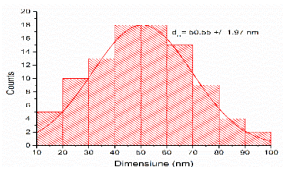

Fig.6: *Dispersion diagram nano-Ag*

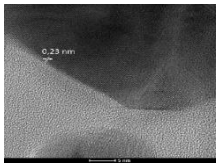

Fig.7: *.HR-TEM nano-Ag*

The images show that the sample is composed from particles of spherical and polyhedral shapes, having a mean dimension per particle of 50,55 nm ± 1,97 nm. The distribution diagram of the Ag nanoparticles dimension is presented in figure 6, proving that these are very well dispersed. The HR-TEM image on the Ag sample is presented in figure 7.

The electronic transmission microscope image of high resolution for the Ag sample showed crystalline surfaces with an inter-surface distance of 2.3 Å, corresponding to the family of crystalline surfaces (1 1 1), which are specific to silver nanoparticles. The TEM images in bright light obtained on the CeO2 sample, showed the polyhedral shape of the particles, having a mean dimension per particle of 11,86 nm ± 0,49 nm. The regular sequence of the crystalline surfaces indicated the uniformity of the nanocrystals, without amorphous structures.

2.3 The functionalization of textile materials

The woven and knitted samples from 100% cotton, cotton/PES blend and 100% PES were treated by impregnation on the laboratory padding machine, drying and condensing on the machine for drying-condensing-heat setting, with the following recipes: 50g/l RUCOSTAR EEE6+20 ml 5% nano-Ag dispersion, or 10% nano-CeO_2 in ethylene glycol, respectively water and 0,5ml acetic acid 60% for products from 100% cotton and PES/cotton and 50g/l NUVA N 2114 liquid with the same percent of nanoparticles but with 1 ml/l acetic acid 60%, in case of 100% PES samples.

3. THE CHARACTERIZATION OF THE FUNCTIONALIZED FABRICS

3.1 Physical-chemical characterization

The following aspects were evidenced when compared to the non-functionalized (hydrophobic / oleo phobic) samples:

-The oleo phobic property reached good and very good results (grades of 6 and 6-7) for the treatment with nano-Ag and with nano-CeO_2 for all variants of woven and knitted fabrics, at the same level with the non-functionalized variants;

-The hydrophobic property determined by contact angle measurement proved very good values for all variants of woven and knitted fabrics treated with nano-Ag and nano-CeO_2, at the same level with the initial variants.

3.2 DSC analysis of the fabrics functionalized with nano–Ag and nano-CeO_2

The DSC analysis [6] was performed in specific conditions (mass and temperature) for each variant of woven and knitted fabric by determining: the DSC thermogram, the processed DSC thermogram and the superposed thermogram: untreated sample (N-green), treated (T-blue) and treated /

functionalized (T/F-nano-Ag or nano -CeO_2- red) – figure 8.

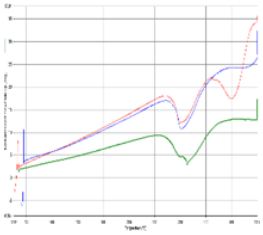

***Fig.8**: Thermogram of superposed samples*

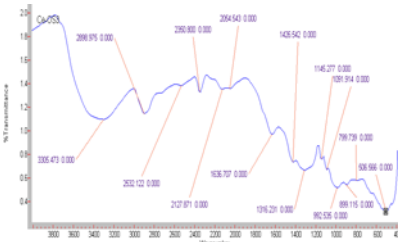

***Fig.9:** FT-IR spectru m*

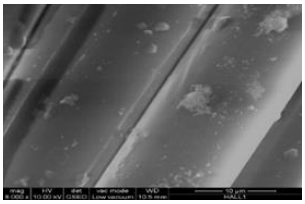

***Fig.10:** SEM images*

The DSC analysis evidenced the modification of the thermal behavior of the samples treated with nanoparticles.

3.3 Infrared spectrometry analysis with Fourier transformation (FT-IR)

This analysis was accomplished by means of spectral determination proved specific functional groups [7] in correlation with the wave number (cm^{-1}) - figure 9.

3.4 Scanning electronic microscopy analysis SEM Analysis

Figure 10 proved agglomeration of nanoparticles with various dimensions: 56-106 nm, 60-177 nm and 95-99,1 nm on the woven and knitted fabrics treated with nano-Ag and nano -CeO_2.

3.5 Anti-fungal characterization of the functionalized textile materials

The textile materials treated with nano-Ag and nano-CeO2 evidenced a weak influence upon this property for nano-Ag, well known for its anti-bacterial action, due to the influence of the oleo phobic product.

4. CONCLUSIONS

The complex characterization: hydrophobic and oleo phobic properties, color change, whitening degree, DCS, FT-IR, SEM and microbiology, evidenced through the obtained results the justness of the selection for: the raw materials (100% cotton, cotton/PES, 100% PES), the weave (plain, twill, rib, pique), the fabric tightness and fabric cover etc. These data allowed the elaboration of textile material's specifications for impact plates.

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TEXTILE SURFACE MODIFICATION BY PYHSICAL VAPOR DEPOSITION – (REVIEW)

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Abstract: *Textile products are used in various branches of the industry from automotive to space products. Textiles produced for industrial use are generally referred to as technical textiles. Technical textiles are nowadays applied to several areas including transportation, medicine, agriculture, protection, sports, packaging, civil engineering and industry. There are rapid developments in the types of materials used in technical textiles. Therefore, modification and functionalization of textile surfaces is becoming more crucial. The improvements of the properties such as anti-bacterial properties, fire resistivity, UV radiation resistance, electrical conductivity, self cleaning, and super hydrophobic, is getting more concern with respect to developments in textile engineering. The properties of textile surfaces are closely related to the fiber structure, the differences in the polymer composition, the fiber mixture ratio, and the physical and chemical processes applied. Textile surface modifications can be examined in four groups under the name mechanical, chemical, burning and plasma.*
Surface modifications are made to improve the functionality of textile products. Textile surface modifications affect the properties of the products such as softness, adhesion and wettability. The purpose of this work is to reveal varieties of vapor deposition modifications to improve functionality. For this purpose, the pyhsical vapor deposition methods, their affects on textile products and their end-uses will be reviewed.

Key words: *Vapor, Deposition, Textile, Functionality, Adhesion, Softness*.

1. INTRODUCTION

Textile products are used in various branches of the industry from automotive to space products. Textiles produced for industrial uses are generally referred to as technical textiles. The natural structures of the textile products to be used for technical textiles may be poor in terms of the properties to be used (anti-static, optic etc.). For this reason, it may be necessary to change the surface properties of these products by physical or chemical methods. This changing/development process can also be described as surface modification.

Textile surface modifications are divided into four groups as mechanical, chemical, incineration and plasma. Since the fiber diameter is a few micrometers, incineration and mechanical methods can not be used for surface modification of fibers [1]. Chemical modification processes can be used for better adhesion of fiber and polymer matrix in fiber reinforced composite materials [2]. However, the chemical modification has some disadvantages, such as the risk of corrosion, the ability to modify the surface in a controlled manner, thereby reducing fiber strength and causing environmental pollution. Plasma technology has been reported to have positive effects on wettability, shrinkage, desizing, adhesion, surface cleaning, dye affinity and printing properties. At the same time, it is an environmentally friendly technology [1], [3].

In this study, physical vapor deposition method which is one of the surface modification types is investigated. The general framework of physical vapor deposition, its application to textile products as well as its usage areas in textile has been examined on literature basis.

2. PHYSICAL VAPOR DEPOSITION (PVD) METHOD

Physical and chemical vapor deposition techniques are types of coatings made on the substrate from the gas phase (vapor phase). Physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques, which are coating techniques made in the gas phase, have a wide range of applications in industrial applications [4].

Physical vapor deposition coating technology has been known since 1800 years, but it is the thin film coating technique used in the industry last 50 years. In this technique, solid raw material is converted into plasma with high energy and then bonded on the substrat to be coated in a controlled way from the raw material [5]. Advantages of this technique include the following: It can be applied on all kinds of materials, the coatings show excellent adhesion properties, the coating thickness can be made very thin and very thick intervals, high speed production can be achieved, environmental friendliness and can be done at low temperature so that the coated material is not damaged [6], [7]. The working cycle of this method is given in Figure 1.

There are two types of parameters that affect the coating process These are: the thickness of the coating and the temperature of the coating process. [8]. The PVD method has a wider range of uses than other methods because it can be made at lower processing temperatures and a wide range of coating thicknesses can be achieved [9].

The working principles of the PVD method include; vacuum evaporation, ion implantation, magnetron sputtering methods [10]. Vacuum evaporation is the simplest of PVD techniques. The material to be coated is evaporated by any heat effect and the evaporating atoms gradually condense on the substrate [11]. Ion implantation is a material surface modification process by which ions of a material are implanted into another solid material, causing a change in the surface physical and chemical properties of the materials. Ion implantation involves an ion source (ions of the desired element), an accelerator (accelerating the ions electrostatically with a high energy), and a target (ions impinging on a target) [10]. The magnetron sputtering technique provides coatings with high chemical and structural complexity [12].

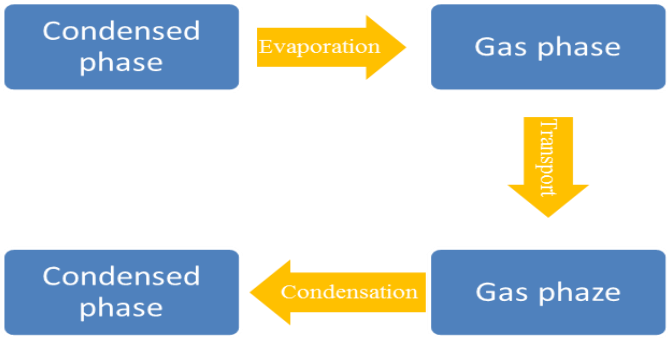

Fig. 1: *Schematic representation of the physical vapor deposition method*

2.1. Use of Physical Vapor Deposition Technique in Textile

Physical vapor deposition technique is a method used to develop functional textiles. With this method, fabrics can be given different properties such as anti-static, protection against electro-magnetic radiation, antibacterial, water-oil repellency, chemical resistance, UV protection, conductivity [13], [14], [15], [16], [17].

Almost all metallic materials can be transferred to textile surfaces by sputtering [10]. The most commonly used PVD technique in the textile industry is sputtering method [18]. The magnetron sputtering technique is one of the most efficient of film coating techniques due to better adhesion on the substrate, environmental friendliness and low storage temperatures [12]. Magnetron sputtering technology can impart conductivity to textile products [17]. Conductive yarns are rapidly gaining importance for areas such as need, static applications, data transfer, imaging, protection against corrosion and electromagnetic shielding [16]. Metals such as Zn, Ti, Cu, Ag and Al; properties such as conductivity, electromagnetic shield, antibacterial textiles can be imparted to fabrics [13], [19].

Silver (Ag) is a coating material that can impart conductivity, antibacterial, UV protection and hydrophobic properties to textile products (Figure 2) [10], [20]. Silver-containing fibers have potential applications ranging from conductive shielding, packaging and protective materials to electronic sensors [21]. Silver and copper coatings can impart both visible light (300-600 nm) and UV light reflection to fabrics. Metallic nanocomposite coated textile materials have great potential for applications such as antistatic fabric, explosion-proof filters, UV absorbing materials and electromagnetic shielding materials [22]. Aluminum nano coatings have also been shown to reduce the electrical resistance of textile products (nonwoven surfaces) [23].

Metal oxide coatings on textile surfaces have also been demonstrated with various studies [24], [25], [26], [27], [28], [29], [30]. These materials include titanium dioxide (TiO2), zinc oxide (ZnO), indium doped tin oxide, and aluminum doped zinc oxide [10]. Titanium dioxide-coated materials have recently been found to exhibit interesting properties due to their unique dielectric and optical properties [25]. Titanium dioxide-functionalized textiles have great potential for the separation of environmental pollutants or gases [31].

Yu et al. PET Polyester non-woven surfaces are coated with semiconductor zinc oxide (ZnO) by direct current reactive magnetron sputtering. As a result of the study, it has been observed that the UV absorbency and antibacterial properties of ZnO coated polyester nonwoven fabrics are improved [32].

In a study by Dietzel et al. Titanium and zirconium cathodes on polyamide fabrics were coated using physical vapor deposition technology (metallization). As a result of the study, the samples were observed to be antistatic [17].

Wang et al. [13] have attempted to impart anti-bacterial properties by coating the surface of polypropylene nonwoven fabrics with nano-structured silver films. As a result, it has been observed that nonwoven polypropylene fabrics coated with silver film have a serious anti-bacterial property compared to the uncoated. At the same time, the increase in silver film thickness contributed positively to the antibacterial property.

(a) (b)

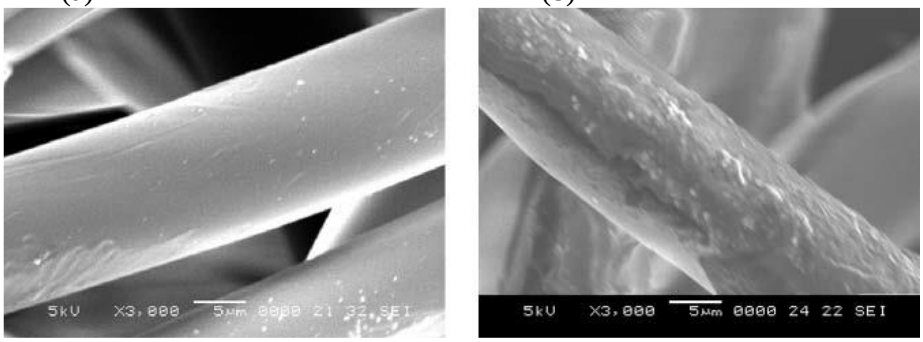

Fig. 2: *SEM images, (a) Original PP fibers, (b) 3 nm thick silver coated PP fibers [10].*

3. CONCLUSIONS

Numerous researches have been carried out to improve the functional properties of textiles and new technologies have been adopted to impart different properties to textile products. An ideal surface modification is to coat the thin and uniform layer on the surface without damaging the fiber. At the same time, the environmentally friendly coating processes are the most desired production technique in today's conditions. For this reason, new technologies tend to take the place of conventional coating techniques. One of these techniques are mentioned in this study.

Physical vapor deposition technique have been mentioned in this study and their use on textile surfaces has been examined. The physical vapor deposition technique can impart properties such as conductivity, antistaticity, radiation protection, antibacterial property, water repellency, UV protection, and resistance to chemicals to textile products.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

POTENTIAL APPLICATION OF HORSE CHESTNUT (*Aesculus hippocastanum* L.) EXTRACTS IN DOUBLE FACE PRODUCTION

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Abstract: *Aesculus hippocastanum L, known as horse chestnut, is generally used for therapeutic, medicinal and pharmaceutical applications and has large seed shells containing aesculin which is responsible for the dyeing property. Due to the lack of information on dyeing characteristics of horse chestnut extracts in leather and also textile engineering field, ecofriendly dyeing process of leathers with the extracts of horse chestnut seed shells has gained an interest. Therefore, in the study the dyeing properties of double face leathers with extracts of Aesculus hippocastanum L were investigated. Seed shells of A. hippocastanum were extracted with sodium hydroxide in different concentrations and the extraction yields were determined. In accordance with extraction results, the horse chestnut extracts were used for the dyeing process of double face leathers. To evaluate the effect of A. hippocastanum extract on dyeing properties of double face leathers, the proportions of the extracts were differentiated. The quality performance of dyed leathers was investigated in terms of colour measurements and to-and-fro rubbing fastness characteristics. The colour measurements were determined with Minolta CM-3600A spectrophotometer and to-and-fro rubbing fastness was examined in accordance with TS EN ISO 11640 standard. The results revealed that A. hippocastanum extract could be used as newly adapted natural dye stuff in eco-friendly double face production.*

Key words: *dyeing, leather, natural colorants, Aesculus hippocastanum L., wool*

1. INTRODUCTION

The use of synthetic dyes in leather and textile industries has occurred in huge amounts that cause severe ecological problems on nature and human health due to their toxic and harmful nature [1, 2]. Ecofriendly dyeing techniques such as use of plant, animal, and microbial sources [1, 2] are in focus of interest for leather and textile industries in recent years due to their better biodegradability, higher compatibility and less toxic characteristics as well as their potential antimicrobial, deodorizing, and insect repellent properties [1, 3]. However, the commercial interest in use of natural dyes is limited because the extraction and color yields, washing and light fastness properties and their color standardization have needed to be improved [3]. But the increasing demand for ecological products and changes in customer demands make the use of natural dyes in trend again for leather and textile industries. Still there have been limited studies in literatures about ecological leather dyeing in contrast to textile materials and up to our knowledge this is the first study about double face leather dyeing with horse chestnut (*Aesculus hippocastanum* L.) extract.

Aesculus hippocastanum, commonly known as horse chestnut, is a plant belonging to the family Hippocastanaceae. It can be found in Balkan region, Turkey, Greece and Bulgaria and mostly planted in Turkey as an ornamental tree due to the flowers and shade bearing characteristics [4]. *A. hippocastanum* has been generally used for pharmaceutical and medical preparations due to the aescin saponin content [5] and aesculin is the dye stuff found in the shells of the seeds [6].

In this research we investigated the dyeing properties of double face leathers with extracts of *Aesculus hippocastanum* L. The quality performance of dyed leathers was investigated in terms of colour measurements and to-and-fro rubbing fastness characteristics.

2. MATERIALS AND METHODS

2.1 Materials

In the study, domestic double face crust leathers were used for the application of the *Aesculus hippocastanum* extracts in the dyeing process. The outer shells of the *Aesculus hippocastanum* were collected from Uşak/Turkey and dried at room temperature prior to grinding [7].

2.2 Methods

Sodium hydroxide was used as the extraction chemical for the eco-friendly dyeing trials. Different concentrations of sodium hydroxide such as 0.1, 0.5 and 1% were used for the extraction and the temperature was set to 90ºC for 1h in a ratio of 1/20 (solid/liquid). Later, the suspensions were filtered using Whatman filter paper (no. 1) and dried in an air oven at 102±2°C to calculate the extraction yield as the percentage weight loss of the starting raw material [8]. The dyeing recipe was given in Table 1 and the visual displays of the leathers were shown in Figure 1 - 7.

Table 1: *Dyeing recipe of double face crust leathers by Aesculus hippocastanum extracts*

Process*	**g/l**	**Material**	**˚C**	**Time (min)**	**pH**
Re-wetting	1/30	Water	45	60	5.5
Dyeing	1/15	Water	40		
	x*	*A. hippocastanum* extracts		60	
	x	HCOOH		30	4
Washing and Drying					

The dyeing process of double face crust leathers were based on dry weight; x; 10; 20; 40; and 60 g/l

Fig.1: *The leathers dyed with horse chestnut extracts (0.1 %NaOH; A 10; B 20; C 40; D 60g/L; suede side)*

Fig.2: *The leathers dyed with horse chestnut extracts (0.1 %NaOH; A 10; B 20; C 40; D 60g/L; fur side)*

Fig.3: *The leathers dyed with horse chestnut extracts (0.5 %NaOH; A 10; B 20; C 40; D 60g/L; suede side)*

Fig.4: *The leathers dyed with horse chestnut extracts (0.5 %NaOH; A 10; B 20; C 40; D 60g/L; fur side)*

Fig.5: *The leathers dyed with horse chestnut extracts (1 %NaOH; A 10; B 20; C 40; D 60g/L; suede side)*

Fig.6: *The leathers dyed with horse chestnut extracts (1 %NaOH; A 10; B 20; C 40; D 60g/L; fur side)*

Fig.7: *The pseudo colors of crust double face leathers (A: suede; B; fur side)*

The color measurements were determined with Minolta CM-3600A spectrophotometer (Konica, Japan). The measurements were performed according to the Commission Internationale de l'Eclairage (CIE) Lab color system [9]. The rubbing fastness properties of the leathers were examined by Bally Finish Tester 9029 according to TS EN ISO 11640 standard (50 rubs in dry and 25 rubs in wet) [10].

3. RESULTS AND DISCUSSION

3.1. Extraction yield results

The different concentrations of NaOH resulted different extraction yield results. The higher concentration led to higher extraction yields (Table 2).

Table 2: *The extraction yields of Aesculus hippocastanum L.*

Extraction substance	Extraction yield %
Water	18.2
0.1 % NaOH	24.6
0.5 % NaOH	30.2
1 % NaOH	36.4

3.2. Color measurement values

The spectrophotometric color measurements of dyed leathers with extracts of *Aesculus hippocastanum* L. are shown in Table 3 - 8. A direct proportional was found for ΔE and "a" values of 0.1% concentration for the suede side in contrast to fur side of the leathers (Table 3and 4).

Table 3: *Color measurement values of double face leathers (0.1% NaOH)*

	L	a	b	dL	da	db	dE
10g/L_Suede	61.19	2.31	13.22	-37.73	2.42	13.56	40.17
20g/L_Suede	59.04	3.93	14.65	-39.88	4.04	15.00	42.80
40g/L_Suede	60.70	4.98	14.55	-38.22	5.09	14.90	41.33
60g/L_Suede	58.93	6.55	15.34	-39.98	6.66	15.69	43.46
Crust_Suede	69.85	-4.20	5.88	-29.07	-4.08	6.24	30.01

Table 4: *Color measurement values of double face leathers (0.1% NaOH)*

	L	a	b	dL	da	db	dE
10g/L_Fur	73.10	0.75	10.56	-25.82	0.86	10.90	28.05
20g/L_Fur	72.57	1.28	12.11	-26.34	1.39	12.46	29.18
40g/L_Fur	72.70	0.30	11.91	-26.21	0.41	12.26	28.95
60g/L_Fur	71.73	0.96	14.33	-27.18	1.07	14.68	30.93
Crust_Fur	78.59	-1.52	6.36	-20.33	-1.41	6.72	21.48

Table 5: *Color measurement values of double face leathers (0.5% NaOH)*

	L	a	b	dL	da	db	dE
10g/L_Suede	55.44	7.2	19.05	-43.48	7.31	19.41	48.18
20g/L_Suede	56.83	6.79	18.7	-42.09	6.9	19.06	46.72
40g/L_Suede	58.9	6.47	18.41	-40.02	6.58	18.77	44.7
60g/L_Suede	58.7	7.15	18.88	-40.22	7.26	19.24	45.17
Crust_Suede	69.85	-4.20	5.88	-29.07	-4.08	6.24	30.01

*L, a, b values of white color as a target given as respectively; 98.92; -0.1; -0.37

The color measurement values of double face leathers showed that there was a significant difference between the suede sides of control and dyed leathers (ΔE; 0.5% NaOH; Table 5). However, the concentration increase didn't affect the ΔE values significantly. The concentrations of 20, 40 and 60 g/L extracts gave similar colors to suede side of the leathers.

Table 6: *Color measurement values of double face leathers (0.5% NaOH)*

	L	a	B	dL	da	db	dE
10 g/L_ Fur	69.67	0.95	10.41	-29.25	1.06	10.77	31.22
20 g/L_ Fur	73.39	0.97	12.83	-25.53	1.08	13.19	28.77
40 g/L_ Fur	74.24	0.95	14.53	-24.68	1.06	14.89	28.85
60 g/L_ Fur	75	1.26	14.48	-23.92	1.37	14.84	28.19
Crust_Fur	78.59	-1.52	6.36	-20.33	-1.41	6.72	21.48

For the fur side of the leathers, the highest color difference value was obtained from 10g/L concentration and similar ΔE values were determined for the other concentrations. The a value was found significantly lower than the values obtained from the suede side and the intensity of b value was found lower than the suede sides but higher than the control leather (Table 6).

Table 7: *Color measurement values of double face leathers (1% NaOH)*

	L	a	b	dL	da	db	dE
10 g/L_Suede	51.81	9.66	20.18	-47.11	9.77	20.55	52.31
20 g/L_Suede	47.12	11.11	20.74	-51.8	11.22	21.1	57.06
40 g/L_Suede	53.78	10.09	20.49	-45.14	10.19	20.85	50.76
60 g/L_Suede	55.73	10.31	21.46	-43.19	10.41	21.83	49.5
Crust_Suede	69.85	-4.20	5.88	-29.07	-4.08	6.24	30.01

The 1% extraction provided darker colors compared to 0.5 and 0.1%NaOH extraction. No significant color differences were observed among the different concentrations except 20g/L. Similar b values were determined from the leathers derived by 0.5 and 1% NaOH extraction (Table 7).

Table 8: *Color measurement values of double face leathers (1% NaOH)*

	L	A	B	dL	da	db	dE
10 g/L_ Fur	71	4.14	13.99	-27.92	4.25	14.36	31.69
20 g/L_ Fur	69.66	5.65	15.42	-29.26	5.76	15.78	33.76
40 g/L_ Fur	69.48	5.96	17.39	-29.44	6.07	17.76	34.92
60 g/L_ Fur	70.54	7.32	19.74	-28.38	7.42	20.11	35.57
Crust_Fur	78.59	-1.52	6.36	-20.33	-1.41	6.72	21.48

The higher concentrations of NaOH led to higher ΔE, a and b values indicating the colorant effect of the extracts for the fur side. The dyeing property of the extracts were also supported by the low L values.

3.3. Rubbing fastness values

Depending on the NaOH concentration, the rubbing fastness values were decreased and lower fastness results were obtained from the dry rubbings (Table 9).

Table 9: *To and fro rubbing fastness values of double face leathers dyed with different concentrations*

0.1%	Dry		Wet		0.5%	Dry	Wet		1%	Dry	Wet	
	F*	L*	F	L	F	L	F	L	F	L	F	L
10 g/L	3	2/3	3/4	3/4	1/2	2	3/4	3	2	2	3	2
20 g/L	2/3	2/3	4	4	1/2	2	2/3	3	2/3	1/2	3	2
40 g/L	2/3	3	4	4	2	2	3	3	2	2	3	3
60 g/L	2/3	2/3	4	4	2	2	3	3	1/2	2	3	2/3

*F: felt; L: leather

4. CONCLUSIONS

In this study, the dyeing characteristics of horse chestnut extracts for double face leathers were investigated. The results revealed that the horse chestnut extracts treated with different concentrations of NaOH provided good dyeing propery of suede side of the leathers. The higher concentrations didn't give significant correlations and the increase in NaOH concentration led to lower rubbing fastness characteristics.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

INFLUENCE OF REACTION CONDITIONS ON THE ALKALINE HYDROLYSIS OF CHAMOIS LEATHER WASTE

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Abstract: *The leather processing industry is known as an important source of environmental pollution, due to the large amount of waste generated. In this respect there are efforts concerning recovering and capitalizing of these wastes in order to subsequently use them in different applications. This work aimed to obtain collagen forms with convenient features starting from Chamois leather waste resulting from the buffing operation, by alkaline hydrolysis at different temperatures (60°C, 90°C, and 120°C) and reaction time (4, 6 and 8 hours), in a solution of 30% NH_4OH with a pH=11. The effects of the reaction conditions (temperature and reaction duration) on the hydrolysis yield and molecular weight of the extracted polypeptides were investigated. The working version no. 8 (temperature = 120^0C, and reaction time = 6h) was chosen as optimal for obtaining a protein product suitable from the point of view of hydrolysis yield and molecular weight, respectively. For this sample no. 8, tests for checking physical-chemical characteristics were carried out, and also the influence of the hydrolysis upon certain structural changes caused by the reaction conditions was investigated by IR analysis. The reaction conditions led to obtaining polypeptide mixtures with different molecular weights and polydispersity that can be used as auxiliaries to obtain composite materials or as additives for new building materials.*

Key words: *hydrolysis yield, polipeptide mixtures, structural characteristics, IR analyses.*

1. INTRODUCTION

The large amount of solid waste provided by the leather processing industry is a major concern of the researchers in the field. In this respect there are efforts concerning recovering and capitalizing of these wastes to be used as: soil fertilizers [1,2], auxiliaries for leather treatment [2-5], adsorbents for dyes and heavy metals [6,7], adjuvants for preparation of cosmetic products [8,9], biomaterials with applications in medicine [10,11], biosensors [12,13] auxiliaries for building materials [14-18], biodegradable plastic materials [19-21], biofuels [22], composite materials [23].

The hydrolysis of the collagen material as the main component of leather and/or leather waste is based on the general principle of the substitution reactions, according to which chemical function to be modified must be in a non-ionized state. This requires that the protein solutions to be brought at a pH different from the isoelectric point; in this case the consumption of acidic or basic functions of these solutions will take place by conducting the reaction in an acid or alkaline medium, respectively. Depending on hydrolysis conditions, the process leads to a change of the leather

substrate reactivity, a loss of proteinaceous material, associated with a specific molecular weight distribution of polypeptides and a corresponding hydrolysis yield [24].

This work aimed to obtain collagen forms with convenient features by alkaline hydrolysis of Chamois leather waste resulting from the buffing operation, and investigated the effects of the reaction conditions (temperature and reaction duration) on the hydrolysis yield and molecular weight of the extracted polypeptides. The structural changes caused by hydrolysis were also highlighted through IR analysis.

2. MATERIALS AND APPARATUS

The experiments were conducted using the following materials: Chamois leather waste with the following composition: dry matter: 87.98%; protein matter: 63.64%; total nitrogen (TKN): 10.13% (relative to dry matter); Chemical reagents and chemical auxiliaries as: trichloroethylene, NH_4OH, NaOH, nonionic surfactant Boron SE type; acetone, ethyl alcohol; distilled water.

Equipment used: VELP Scientifica UDK 132 with semi-automatic Distillation unit for total nitrogen determination; Krebs Viscometer; Digital balance KERN 474; Laboratory Oven MLW WS100 (Hungary); Laboratory centrifuge, DIGILAB – SCIMITAR Series FTS 2000 spectrometer with ZnSe crystal, 750 - 4000 cm^{-1} range, 4 cm^{-1} resolution.

3. EXPERIMENTAL

Scleroproteins from wastes generated in leather processing are present in a more or less distorted chemical form. Chamois leather waste (dust from buffing operation) is a strong stabilized protein structure as a result of two technological operations: a pre-tanning operation consisting of crosslinking of collagen matrix with glutaraldehyde, followed by the actual tanning using fish (cod) oils as tanning agent. Bringing scleroproteins to a usable form that can be subject to chemical modification requires their release from supramolecular matrix, and liquid phase transition. There are thus obtained the so-called processable protein shapes.

The easiest way to bring scleroproteins in liquid phase is by alkaline hydrolysis; in this respect the laboratory experiments consisted in nine working variants involving autoclaving at different temperatures (60°C, 90°C, and 120°C) and reaction time (4, 6 and 8 hours), in a solution of 30% NH_4OH with a pH=11. Thus, each sample consisting of 250 g of Chamois powder waste was subjected to a wetting/swelling and degreasing process with a non-ionic surfactant/trichlorethylene (1:5 wt/wt) mixture at 20ºC, for 24 hours, and then was dried in a thermo-regulated oven at 50ºC, followed by cooling to 20ºC. Subsequently, the degreased product was placed in a batch reactor (Fig.1) equipped with a stirring system, a vapor condenser and pressure automatic control at 2 atm, and subjected to hydrolysis process under the above-mentioned conditions.

The resulting mixture was cooled to 20ºC, and then separated by centrifugation at 6000 rpm for 30 min. The obtained liquid component was then subjected to the operations of extraction, separation, purification, and drying by lyophilization resulting thus a fine powder mixture. The process flow for obtaining the hydrolyzed polypeptide mixture is shown in Fig. 2.

4. RESULTS AND DISCUSSIONS

The hydrolysis yield of the lyophilized samples resulting from experiments was determined by the following equation:

$$Y = \frac{W_h}{W_i} 100 \quad \textbf{(1)}$$

where Y is the hydrolysis yield (%), W_h is the weight (g) of the dried hydrolysate powder and W_i is the weight (g) of the initial sample in the dry state.

The results obtained for the nine experimental variants are presented in Fig. 3. In order to determine the average molecular weight of the lyophilized protein mixture Sörensen method (AOAC 1995) [25] was used and the results are presented in Fig. 4.

Fig. 1: *Batch reactor for carrying out alkaline hydrolysis (autoclave)*

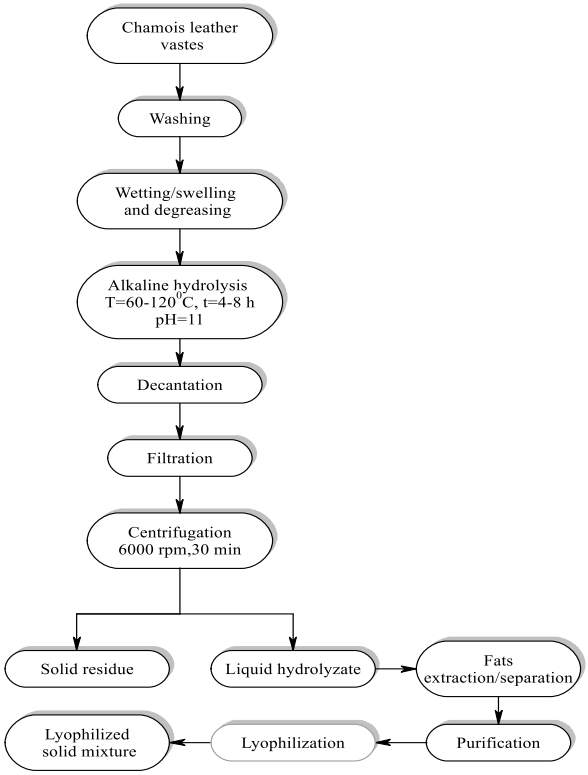

Fig. 2: *The sequence of operations for obtaining polypeptide hydrolysates by alkaline hydrolysis*

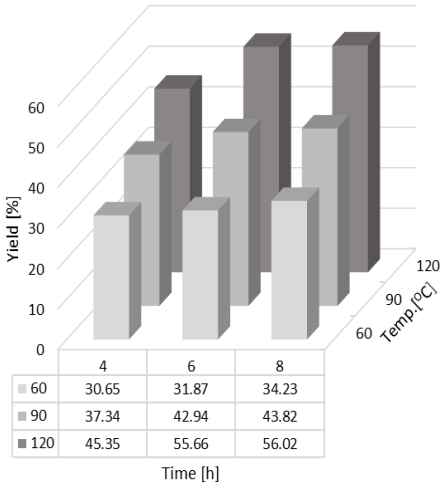

Fig. 3: *Dependence of hydrolysis yield on temperature and time*

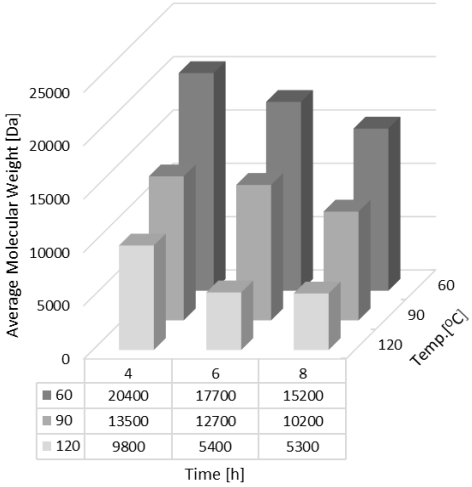

Fig. 4: *Dependence of average molecular weight on temperature and time*

Analyzing data in Figure 3 and 4 it can be seen a noticeable increase in the yield of protein hydrolysis with the increasing of reaction time and temperature; at the same time occurs a most advanced fragmentation of polypeptide chains demonstrated by molecular weight reduction. The composition of the amino nitrogen (according Sörensen method) of the extracted hydrolysates indicates the presence of polypeptides with average molecular weight of 5300 - 20400 Da.

Obtaining mean polypeptides with average molecular weight exceeding 10,000 Da, in conjunction with lower hydrolysis yields at a reaction temperature of 60^0C-90^0C, can be attributed to the so-called effects of "superficial erosion" due to possible the existence of cross-linking bridges resulting from the tanning of Chamois leather with cod oil. This range of molecular weights will be studied further in order to obtain products with potential applications in composite materials.

By increasing the hydrolysis temperature to 120^0C together with the reaction time (up to 8 hours) occur so-called "erosion in volume" processes that determine obtaining polypeptides with low molecular weight and low polydispersity. At this temperature, no significant differences were observed for the yield values and the average molecular weights obtained for a reaction time of 6 and 8 h, respectively. This aspect can be valorized to obtain new value-added products based on Chamois leather waste, with potential applications in building materials.

Given the above results, the working version no. 8 (temperature = 120^0C, and reaction time = 6h) was chosen as optimal for obtaining a protein product suitable from the point of view of hydrolysis yield and molecular weight, respectively. For sample no.8 tests for checking physical-chemical characteristics were carried out and the results are shown in Table 1.

Table 1. *Physical and chemical characteristics of hydrolyzed product no.8*

Property	**Value**
Average Molecular Weight , Da	3400
Density (related to dried protein form), g/cm^3	0.42
Components (relative to dry matter) %	
- total dry matter	34.62
- water soluble components	9.20
- total fats	19.39
- protein matter	36.79
Total nitrogen (Kjeldahl Method), %	14.62
Total ash, %	4.74
Hydrolysis yield **(**related to total protein), %	55.66

In order to study the the structural changes caused by the hydrolysis in an alkaline medium, IR analysis of the hydrolyzed sample no.8 along with Chamois leather powder as control sample was performed (fig.5).

Spectra from figure 5 show typical bands of collagen such as: the amide A band associated with the free N-H stretching vibration, and free water in the range of 3400 to 3440 cm^{-1}; amide B related to the stretch of CH_2, was found at ~ 2900 cm^{-1}; amide I band with its characteristic frequencies 1600-1700 cm^{-1}, mainly associated with the stretching vibrations of the C=O group along the polypeptide backbone, is a sensitive marker of the peptide secondary structure; amide II at 1500–1550 cm^{-1} corresponding to N-H bending vibrations; and amide III at 1200–1300 cm^{-1} related to C-H stretching. Normally, the amide I band is strong, the amide II band is weak and the amide III band is moderate. Area and location of individual peak is changed according to the changes in the structure of collagen. Fibril formation, which increases intermolecular interactions in collagen, is associated with broadening and slight shift to lower wavenumber of the amide A (at ~ 3300 cm^{-1}), as we can see from the spectrum of the control sample, suggesting that more NH groups were involved

in the hydrogen bonding, in contrast to the hydrolyzed samples where this band is more intense and occurs at ~ 3400 cm^{-1}; this could be also associated with an increase of free –OH groups content. On the other hand, the amide II and III adsorption show a lower signal for hydrolyzed sample that can be attributed to the conformational changes in the secondary structure of collagen, with the increasing of random-coil structures.

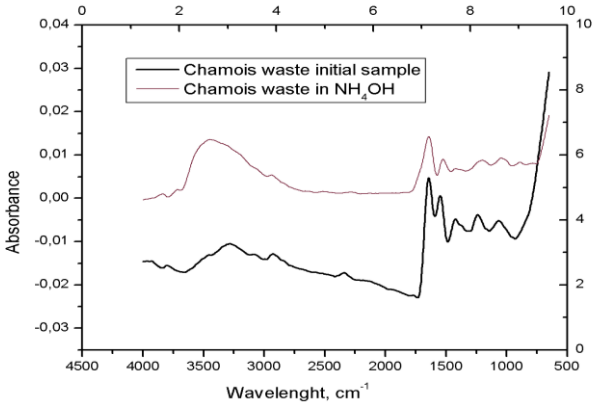

Fig. 5: *IR spectra of Chamois powder and his hydrolysate in NH_4OH (120^0C, 6 h reaction time)*

5. CONCLUSIONS

1. Starting from waste resulting from buffing operation of chamois leather, were obtained polydisperse colloidal solutions containing protein fractions with an average molecular weight of 5300 - 20400 Da.
2. A noticeable increase in the hydrolysis yield with the increasing of reaction time and temperature occurred, at the same time with a most advanced fragmentation of polypeptide chains, demonstrated by molecular weight reduction. The structural changes were also revealed by infrared analysis performed.
3. Polypeptides with low molecular weight and low polydispersity resulting at high temperature can be valorized to obtain new value-added products based on Chamois leather waste, with potential applications in building materials.

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Two of the authors (M. Pruneanu, and T. Balau Mindru) acknowledge the financial support of PNII-PT-PCCA-2013-4, nr. 216 / 2014, with the title “SISTEM INOVATIV DE PRODUSE SI TEHNOLOGII DESTINAT STIMULARII CRESTERII ECO-EFICIENTEI INDUSTRIEI DE PIELARIE”(PROECOPEL) (TUIASI – P2).

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

SUSTAINABLE PRODUCT DESIGN AND EXAMPLES OF LEATHER MATERIAL RECYCLING

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Abstract: *Many garments made of leather, end up in landfills as waste following the end of its useful life. However, in the flow of production of a leather product, intense energy, chemicals, high volumes of water are consumed. This means that the carbon footprint and environmental loads are high. There are many research activities related to the recycling of textile products, and recycling chains, in this regard famous clothing brands have been organizing grand campaigns. In order to assess the case for leather products that have an important place in the ready-to-wear segment, one should ask the following questions: "How do the big companies and brands in this sector participate in the environmental movement? And importantly, what are the best attempts to recycle leather products? What can be done about the future of leather products recycling and innovative sustainable designs?" when considering sustainable design using recycled leather from end-of-life leather products. In this study, examples of innovative best practices, which were adopted by new brands for recycling and reuse of various types of waste, in order to perform a sustainable product design were presented with the attempt of clarifying aforementioned questions. These new initiatives and practices can develop a novel perspective for academicians and professionals engaged in the field of leather and fashion design, and the concept of sustainable design can be introduced to wider masses.*

Keywords: *leather materials recycling, sustainable design, innovative design, fashion design*

1. INTRODUCTION

1.1 Methods of Leather Materials Recycling

Leather clothings, shoes and scraps generated during the leather production process are important materials that can be used for designing new products through diversified methods. Throughout this cycle different recycling scenarios and methods are practiced considering the required end-product. These may be classified as four main methods which emphasized in Figure 1.

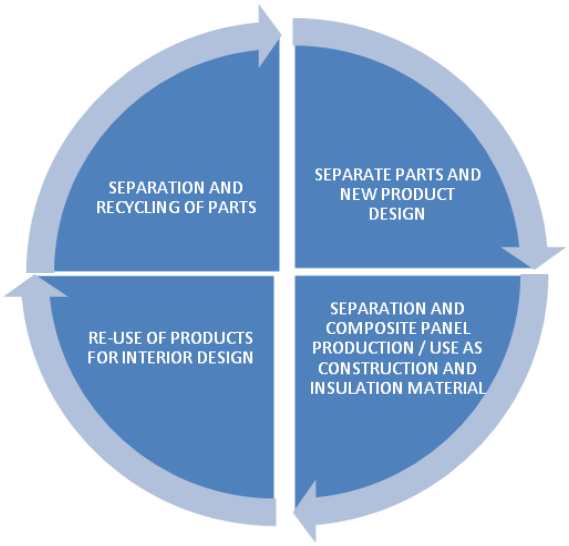

Figure 1: *Recycling methods of leather materials*

1.2. Innovative Designs of Recycling

Innovative designs of recycling are remaining on the agenda as a global movement around the world. Both fashion and industrial designers are using the concept of nature friendly, ecological and sustainable design in their works and reflecting on their products.

Beyond being a new and interesting movement, this intention is an important trend which involves concept of social responsibility and supports the idea of preserving the environment along sensibility and conscious approach on use of natural resources. There are intensive work and outturn samples of sectors and giant brands in this context. However, featuring, popularizing and promotioning outputs, along both professional areas and ones formed by consumer profile, can be named as a green innovator project concerning whole planet.

It is an important subject that shared samples and products creating a prudential vision for all designers, engineers and related domain experts and this trends becoming a remaining method rather than being a short-tempered but disappearing mainstream, and increasing of innovator designs and products.

The U.S. EPA found that two million tons of textiles were recovered for recycling and reused in 2010. The leather jacket in the back of your closet is a bulky item that should not go directly into the trash. The item would join billions of textiles congesting American landfills. According to the U.S. Environmental Protection Agency, in 2010, more than 13.1 million tons of textiles were generated, but only 14 percent of clothing and shoes were recycled [1, 2].

EcoDemo Leather Surfacing Fabrication Company designs new surfaces for doors composed from belt panels, bedrails and similar furnitures in segment of recycling leather. They also, put floor made from leather clothing cut into pieces, surface dressing for wardrobes, leather furniture, pouf on the market and bring into use, and produce an environmentalist production emphasized company name [3, 4].

Figure 2: *Eco-Demo recycling leather products [5]*

Daniel L.Vermeer has developed social innovation strategies using data and storytelling to help transform companies, nonprofits, and the communities in which they work and projects. In the article entitled "7 upcycling companies that are transforming the fashion industry" emphasized the alternatives of recycling in leather garments within the scope of recyclable, fashionable fashion products [6].

Despite the stereotypes, "eco-friendly footwear" doesn't have to mean hemp sandals or Birkenstocks. British shoe company Terra Plana has been putting its own unique stamp on eco-friendly style since 2001, with their quirky shoes made from environmentally sustainable materials like recycled rubber, vegetable tanned leathers, and recycled Pakistani quilts [7].

Figure 2:*Terra plana eco-friendly shoes [7]*

Verdura Shoes and Sandals are handcrafted in Tuscany, Italy, by master shoemaker Andrea Verdura. The use of recycled and vegan materials, together with the eccentric, boundary-less design, make the shoes and sandals a unique walking experience. Each pair is a vibrant, pulsing creation, born from the unrivalled tradition of Tuscan shoemaking. They aim is to offer a wide range of quality footwear with all the crucial elements a great shoe needs to have: standards of beauty, comfort and durability – while prioritizing environmental impact. It has taken years of research, the best natural and vegan materials, knowledge of manual skills, innovative designs to create Verdura Net Sandals. Verdura's designers cut the net and wash it several times to soften the fabric. They dye it with natural pigments and then combine it with cork, recycled rubber sole and waste leather left over from shoe production.

The insole is anatomic, made of natural cork. The sole itself is available in two different versions, one composed of recycled Vibram rubber and the other of recycled, vegetable-

tanned leather. They use these eco-conscious materials to craft stylish, comfortable footwear for women, men and kids [8].

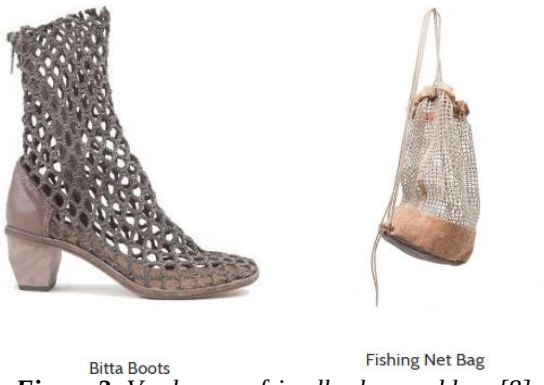

Figure 3: *Verdura ecofriendly shoe and bag [8]*

3. CONCLUSIONS

Adoption of clean production technologies within all sectors that support national economies, optimization of sustainable designs and resource utilization in all areas and when following this track, production of consumer goods from recycled materials is a mega project, which can be performed with the participation of financial environments and academia.

These new production systems, concerning our planet and living areas directly, exhibit its reflections in all areas related leather, textiles and leathercraft products. However, it is required to popularize best application samples and brands, and adopt this logical framework. Consequently, researches and outputs should be intensified by addressing innovative and ecological designs in every aspect. Leather is a recyclable or reusable material and end of life leather products are potential resources for various innovator products.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

HEAVY METAL CONTENTS OF NATURAL AND ARTIFICIAL UPHOLSTERY LEATHERS

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Abstract: *Textile products and natural and artificial leathers are used as flooring materials in upholstery products. Due to the expensive materials as natural leather upholstery, today. Therefore, the demand for artificial leather has increased. Because artificial products are easy to clean, light, and have good features like natural leathers, they are used as an cheap alternative to natural leather especially in furnishing industry. In this study, the amounts in natural and artificial leathers of heavy metals such as cadmium, cobalt, chrome, copper, mercury, nickel and lead, which are limited in many goods due to their harmful effects, and of aluminum and zinc, which are unlimited, were evaluated. In this research, the total heavy metal contents of the leathers were specified in ICP-OES. Then, the amount of heavy metal manifesting when the leathers were exposed to sweat and water was determined using ICP-OES. Heavy metal contents of all leathers were compared with standard limit values. Small amounts of aluminum, cobalt, copper, nickel and zinc were also found due to the chemical and physical reactions during the wet and dry finishing processes. The heavy metal detected in the greatest quantities in natural and artificial leathers was chromium. However, neither hexavalent chrome, cadmium, mercury nor lead were found in either of the leather types.*

Key words: *Genuie Leather, Faux Leather, Furniture, ICP-OES, Elements, Environment*

1. INTRODUCTION

Many different organic and inorganic materials are used during the manufacture of natural leather, and pollution is caused by the intense use and discharge these chemicals [1]. The manufacture of aproximately 90% of the natural leathers produced in the world involves the use of chrome salts [2]. However, chrome cannot give the leather all the properties and qualities desired, and so different metal salts are used in various phases of leather are not subjected to a lengthy tanning process in which heavy metals are used in large quantities.

Today, the increasing price of natural leather around the world has caused consumers to shift towards goods manufactured from artificial leathers. Since these products are easy to clean, light, and have good waterproof features, they are used as an alternative to natural leather especially in shoes and furniture.

In the manifesto of the European Union Commission dated July 12 2002, a complete ban was placed on Pb, Cd, Cr (VI), As, Hg and their compounds in textile and leather products, and concentrations of other heavy metals were limited [3]. Therefore, the aim of this research was to determine the heavy metal contents of natural and artificial leathers used in furniture. The total

heavy metal ions in leathers and the heavy metal ions that can be extracted in artificial sweat solution were determined using ICP-OES. Later, an evaluation was made of the difference between the total amounts of heavy metal in the natural and artificial leathers and their extraction levels in artificial sweat solution.

2. MATERIALS AND METHODS

Ten natural and ten artificial different finished upholstery leathers of different colors were randomly selected as research material and obtained from the Istanbul Leather Industrial Area and Menemen/Izmir Leather Free Zone, and from leather furniture manufacturers.

In order to determine the amounts of heavy metals in the leather products which could be extracted in damp conditions, extraction in water (EW) was carried out on the samples in accordance with ISO 4098:2005, and extractable heavy metal levels were determined with ICP-OES (Perkin Elmer Optima 2100 DV) [4]. In order to determine the amounts of heavy metal which can get into human sweat due to its dissolving effects when the leathers are in use, an artificial sweat solution was prepared in accordance with ISO 105-E04: 2014 [5]. After the extraction process was performed on leather samples in the artificial sweat solution (EAS) in accordance with ISO 17072-1:2011, the concentration levels of heavy metals other than hexavalent chrome were determined by ICP-OES [6]. The total amount of heavy metals (THM) other than hexavalent chrome within the samples was determined by ICP-OES in accordance with ISO 17072-1:2011 [4]. The amount of hexavalent chrome in the samples was determined in accordance with ISO 1705:2007 [4].

3. RESULTS AND DISCUSSION

It was found in this study that the values of all heavy metals in the leathers determined by wet decomposition were higher than those which could be extracted in water or sweat [7, 8]. As seen in Table 1, cadmium, mercury and lead were not found. They stated that the amounts of cadmium determined at low levels varied according to the color of leathers, and that this resulted from pigments used in the leather production process [6]. Besides, the very low levels of lead and mercury which can sometimes be determined in natural leather samples may come from the environment of the animal or the slaughterhouse.

Table 1: *Heavy metal content of leathers*

	Natural Leathers			Artificial Leather		
	EW (ppm)	EAS (ppm)	THM (ppm)	EW (ppm)	EAS (ppm)	THM (ppm)
	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD	Mean±SD
Cd	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Pb	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Hg	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Co	0.85±0.46	2.94±2.86	31.74±29.86	0.07±0.03	0.08±0.01	0.55±0.37
Cr	72.57±31.12	168.42±38.24	16 549.00±207.25	2.09±2.01	11.48±4.69	96.90±46.48
CrVI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Cu	4.11±3.47	6.57±11.10	53.74±40.60	0.00±0.00	0.03±0.01	0.35±0.88
Ni	0.00±0.00	0.11±0.25	0.89±2.72	0.00±0.00	0.00±0.00	0.01±0.01
Zn	0.13±0.10	1.23±0.86	11.93±10.45	0.00±0.00	0.01±0.02	0.001±0.00
Al	40.87±39.12	77.13±54.41	602.33±284.65	0.78±0.52	1.32±0.22	4.73±4.25

Table 2: *Heavy metal standards of leathers*

	Eko-Tex 100 (ppm)	SG (ppm)
Cd	0.10	
Pb	1.00	0.10
Hg	0.02	0.80
Co	4.00	0.02
Cr	2.00	4.00
Cr(VI)	0.50	-
Cu	50.00	0.30
Ni	4.00	60.00
Zn	-	1.00
Al	-	-

EW and EAS cobalt concentration values of natural leathers have been found below the standard values and THM cobalt concentration values have been found which were above the standards (Table2), [7, 8]. Cobalt may have originated from bioaccumulation while animal was alive; from the dyes and pigments, or from the machines used during the manufacturing of the leathers [6, 9, 10, 11]). Also, it has been observed that total cobalt concentration values of artificial leathers were below the limits in Eko-Text 100 and SG standard values [7, 8]. This low cobalt content of artificial leathers may be a result of metal complex pigments and contamination during processing [11, 12].

EW and EAS copper concentration values determined in natural leathers have been found to comply with limit values set by Eko-Tex 100 and SG, and the THM copper value of natural leathers has been determined to be above the 50ppm indicated by Eko Tex 100, and below the 60ppm required by SG [7, 8]. The copper detected in natural leathers may be caused by contamination during the production of leathers and metal complex based dyes used in coloring leathers [6, 11]. When Table 1 and 2 is examined, it can be seen that the entire copper concentration values of artificial leathers are much lower than the standard values [7, 8]. while the copper concentrations detected in artificial leathers, may result from contamination during production and copper based dyes.

Nickel concentration values of EW, EAS and THM present in natural and artificial leathers have been found to be below the standards [7,8]. Nickel values detected in both leather types might be caused by colorants used in leather production or stainless steel based machines and tools [6,10, 11].

Because of a lack of limit values for zinc and aluminum by both SG and Eko-Tex 100, it was not possible to evaluate conformity with standards for the Zn and Al values detected in our study (Table 2). The presence of these metals determined in both leather types may have been caused by contamination, inorganic pigments, or the water used in the production of the leathers [6,10, 11]. Besides Zn may have originated from the metabolic activities of the animal while it was alive, and aluminum is used during the tanning and retanning of the natural leathers [9].

4. CONCLUSIONS

The results for heavy metals in artificial leathers are similar to those for heavy metals in natural leathers. However, the heavy metal contents determined in artificial leathers are much lower than those in natural leathers. This is because mineral tannins are not used in the production of

artificial leathers. Although cadmium, lead, mercury and hexavalent chrome were not found in artificial leathers, and nickel element was detected at very low levels, only chrome was found in high quantities. The occurrence of these heavy metals in artificial leathers may be caused by chemical substances, dyes and pigments used in production process and by contamination from various sources. To conclude, it is expected that in the future the trend towards a demand for ecological products will have a greater effect on leather producers but that the suggested limit values may be decreased further. Therefore, the leather industry and especially natural leather processing should be prepared for these new lower limit values. Otherwise, the natural leather industry will be unable to keep up with worldwide competition, and may be affected adversely.

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ANNALS OF THE UNIVERSITY OF ORADEA
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COMPOSITES FROM LEATHER INDUSTRY BUFFING DUST: A REVIEW

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Abstract: *Leather buffing dust is a fine powder of collagen fibril waste from milling and buffing operations and constitutes an important part of solid wastes generated from chrome tanned leather production processes. It is one of the difficult tannery wastes to manage and current practice of its disposal includes its incineration and disposal in landfill. The scientific literature reports numerous studies on its utilization in composites formulations. Chrome tanned buffing dust has been used as filler for various polymeric matrices with the aim of producing leather-like composites for potential applications such as hand bags, wallets, key chain holder and purses and footwear products such as shoe soles, insole, heels etc. This paper compiles different research works done by researchers regarding composites made from leather industry buffing dust. The characteristics of composites are also presented by making use of previously published studies carried out with different polymer matrices. Reviewed studies reveal that fiber-reinforced composites utilizing buffing dust provide landfill avoidance, energy conservation, decrease depletion of virgin raw material, enable production of low cost composites with improved mechanical properties that can be used for multifunctional applications and moreover they provide solution to the environmental problems associated with the waste management of the leather industry.*

Key words: *leather industry waste, composites, recycling, buffing dust*

1. INTRODUCTION

Leather industry is responsible for generation of large amount of solid tanned waste throughout tanning process, which converts raw skins/hides into leather. These solid wastes can be generally classified as untanned hides/skins, tanned leather and wastes from finished leather [1]. The transformation of 1000 kg of rawhide into leather provides only 200 kg of leather final product, along with 250 kg of non-tanned and 200 kg of tanned waste [2]. Among the tanned wastes solid waste from chromium-tanned leather, which includes shavings and buffing dust (BF), constitutes an important part and its disposal cause serious environmental problems.

Buffing dust is a fine powder of collagen fibril, which is generated when the finished leather is subjected to abrasion process in order to get a smooth and fine feel. For every tone of skin or hide

processed, about 2–6 kg of buffing dust is generated as a solid waste. The characteristics of buffing dust are listed in Table 1.

Table 1: *Characteristics of buffing dust [3]*

Parameter	Value
Humidity (wt%)	7.92
Ash (wt%)	12.86
Chrome oxide (wt%)	3.41
pH	4.15
Nitrogen (wt%)	9.71
Protein (wt%)	54.58
Decomposition temperature °C	323
Diameter average (μm)	4.52
Length average (μm)	258.5

Management of buffing dust from chrome-tanned leather is difficult, and current practice of its disposal includes its incineration and land codisposal. However incineration causes serious air pollution problems because of the release of toxic gases, and on the other hand land disposal method poses a threat to groundwater resources [4]. Therefore various attempts have been made for finding beneficial uses of this waste and numerous researchers reported alternative processes to recycle and utilize buffing dust waste as fillers in a polymer matrix to produce composites, instead of landfilling or incineration in the literature. The aim of this study is to present an overview of the previous researches carried out on the reuse of buffing dust as filler in composites, in order to propose potential application areas and overcome environmental issues associated with its disposal.

2. UTILIZATION OF BUFFING DUST AS REINFORCING FILLER FOR COMPOSITES

In the literature there are numerous leather fiber composite studies, which utilize chrome tanned leather wastes in the form of both chromium shavings, and buffing dust. However in case of chromium shavings, wastes have to be subjected to grinding or milling procedure, prior to incorporation into the composite blend. Therefore in this paper, studies handling exclusively buffing dust as filler were reviewed.

2.1. Literature survey on leather fiber composites from buffing dust

Rubber matrices such as natural rubber, scrap rubber, carboxylated butadiene acrylonitrile rubber, various polymers such as poliamide, poly vinyl butryral are used as matrix where leather-buffing dust was utilized to prepare leather fiber composites. And more recently due to the increasing demand of the eco-biocomposites made from the natural biodegradable material to replace conventional composites naturally-derived polymers such as Polylactic Acid (PLA) [3] and Polycaprolactone (PCL) [5] have been investigated with attempt of replacing nonbiodegradable polymeric materials with biodegradable polymers. Table 2 summarises the studies conducted on composites from leather industry buffing dust, the polymer matrices, mixing ratios and methods for preparing composites, and analysis performed for the characterization of composites for each study were also presented.

***Table 2**: Studies conducted on buffing dust composites*

Polymer matrix	Method	Mixing ratios	Analysis performed for composites	Authors
Carboxylated butadiene-acrylonitrile rubber (XNBR); butadiene-acrylonitrile rubber (NBR)	Vulcanized	100phr XNBR: 5phr ZnO: 5phr BF	Hardness, elasticity, shock absorbing capacity, electrical conductivity, SEM, mechanical properties, resistance to thermal ageing	Chronska et al., 2008 [6]
Poly vinyl butryral (PVB)	Extruded and compression molded	30-50-70% BF	Mechanical properties, hardness, abrasion resistance	Ambrosio et al., 2011 [7]
Natural rubber latex (NRL)	Compounded and hydraulic pressed	400g BF: 150, 300, 450 mL NRL	FTIR, TGA, SEM, mechanical properties, water absorption	Senthil et al., 2015[8]
Polycaprolactone (PCL)	Extruded and compression molded	2-5-10-20-30-40% BF	DSC, mechanical properties, XRD, SEM, TGA, water absorption	Joseph et al., 2015 [5]
Natural rubber (NR)	Vulcanized	100phr NR: 15phr ZnO: 2phr Stearic acid: 10, 20, 30phr BF	Rheometric characteristics	Cardona et al., 2016 [9]
Polylactic Acid (PLA)	Extruded and compression molded	2-5-10-20-30% BF	Mechanical properties, SEM, DSC, water absorption, contact angle, TGA	Ambone et al., 2016 [3]
Epoxy polymer; Titanium dioxide	Mixed and cured	10% BF	SEM, Hhardness, DSC, TGA, FTIR, mechanical properties, chemical resistance test	Sivakumar et al., 2015 [10]

***Phr**: Parts per hundred rubbers*

Authors carried out the structural characterization of the composites using Fourier-transformed infrared (FTIR) spectroscopy and X-ray diffraction spectroscopy (XRD). Scanning Electron Microscopy (SEM) was used to analyze morphological structure and distribution of BF in the matrix. Differential Scannig colorimetry (DSC) and thermogravimetric analysis (TGA) were used for investigation of thermal properties of composites. And in some researches biological stability [8], and chemical resistance of compositeswere also analyzed [10].

2.2. Characteristics of leather fiber composites from buffing dust

Table 3 provides the general characteristics of leather fiber-reinforced composites developed by researchers. Utilization of BF in rubber mixes improved processibility and mechanical properties of composites. Chronska and Przepiorkowska (2008) reported that incorporation of BF as filler for rubbers such as carboxylated butadiene-acrylonitrile rubber (XNBR) and butadiene-acrylonitrile rubber (NBR) has improved their mechanical properties, increased thermal aging, provided higher cross-linking density, and higher hardness. Cardona et al. (2016), observed that incorporation of BF into natural rubber formulations improved processibility and facilitated the vulcanization process during mixing, diminishing the viscosity and vulcanization time. Senthil et al., (2015), developed a

composite material in board form from buffing dust using different concentration of natural rubber latex. Among the different concentrations of NRL used, 450 mL (w/v) provided significant mechanical properties, which may find application in footwear, leather goods, and household interior applications.

Table 3: *Properties of fiber-reinforced composites*

Polymer	**Tensile strength (Mpa)**		**Elongation at break (%)**		**Shore A hardness (◦Sh)**	**Water absorption (%)**	**Reference**
	Neat polymer	**Composite**	**Neat polymer**	**Composite**			
XNBR vulcanizates (100phr XNBR: 5phr ZnO: 5phr BF)	8.5	14.88	45	58	355.15	-	[6]
NBR vulcanizates (100phr NBR: 5phr ZnO: 5phr BF)	2.1	3.45	50	46	458.6	-	[6]
Natural rubber latex (NRL) (400gr BF: 450 mL NRL)	-	4.19	-	3.99	-	50	[8]
PLA (90 PLA: 10 BF)	43.15	45.05		-	-	2	[3]
PVB (70 PVB: 30 BF)	21	8	63	75	175	-	[7]
PCL (80 PCL: 20 BF)	15	16	-	-	40	3.8	[5]
Epoxy (10gr Epoxy:0.005 Nano TiO_2:1gr BF)	4.43	15.08	9.44	6.11	-	-	[10]

Incorporation of buffing dust into polymer matrices resulted in increase in mechanical properties and hardness. This increase in hardness derived from higher hardness of tanned leather fibers than the plasticized polymer matrices. Ambrosio et al., (2011) reported that increasing the incorporated buffing dust leather content in the poly (vinylbutyral)–leather fiber composites led to a significant increase in the elastic modulus and shore hardness of the composites, whereas tensile strength and abrasion resistance decreased [7] .

Joseph et al (2015), developed Polycaprolactone (PCL) biocomposites filled with waste leather buffing dust, which could be used to produce low cost materials suitable for applications in footwear industry, for making bags and suitcases [5]. Incorporation of BF with increasing concentrations into PCL resulted in improvement of tensile modulus, increase in percentage of water uptake and reduction in percentage crystallinity of PCL matrix. Similarly Ambone et al., (2016) also reported that addition of BF in increasing contents improved tensile properties of biodegradable polymer based biocomposites and led to a reduction in percentage crystallinity of PLA matrix [3]. BF/PLA biocomposite showed increase in water absorption with BF addition.

2.3. Application areas of leather fiber composites from buffing dust

Numerous application areas and benefits for utilization of buffing dust for the production of leather fiber-reinforced composites were listed in Table 4.

Properties of composites studied here varied with the type of polymer matrix and content of leather wastes. Type of polymer matrices must be selected according to the desired final properties of the material to be manufactured. For instance mechanical properties and water absorption capacity of a composite material play a major role in deciding its use in footwear and leather goods

manufacture. Comfort footwear could be made from leather boards with tensile strength of 5.5 Mpa while inexpensive and light foot wears could be made from leather boards with tensile strength of 4.0 Mpa and the water absorption (%) should be minimum of 35% [8]. On the other hand composites with high chemical resistance and hardness can be required for construction materials and mechanical automobile body parts.

Table 4: *Application areas of fiber-reinforced composites*

Application areas of composites	**Benefits of utilization of buffing dust as a filler in composites**
• Footwear, • Handbag, • Suitcase, • Shoe sole shoe last, shoe heel, • Clothing • Household interior • Construction materials • Automobile interior moldings • Heat-sound insulating boards • Flooring materials	✓ Decrease depletion of virgin raw material ✓ Landfill avoidance ✓ Energy conservation ✓ Low cost composite production ✓ Reduction of waste volume ✓ Reuse waste ✓ Improve/increase of mechanical properties of composition ✓ Profitable use of waste ✓ Air permeability

Utilization of buffing dust enables saving of depletion of virgin raw materials avoids landfilling of wastes and reduces waste volume. Due to environmental issues arising from tanned leather wastes the demand for cost effective, environmental friendly materials continues to increase. The driving forces behind the utilization of the leather industry buffing waste are environmental benefits, cost, and renewable resource utilization.

3. CONCLUSIONS

Incineration and landfill of chrome tanned leather wastes pose significant environmental problems. Numerous studies have been carried out on utilization of buffing dust as filler for fiber-reinforced composites. Various polymeric matrices have been usedwith the aim of producing leather-like composites, which may find application in footwear, leather goods, and household interior applications.

This paper presents an overview of the previous researches carried out on the reuse of buffing dust as filler in composites, in order to overcome environmental issues associated with its disposal and propose a profitable use of chromium tanned leather waste. Studies reveal that fiber-reinforced composites utilizing buffing dust have good mechanical properties, acceptable water absorption values which can be used for multifunctional applications. The developed composites also provide solution to the environmental problems associated with the waste management of the leather industry. Leather wastes composites exhibited a homogeneous distribution within the

polymer matrix, which makes it feasible to develop low cost eco-friendly composites for shoes, bags and upholstery manufacturing.

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ANNALS OF THE UNIVERSITY OF ORADEA
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EFFECTS OF FATLIQURING PROCESS ON LEATHERS COLOURED WITH IR REFLECTIVE DYES AND PIGMENTS

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Abstract: *Black coloured materials and consumer goods are known to be heating up more, because they absorb sun radiation more than light colours. This heating is a problem for the users for black automotive or motorcycle leathers and also for dark shoes and boots which are exposed to sun heat. Human vision system can distinguish visible colours between the wavelengths of 390-700 nm. So reflecting the sun radiation in the infrared area of radiation spectrum higher than 700nm, is a solution for heating problem without affecting the visible colour. For this reason IR reflective dyes and pigments are designed. A leading Leather Chemical Company has developed an IR reflecting dyeing system for leather keeping the dark coloured leathers cooler under sun radiation. Additionally in theory, fat and water content of leather affects its heating properties. In this study, effect of natural, synthetic and waterproof fatliquoring systems on heating properties of leathers coloured with IR reflective dyes and pigments are investigated.*

Key words: *Leather, IR Reflective, Dyes, Pigments, Fatliquoring*

1. INTRODUCTION

Colours almost always align with certain emotions and they have their own meanings for most people. For example black colour is associated with power, elegance, formality, death, evil, and mystery. Fashion industry uses this simple colour strategy in almost every item. Black is the indispensable colour for motorcycle seats, motorcycle clothes, car interiors, elegant shoes and boots.

Let's have a look how black colour is formed: Light is an electromagnetic radiation within a certain part of the electromagnetic spectrum. Human vision perceive the light reflections which have wavelengths between 390-700nm as colours. If all the radiation is reflected we see the white colour and if all the radiation is absorbed we see the black colour.

The electromagnetic radiation below 390 nm is called ultraviolet (UV) and beyond 700 nm is called Infrared (IR). Infrared radiation in sun was discovered by Herschel at 1800. Herschel was testing filters for the sun so he could observe sun spots. When using a red filter he found there was a lot of heat produced. Further experimentation led to Herschel's conclusion that there must be an invisible form of light beyond the visible spectrum [1]. Nearly half of the solar radiation consists of near-infrared (NIR) radiation (700–2500 nm) which is a direct consequence of heat [2].

Black coloured products absorb all the sun radiation including near IR and cause a heating problem. This causes comfort problems for motorcycle, automobile drivers and black shoe wearers. So reflecting the sun radiation in the infrared area of radiation spectrum higher than 700nm is a solution for heating problem without affecting the visible colour. For this reason IR reflective dyes and pigments are designed.

Modern IR-reflecting pigments enable formulators to create products showing less interaction with solar radiation compared to using normal pigments, and therefore showing lower heat build-up [3]. This technology is finding use in the area of coil coatings for facades and roofs and also in transportation and other areas where the ability to stay cool is a valuable benefit [4]. A leading Leather Chemical Company has developed an IR reflecting dyeing system for leather keeping the dark coloured leathers cooler under sun radiation [5].

However leather production is a result of continuous process steps which effect on the produced leather. Among these processes, tanning has its major importance; because the tanning process is the stabilization of the collagen matrix to retain a separated fibre structure and to increase the hydrothermal stability [6]. Another important process in leather making is the fatliquoring process which these separated fibres structure is kept during drying, thus allowing the fibres move laterally over each other. In essence, fatliquoring is a simple lubrication phenomenon [7]. However the chemical industry has many different raw materials available for the production of fatliquors. Fatliquors can be classified according the ionic character, composition or origin of raw material. Based on origin of raw materials, fatliquors can be classified as in two main groups as: Natural raw oils and fats, and synthetic oils. [8, 9]. Each fatliquoring class like sulfited natural and synthetic products, sulphated natural and synthetic products, lecithin-based sulphated natural and synthetic products, polymeric acrylic syntans, water-proofing fatliquors, etc. has their own characteristic effect on properties of leathers [9], [10], [11],[12].

In this study, effect of natural, synthetic and waterproof fatliquoring systems on moisture content, water absorption properties and heating properties of leathers coloured with IR reflective dyes and pigments are investigated.

2. EXPERIMENTAL

2.1. Material

2 wet blue sides each weighting approximately 10 kg were used as the raw material for wet-end processes. The thicknesses of leathers were adjusted to 1.2-1.4 mm by shaving.

The IR reflecting dyes & pigments, mixture of natural and synthetic fatliquors and waterproofing fatliquors were provided from TFL Turkey. Natural and synthetic fatliquors were provided from Zschimmer & Schwarz

2.2. Method

Each side of wet-blue leathers were divided into 8 pieces, totally 16 pieces. The study was conducted with two parallels. 4 different fatliquoring systems:

1- Combination of Selected Natural and Synthetic Fatty Substances (Lecithin)
2- Synthetic Fatliquoring Agent
3- Natural Fatliquoring Agents
4- A Waterproof Fatliquoring system

And 2 dyes were used in trials :

A- Standard acid dye
B- IR reflecting acid dye

2.2.1. Wet-end Process

The wet-blue leathers were processed according recipes given in Table 1 and Table 2. Then the leathers were hang-dried and mechanical processes like milling and toggling were carried out.

Table 1: *Standard wet-end process*

Process	Product	Dosage (%)	Temperature (°C)	Duration (min)	Remarks
Washing	Water	200	40		
	Oxalic Acid	0.2		45	
Washing	Water	100			
Neutralization	Water	150	35		
	HCOONa	1.5		20	
	$NaHCO_3$	1		45	pH:5.5
Washing	Water	100	40	30	
Dyeing / Fatliquoring	Water	100	35		
	Anionic Neutralization Syntan	1.5		30	
	Standard Dye / IR Reflecting Dye	3		30	
+	Water	50	55		
	Fatliquoring*			90	
	HCOOH	1.5		20	
	HCOOH	0.5		30	pH:4
Washing	Water	100			

* Fatliquoring variations:
1- 10% Fatliquoring Agent (Combination of natural and synthetic fatty substances (Lecithin))
2- 10% Synthetic Fatliquoring Agent
3- 7 % Natural Fatliquoring Agent (Combination of sulfonated and sulfited natural fats)
+ 3 % Natural Fatliquoring Agent (Sulfited fish oil)

Table 2: *Waterproof wet-end process*

Process	Product	Dosage (%)	Temperature (°C)	Duration (min)	Remarks
Washing	Water	200	40		
	Oxalic Acid	0.2		45	
Washing	Water	100			
Neutralization	Water	150	35		
	HCOONa	1.5		20	
	$NaHCO_3$	1		45	pH:5.5
Washing	Water	100	40	30	
Dyeing / Fatliquoring	Water	100	35		
	Anionic Neutralization Syntan	1.5		30	
	Standard Dye / IR Reflecting Dye	3		30	
+	Water	50	55		
	Waterproof Fatliquoring Agent A*	10			
	Waterproof Fatliquoring Agent B**	5			
	Waterproof Fatliquoring Agent C***	3		90	
	HCOOH	0.8		20	
	HCOOH	0.8		30	pH:4
Washing	Water	100			
Metal Capping	Water	200			
	Chromium (%33)	3		60	
Washing	Water	100			
	Water	200			

	Waterproof Fatliquoring Agent C***	1.5		30	
	HCOOH	0.5		20	
Washing	Water	100			

*Waterproof Fatliquoring Agent A : (Milky Emulsion Based on a Combination of Synthetic Fatty Substances)
**Waterproof Fatliquoring Agent B : (Milky Emulsion of an Acrylic-Based Polymer)
***Waterproof Fatliquoring Agent C : (Water Miscible Fluorochemical Compound)

2.2.1.Finishing processes

The leather samples dyed with standard dye were finished with a standard upholstery finishing recipe while the IR reflective dyed samples were finished by using IR reflective pigments according to Table 3.

Table 3: *Finishing recipe of leathers*

Product	**1st Coat**	**2nd Coat**	**3rd Coat**	**Procedure / Remarks**
Water	150	150	50	Drying After 2nd Coat
Binder (Compact)	500	500		Press After 3rd Coat (200 bar, 125 °C, 2 second)
Black Pigment / IR Reflective Black Pigment	100	100		
Binder (PU, Dull)			250	
Binder (PU, Glossy)			100	
Crosslinker (%3)			10	

2.2.3.Tests

The leather samples were exposed to IR radiation by using Rotlichtlampe, Typ IR 150 W lamp and temperatures were measured with a portable IR thermometer (Benetech GM320).

Measurement of static absorption of water (IUP 7) [13] and Determination of volatile matter (IUC 5) [14] analysis were done related to standards to determine the moisture and water content of leathers which were processed with different fatliquoring materials.

3. RESULTS AND DISCUSSION

The Volatile Matter % of leather samples are given in Fig.1. According to the findings, leather samples with waterproof fatliquoring system had the least volatile matter (8.42%), while the combination of natural and synthetic fatty substances (Lecithin) had the most volatile matter % (10.12%). The volatile matter% is also an indication of the moisture content of the leather.

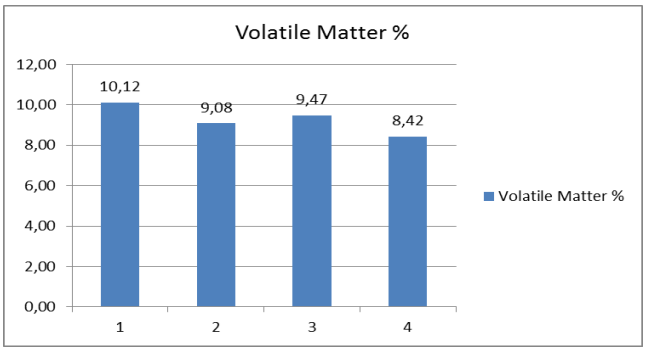

Fig.1: *Volatile Matter% of leather samples with various fatliquoring*

Static water absorptions of leather samples for 30, 60 and 120 minutes are given in Figure 2. At the end of 2 hours, leather samples proccesed with waterproof fatliquoring system had the minimum absorption of 29%. Leathers processed with natural fatliquoring agents, combination of selected natural and synthetic fatty substances (lecithin) and synthetic fatliquoring agent had higher water absorption at the end of 2 hours as 248%, 192% and 149% respectively.

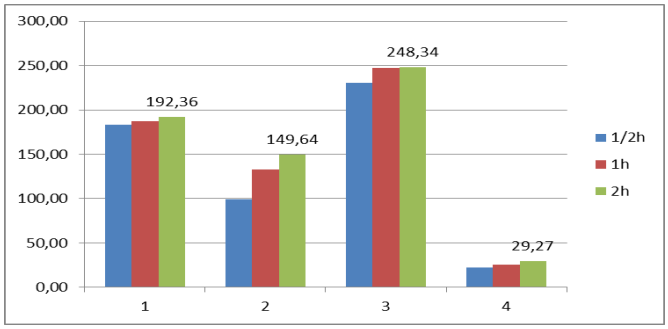

Fig.2: *Static absorption of water %*

The surface temperatures of leather samples dyed with standard dyes and pigments (A) and samples dyed with IR reflective dyes and pigments (B), and further processed with different fatliquoring systems (1-4) are given in Fig. 3. When the surface temperatures of leathers dyed with standard dyes and pigments are investigated, it is seen that waterproof leathers heat up the least 102°C, and all other fatliquoring systems heat up similar around 118°C. This can be related to the moisture content of leathers.

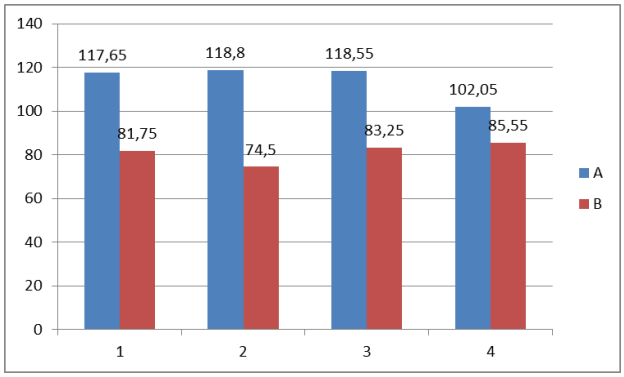

Fig.3: *Surface temperatures of leather samples*

Surface temperatures of leathers dyed with IR reflective dyes and pigments change between 75-86 °C. When the surface temperatures of leathers dyed with IR reflective dyes and pigments (B) are compared with the samples dyed with standard dyes and pigments (A), it is seen that IR reflection theory works and the leathers are cooler. However the temperature relation between moisture content cannot be seen here as seen in standard colours. This can be explained as the cool system works dominantly and take away the fatliquoring process differences.

4. CONCLUSIONS

The fatliquoring materials and system has an important effect on final properties of leathers like softness, physical & mechanical properties, touch properties, water-proofing, etc. [9]. Additionally fatliquoring materials also affect heating properties of leathers. From the findings of

this study, it can be said that waterproofing fatliquors decrease the moisture and water absorption of leathers and they heat up less than standard fatliquors.

IR reflective dyes and pigments can be a solution for heating up problems of dark coloured leathers and leather products. This will ensure higher wearing and usage comfort of leather products without heat complaints of the customer. This technology can be used for car upholstery, steering-wheels, motorcycle upholstery, boots, military, horse-riding, sports & golf. From the test results it is found that leather samples dyed with IR reflective dyes and pigments heat up less than the standard coloured samples, and the leathers stay cooler. However the fatliquoring technology which determines the moisture content of leathers cannot be distinguished when IR reflective dyes and pigments are used. The authors will continue this study on IR reflectance characteristics of leathers, real-time in car tests and effects on aging.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

TANNED LEATHERS PROPERTIES MODIFICATION AS A RESULT OF ARTIFICIAL AGEING

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Abstract: *Leather is a high tech material with different application fields, such as automotive, manufacturing of leatherwear articles or clothing and footwear. Leather is a biomaterial obtained by processing animal skins. Unfortunately, raw animal hides are practically inutilizable, due to their microbiological instability and are affected by rotting. Microbiological stability is achieved by tanning, when the protein is crosslinked, followed by drying. After crosslinking and drying, the new material shows the required properties of sustainability, availability and an esthetically pleasing aspect to the touch, making it available across its entire range of applications. From a structural point of view the animal skins are constituted of collagen, which is a fibrilar protein with a high degree of supramolecular organization in triple helix form that endows softness, elasticity and mechanical strength. High quality standards and lack of toxicity are required in all cases. Leather colour changes during exposure to light radiations are considered a consequence of the presence of some products with weak photochemical resistance during fabrication. The study aims to compare changes in properties of leathers obtained using mineral tanning agents such as Cr III salts and those obtained with the more environment-friendly technology using acid hydrolysis. Accelerated aging studies were conducted on tanned leathers by exposing the samples to UV radiation with different irradiation doses and two wavelengths (254 and 365 nm) under controlled humidity and temperature conditions. Structural changes caused by irradiation were studied by FTIR. Colour changes on the sample surfaces were assessed during irradiation with the CIEL a^*b^* system. The colour parameters variation (L^*, a^*, b^*) and colour differences have been discussed in correlation with structural changes, tanning method and irradiation conditions.*

Keywords: *Bovine skin, Tanning process, Titanium, Leather, UV radiation*

1. INTRODUCTION

Leather is a biomaterial, mostly comprised of collagen and obtained by processing animal skins with various uses, ranging from manufacturing of clothing, footwear and other accesories of daily use [1], [2]. Unfortunately, the raw animal hides are practically inutilizable, due to microbiological instability and rotting. Microbiological stability is achieved by tanning, when the protein is crosslinked, followed by drying. After crosslinking and drying the new material shows the required properties of sustainability, availability [3]. Chromium III salts are the best known tanning agents used for crosslinking of collagen based materials. It is well known that the manufacturing of

leather is one of the most polluting activities due to the inorganic chemical waste levels resulted during chemical operations. Chromium is known as the main source of pollution with heavy metals of the wastewaters resulted from tanning, wet finishing and mechanical processing of leathers. Therefore, the practical significance of chromium-free leather is constantly expanding. Attempts to replace chromium salts in the tanning process of hides with waste resulted from obtaining of ultrapure titanium technology are presented in literature [4], [5], [6]. It is expected that leather should be able to withstand exposure to extreme and varying environmental conditions, such as temperature, light, moisture and mechanical loading, over a series of years. The legal and economic consequences arising from any guarantee declaration force the manufacturers to know the ageing properties of their products and of the materials included in these products.

2. EXPERIMENTAL

2.1. Materials

The synthesis method of Ti–Al tanning agent and the obtaining of wet–white and wet–blue products were described in the literature [3].

2.2. Equipment

Material irradiation

The aging studies were conducted by exposing the leather surface samples (70x40x0.5 mm) to UV radiation up to 200 hours in the air. The samples were irradiated with UV filtred light emitted by two high intensity mercury vapor lamps (model R-52G, and B-100AP, manufactured by Analytik Jena Company, with emission maxima located at 254 and 365 nm.

A PMA 2100 radiometer manufactured by Solar Light Company equipped with PMA 2110 and PMA 2122 detectors with response spectral region 320-400 nm and respectively 249-251 nm was used to measure the irradiance and the irradiation dose during photochemical aging. The irradiance values were 23.3 Wm^{-2} for B-100AP lamp and 4.6 Wm^{-2} for R-52G lamp. Hourly irradiation doses were 36.8 kJm^{-2} for B-100AP lamp and 16.7 kJm^{2} for R52G lamp. These values were measured in irradiation chamber at the level of samples holder.

Colour modifications

Colour modifications during irradiation on the sample surfaces were followed with a Lovibond LC 100, RM 200 model apparatus manufactured by Tintometer Ltd., UK, using a white pellet from $BaSO_4$ as standard. The standard DIN 6174 (Farbmetrische 15 Bestimmung von Farbabständen bei Körperfarben nach der CIELAB-Formel, 1979) has been used for colour evaluation using D65 illuminant and the results in CIELAB ($L^*a^*b^*$) system has been expressed. In CIELAB ($L^*a^*b^*$) the colours are described by parameters L^* which defienes lightness, a^* which denotes the red/green value and b^* for yellow/blue value. The colour differences between the irradiated and non-irradiated samples were calculated with Eq. 1, where ΔL^*, Δa^* and Δb^* are the differences between each parameter after and before irradiation irradiation it is noted.

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad \textbf{(1)}$$

Fourier transform infrared spectroscopy (FTIR)

Through FTIR method one can obtain qualitative and quantitative detailed spectral analyses. The FTIR spectra were recorded with a Bruker Vertex 70 apparatus equipped with a MIRacle accessory designed for single or multi-reflection attenuated total reflectance (ATR). The ATR crystal plate was from diamond and the solid material was put in physical contact with the sampling

area through high pressure clamping for recording the spectra with high-quality and reproducibility. The spectra were recorded in the range 4000-600 cm^{-1} at a spectral resolution of 4 cm^{-1} and 64 scans.

3. RESULTS AND DISCUSSIONS

Structural changes during leather samples exposure to UV radiation were monitored by FTIR spectroscopy (Fig. 1). No significant changes were identified between the FTIR spectra of non-irradiated wet blue and wet white samples. Both the FTIR spectra contain specific vibrations of partially denaturated collagen. Thus, the broad signal in the range 3800 and 3000 cm^{-1} with the peak located at 3315 cm^{-1}, is a complex combination between –NH stretching vibrations from peptide linkages and OH groups of water molecules included in collagen structure.

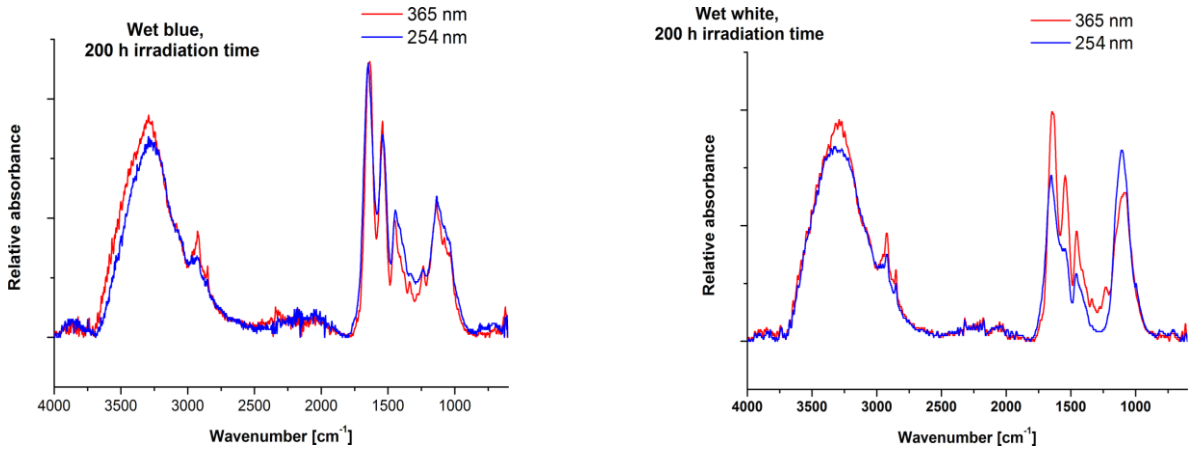
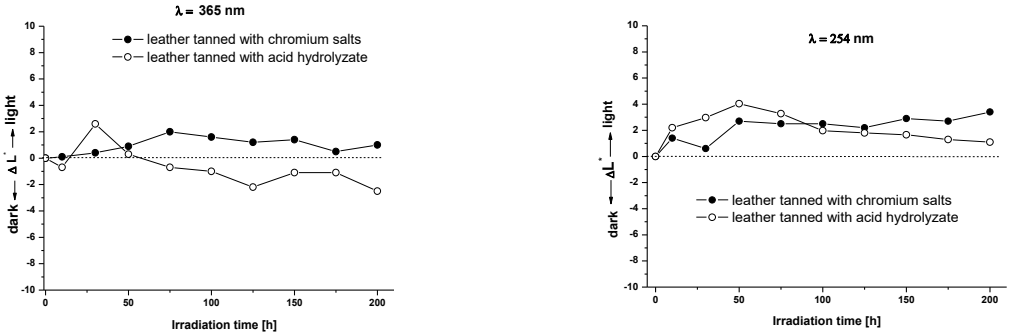


Fig. 1: *ATR-FTIR spectrum of bovine tanned skin*

The peak from 1454 cm^{-1} (Fig. 1a) was assigned to bending of C-H aliphatic groups from collagen structure and fatty acids, included as traces from early processing. The vibrations from 1637 cm^{-1} and 1552 cm^{-1} from Fig. 1(a) are characteristic to the peptide bond. The shifting of the peak from 3315 cm^{-1} to higher wavenumbers was found, regardless of the implied tanning method. The decrease of absorbance and displacement of this singal are indications of hydrogen bonds scission between intermolecular water molecule entities and protein chains. Loss of water molecules by evaporation accompanies the split of hydrogen bonds. Similar aspects were observed for the wet-white leather in Fig. 1(b), however with a more pronounced denaturation of collagen at 254 nm.
Mass losses continously occur during irradiation. In the case of the studied samples the mass losses are between 5 and 8 % after 200 hours irradiation time. These values are dependent on sample type and UV radiation wavelength. Highest mass losses have been recorded for wet blue samples irradiated at λ=254 nm (arround 8 % after 200h exposure time). Lower mass lossess have been recorded for wet blue samples exposed to lower energy UV radiations (λ =365 nm) (around 5 %).
Unlike to the wet blue samples, the wet white samples had comparable mass losses at both wavelengths (4.27% at λ = 365 nm and 3.65 % at λ = 254 nm).

ΔL^* values increase with irradiation time at both wavelengths. At 365 nm samples show similar behavior. The ΔL^* values was below 5 after 200 hours irradiation time. At lower wavelengths (λ=254 nm) the ΔL^* values were higher. The sample tanned with acid hydrolizate is characterized by lower ΔL^* differences. This observation proves a greater sensitivity of leather tanned with acid hydrolyzate. At 254 nm a slight increasing tendency of the lightness factor (L^*) may be observed for

both samples. The acid hydrolyzate tanned leather shows a slight tendency of darkening when the sample was exposed to 365 nm. This behaviour suggests that the wet white leather is more sensitive to photo-oxidation than the wet blue one.



(a) *(b)*

Fig. 2: *Variation of lightness factor differences with irradiation time*

4. CONCLUSIONS

Wet white leather was more sensitive to photo-oxidation than the wet blue one. Samples showed more intense photo-decomposition processes at 254 nm.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

SMART BIOCONVERSION OF PELT WASTE FROM TANNERIES

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Abstract: *The area of interest is the synthesis and study of properties of new types of hydrogels made from pelt waste, in order to recover waste from tanneries. Leather processing in tanneries results in about 500-600 kg of pelt waste from a ton of raw hides.*
These hydrogels are made using smart processes in order to then be applied in agriculture, for preservation of water in the soil or for controlled release of fertilizers, pesticides but also for the development of additivated agricultural film biodegradable over time (between 1 month and 6 months). Hydrogels that are based on biopolymers, compared with hydrogels based on synthetic polymers, have the advantage of biodegradability, biocompatibility, and a low level of toxicity.
The paper presents the production of biodegradable polymer mixtures obtained from hydrolysis and enrichment of the resulting hydrolysate with phosphorus and potassium.
Hydrogels with collagenous structure are tested using a high-performance instrumental analysis system (FT-IR-ATR, UV-VIS-NIR, SEM, EDAX, etc).
The paper presents an experimental model for obtaining hydrogels with collagenous structure from pelt waste resulting from the liming process.

Key words: biopolymers, hydrogels, collagen, tannery, soil.

1. INTRODUCTION

Biopolymers of organic nature are a source of raw materials for agriculture, as protein waste composition provides sufficient elements to improve the composition of degraded soils and plants can harness some elements: nitrogen, calcium, magnesium, sodium, potassium, etc.

This paper presents exploratory research as a starting point to obtain new polymeric complex products - multicomponent - called hydrogels, by processing organic waste with applications in agriculture.

The paper contributes both to the reuse of poor and degraded soils in agriculture and to the recovery of protein waste which is currently disposed of in landfills (processing 1 ton of raw hide results in 75% waste, of which about 50% - approximately 600 Kg - is protein waste that can be used in agriculture) [1-3].

Obtaining hydrogels with collagen structure by pelt waste hydrolysis with applications in agriculture is a novelty, given that collagen is used only in medicine.

Multicomponent absorbent hydrogel-type networks are next generation materials, with three-dimensional structure and high swelling capacity. Hydrogels have a distinct three-dimensional structure [4-7], and although they have a high water content, hydrogels are water-insoluble due to

the crosslinked (physical or chemical) structure of the steric or crystalline linkages. When the hydrogel is in contact with the aqueous solution, there is a swelling thereof.

Hydrogels can be obtained by two major mechanisms: hydrogels with covalent or irreversible links and hydrogels with reversible or physical links [8,9]. The second category includes various subclasses such as ionic interactions (ionic hydrogels or cross-linked polyelectrolyte complexes) and secondary interactions ("entangled" hydrogels, grafted or complexed hydrogels, etc.) [10-11].

In the past decade, interest in different types of gels in areas such as pharmaceuticals, food chemistry, medicine and biotechnology has increased.

2 EXPERIMENTAL

The applications of hydrogels in agriculture aim at water retention in the soil or controlled release of pesticides or fertilizers. In the first case, the application is based on hydrogels' ability to quickly absorb large amounts of water and then release it gradually, supplying plants with water for longer periods after watering the field (rain or irrigation) has ceased.

Currently, most hydrogels are based on synthetic polymers, so this research proposes the use of collagen hydrolysate obtained from pelt waste (HA) and a synthetic copolymer based on polyacrylamide (CAAM).It is known that polyacrylamide is a crosslinked polymer that retains its hydrophilic nature and can absorb a large amount of water and increase its volume. Some of the advantages of hydrogels based on acrylamide include being chemically inert, transparent and stable in a wide range of pH, temperature and ionic strength. CAAM copolymer based on polyacrylamide is a granular anionic polyelectrolyte with high molecular mass produced in Germany.

In this research, synthesis of hydrogels is reported to CAAM and HA by chemical crosslinking using different concentrations and crosslinking agents, polymers of different ratios to determine the effect of variations in the hydrogel and establish the optimal reaction conditions. Then characterization techniques were performed to determine the thermal, structural, morphological and swelling capacity of the hydrogels.

The waste came from fleshing and trimming cattle hides (weight category 35 kg) from SC Pielorex tannery in Jilava, Ilfov County, Romania.

An innovative process is proposed for treating rawhide waste by protein waste hydrolysis in acid or alkaline medium, to obtain a proteinaceous biopolymer which, in combination with other polymers (polyacrylamide, acrylic acid, maleic acid, cellulose, starch, etc.) can be used in agriculture as hydrogels with controlled release of nutrients.

The proposed technological process for obtaining protein hydrogel includes the following:

1. A quantity of 4.5 to 6.0 kg of pelt waste is washed with water at a temperature of 20-25 ^{0} C in a drum for 20-30 minutes (as it is strongly alkaline)

2. Hide waste is then ground using a special grinder (with double knives), yielding a pasty homogenous mass - protein biopolymer.

3. The protein biopolymer is introduced together with 5 to 6.5 % dipotassium hydrogen phosphate (which helps to improve the nutritional properties by the addition of phosphorus and potassium) in an autoclave equipped with heating jacket and agitator. The mixture is stirred for 60-120 min at 85-96 ^{0} C

4. Then to this mixture an amount of 18 to 25 % of a synthetic polymer based on polyacrylamide is introduced and stirring is continued for 120-180 minutes.

5. 0.5-1% boric acid is added and the mixture is removed from the autoclave in plastic drums.

Depending on the fertilizer particle structure, the resulting hydrogel may form the matrix where the fertilizer is embedded or the coating for the solid fertilizer (mono- or multi-layered particles).

2. RESULTS AND DISCUSSIONS

A hydrogel is defined as a polymer network which has the property of absorbing large amounts of solvent causing macroscopic changes in the dimensions of the polymer. The most important property of hydrogels is their degree of swelling as well as dissolution and gradual release of water and nutrients needed for plant growth.

Hydrogels reduce water consumption and irrigation allotted time by 70 %. The hydrogel is an organic soil conditioning substance, which retains the water and diluted nutrients necessary to these plants. Hydrogel in an optimum amount helps plant growth by releasing the necessary water and nutrients.

Hydrogel binds the water and nutrients in the water and continuously provides them to the roots of the plants.

Table 1. *Physical-chemical analyses of hydrogel*

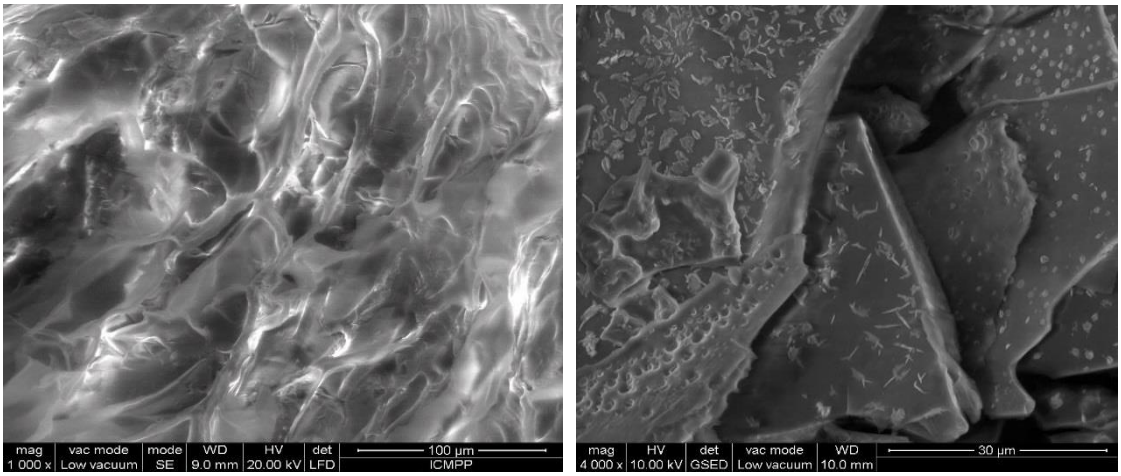
No.	Specification of components	UM	Values reported to relative humidity upon release
1	Total nitrogen (Nt)	%	12,74
2	Phosphorus (P_2O_5)	%	3,64
3	Potassium (K_2O)	%	6,18
4	Sodium (Na_2O)	%	0,37
5	pH	pH units	6,8

- K_2O and Na_2O were determined by atomic emission spectrophotometry
- P2O5 was determined by molecular absorption spectrophotometry
- Nt -mineralization and distillation by the Kjeldahl method

Chemical analysis of collagen structure hydrogel for field experiments resulted in $N_{12}P_9K_{12}$ composition (12.74% total nitrogen, phosphorus, 3.64% P_2O_5, potassium K_2O_5 6.18%)(**Table1**).

Hydrogels were studied in terms of structure and composition using modern instrumental methods. Hydrogels obtained both at laboratory and pilot scale were analyzed using modern equipment at INCDTP and ICMPP-Petru Poni Iasi.

SEM-EDAX micrographs of collagen hydrogels with encapsulated nutrients for soil fertilization, wherein the fibrillar collagen structure is observed, showing crystals of nutrients - phosphorus, potassium, magnesium, etc. are shown in Figures 1 and 2.



2000x 4000x

Fig.1. *SEM micrographs of hydrogel with encapsulated nutrients*

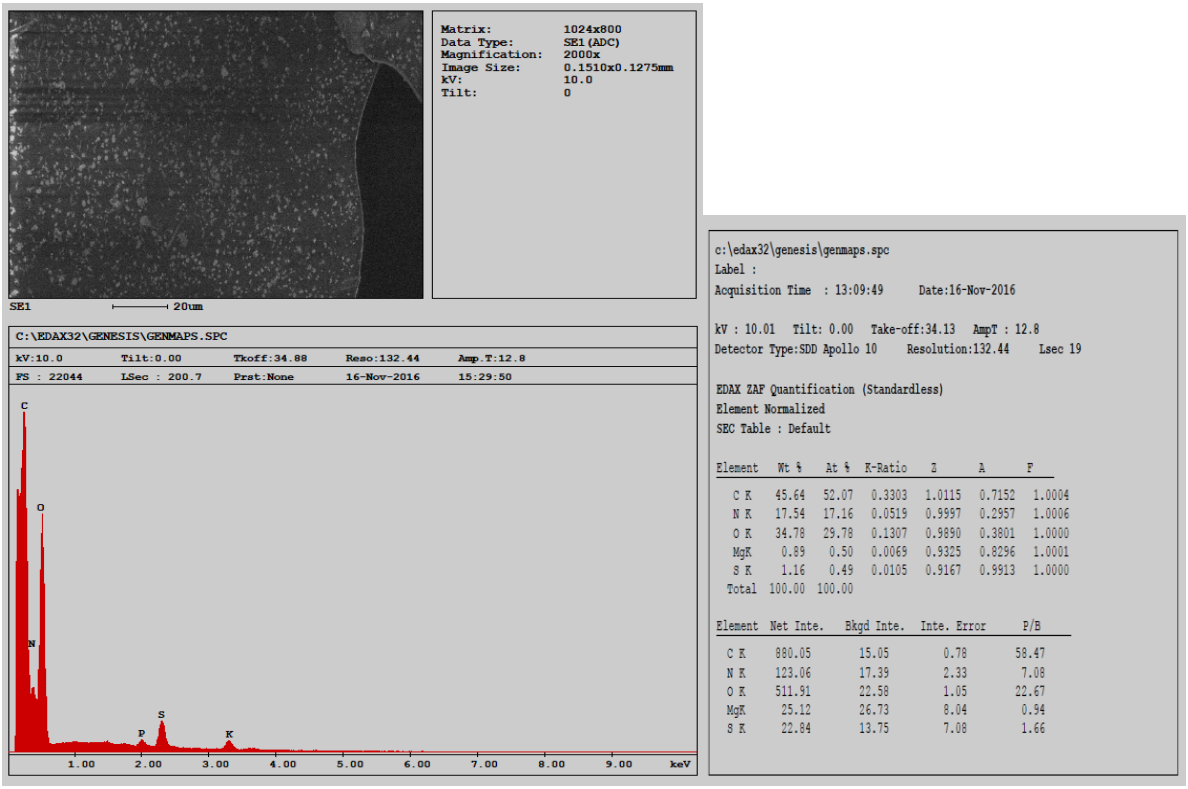


Fig.2. *EDAX analysis of the structural composition of the hydrogel*

In order to highlight the structural changes in the hydrolysis process and the interaction with various synthetic polymers, attenuated total reflectance spectrophotometer FT/IR-ATR Perkin Elmer, USA was used. As Figure 6 shows, all bands specific to the polypeptide matrix of collagen can be identified, such as those at 1658 cm^{-1} and 1541 cm^{-1} (amide I and amide II bands, respectively), while those at 3406 cm^{-1} and 1030 cm^{-1} indicate the C-N bond.

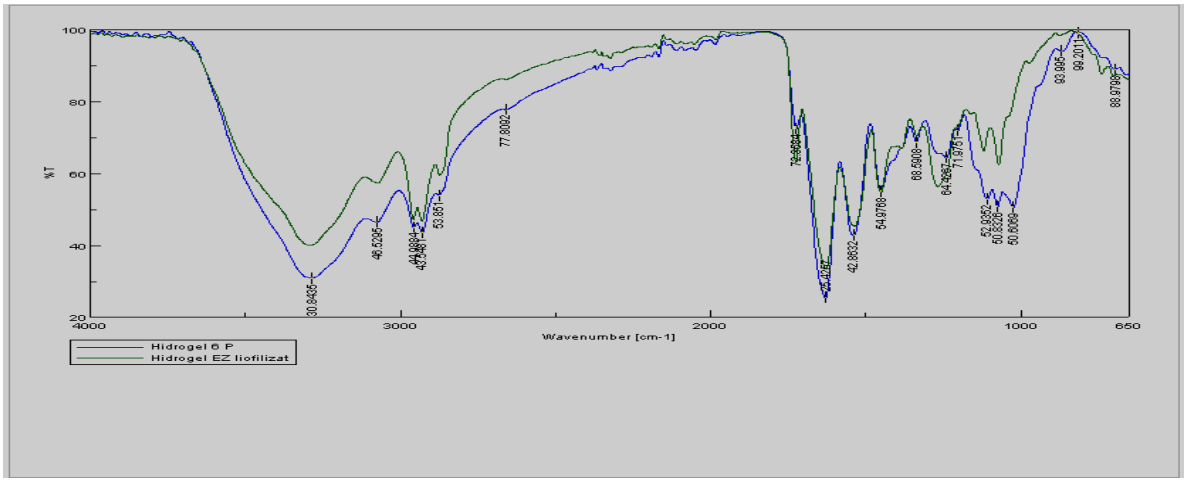


Fig.3: *IR spectra for hydrogels*

The difficulty in interpretation of spectral diagrams arises due to the structural complexity of collagen compositions and the use of trace elements, which have chemical affinity for the same functional groups of the respective macrostructure.Thus, the presence of collagen and acrylamide is confirmed in the molecular structure of the hydrogel.

4. CONCLUSIONS

The paper presented in detail two framework technological pilot-scale processes, of the direct hydrolysis of pelt waste

Hydrogels obtained both at laboratory and pilot scale were studied in terms of structure and composition using modern instrumental methods **(**optical microscopy, scanning electron microscopy SEM-EDAX, FT/IR-ATR, Differential Scanning Calorimetry (DSC)).

In conclusion, the obtained hydrogels show encapsulation of nutrients and the emergence of cross-linking junctions with macro- and microelements introduced in the direct hydrolysis reaction. This confirms the presence of collagen and acrylamide into the molecular structure of the hydrogel by forming collagen-polyacrylamide compounds.

ACKNOWLEDGEMENT

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

RECYCLED TEXTILES USED IN AUTOMOTIVE INTERIORS. CASE STUDY- FORD MOTOR COMPANY

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Abstract: *The environmental movement is affecting all industries, but the textile and automotive industries are two of the few that are constantly being criticized. The automotive industry is the subject of much research, it is the largest manufacturing activity, there is a complex supply chain, is resource intensive and emits various hazardous gases and waste products. The article reviews the current state of automotive industry regarding the textile application. Automotive textiles have been classified as belonging to a category called "Mobiltech" which is one of the main streams of technical textiles. The term means all type of textile components e.g. fibers, filaments, yarns and the fabric used in automobiles. They are classed as technical textile because of the very high performance specifications and special properties required, different from those used in clothing and other applications. The performance of the automotive textiles depends on the fibre properties, fabric structures and various finishes used in the manufacturing processes. After a short presentation of used fibres in car interiors, with advantages and disadvantages it is presented the sustainable textile solutions for the automotive industry. The paper focuses in particular of the use of recycling of textile waste to highlight how the processes of recycled textiles and sustainable textiles production are linked in the automotive sector. A case study with Ford Motor Company outlines and examines their design, development and manufacture process for automotive textiles for car seat coverings and interiors*

Key words: *Recycling, Automotive, Textile, Car interior, Polyester*

1. INTRODUCTION

The environmental movement is affecting all industries, but the textile and automotive industries are two of the few that are constantly being criticized. The primary environmental concerns associated with textile are water use and pollution, hazardous chemicals use, energy use, and solid waste. The main environmental issues associated with automobiles are fuel efficiency and. air pollution and greenhouse gases that climate scientists say are driving global warming. With customer pressure and regulatory constraints for more fuel-efficient and safer vehicles, the automotive industry play a decisive role in driving innovation and reducing environmental and social externalities of vehicles.

2. CURRENT AUTOMOTIVE TEXTILE STAGE

The automotive industry is perhaps one of the leading when it comes to trying new materials in high volume production.The automotive industry is the subject of much research, it is the largest manufacturing activity, there is a complex supply chain, is resource intensive and emits various

hazardous gases and waste products. It employs about 9 million people involved in making 60 million vehicles, about 5 percent of global manufacturing jobs, and 50 million jobs connected indirectly to the auto industry [1].

As automobiles have become more sophisticated and capable, they have also become more complex. A typical modern vehicle might contain up to 10,000 different parts made of about 1,000 different types of materials that in turn are made from about 10,000 different chemical substances [2]. The automotive industry is one of the largest single markets for automotive textiles. The percentage of textile material used in a motor car is 2.2% of the overall weight of the car [3].

Technical textiles are broadly used in transportation vehicles. Given the rise of the automotive industry and the fact that for the modern car today, uses about 20 to 26 kgs of textiles fabric for interior and exterior purposes [4]. Almost two third of the automobile textiles are for interior trim, i.e. seat cover, carpets and roof and door liners and the rest is utilized to reinforce tyres, hoses, safety belts, air bags, etc .

Automotive textiles have been classified as belonging to a category called "Mobiltech" which is one of the main streams of technical textiles. The term means all type of textile components e.g. fibers, filaments, yarns and the fabric used in automobiles. They are classed as technical textile because of the very high performance specifications and special properties required, different from those used in clothing and other applications. The performance of these automotive textiles depends on the fibre properties, fabric structures and various finishes used in the manufacturing processes.

The main criteria involved in the development of textiles and components in automotive are: tensile strength, abrasion and pill resistance, air permeability, compression resistance, elasticity, light fastness at high temperatures, stiffness, ease of cleaning, separation force, dimensional stability, flame resistance, anti-fogging resistant, resistance to adverse climatic conditions. The others processing requirements are mouldability, susceptibility to compression, sewability [5].

Table 1: *Fibe used in car interiors, advantages and disadvantages[8,9,10,11]*

Fibre	**Application**	%	Properties
Nylon, polyester, polypropylene	Carpets (Including Car Mats)	33.3	Light fastness, mouldability, ease of cleaning, thermal and acoustic protection, relatively inexpensive; Disadvantage: Limited compressed resilience of polyester;
Polyester fabric (woven/knitted), nylon,polypropylen wool/polyester	Upholstery (Seating Fabric)	18	Abrasion and UV resistance, attractive design and texture; Disadvantage: Low moisture absorbancy of polyester;
Panox (UCF), Aramid (Nomex, Kevlar-DuPont), Inidex (Courtaulds)	Seat fire barriers	14	Very high FR including restrictions of heat release, toxicity and opacity of fumes;
Polyester, nylon 6	Tyres	12.8	- good thermal absorption, -UV resistance poor unless stabilized;
Polypropylene, nylon polyester	Door trim	9.4	Abrasion and UV resistance, attractive design and texture;
Polyester blends	Luggage carrier liners		UV resistance, decorative and functional, relatively inexpensive;
Polyester , PVC foil	Sunvisor		

Polyester	Seat belts	8.8	Tensile strength, extension(up to 25-30%), abrasion and UV resistance;
Nylon 6,6 multifilament yarns	Airbags	3.7	Resistance to high temperature, inflation gases, durability to storage over many years, tear strength, thermal absorption;

Now almost 90% of the fibres used in car seats are polyester [6]. The excellent UV degradation resistance of polyester combined with very good abrasion resistance and relatively inexpensive price ensure that it will keep its prominent position among the available fibres, even if the low water absorbency can result in thermal discomfort. Although this fibre however requires having UV light-absorbing chemicals are added to the dyebath to pass modern rigorous standards of durability. The use of natural fibres in the production of textile materials for automotive interiors is limited in the main to wool. Wool is used in luxury and up-market cars [7]. (see Table 1). In the drive towards lowering weight for reducing both fuel consumption and CO2 emissions, many current developments are including new uses for fabrics, and by 2020, it is predicted that the same sized car will contain 35 kg of textiles [12]. The global consumption of textiles used in automobile industry is estimated to be over 4.5 hundred thousand tonnes.

Automotive textiles are used for enhanced aesthetic of automotives [13] and for sensual comfort and safety. Additionally, few textile products found their applications as design solutions to engineering problems in the form of composites, tyre reinforcement, sound insulation and vibration control [14].

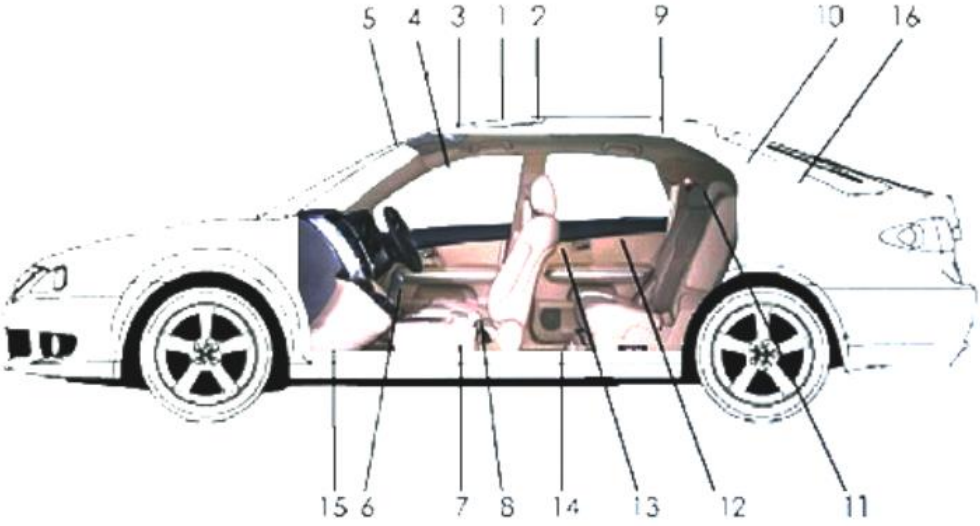

Fig. 1*: Applications of textiles in car (Sunroof-1,headliner-2,convertible tops-3, sunvisor-4,column padding-5, composite panel-6, seat belt anchorage cover-7, seat belt-8,inside roof lining-9, seat cover lining-10, upholstery-11, Insulation-12, windows frames-1, carpet-14,carpet backing-15,rearshelf panel-16) [17]*

The use of textiles (figure 1) in automotive applications includes visible components like floor coverings; upholstery; safety belts; and not visible to the viewers textile materials. The not visible textile materials are mainly used for their functional purpose, and are known as concealed components: tubes and tapes; tyre cord; airbags; components; and filters.

It is estimated that approximately 45 m^2 of textile material is used in the average car for

interior trim, which includes: seats, headliners, side panels, carpets, trunks, door trim, dash mat [15]. There are about 3.5– 4.5 m^2 of carpet in each car, made by either tufting or needle-punching with considerable differences depending on where in the world the car is made. In Western Europe approximately one-third of all cars have carpets tufted mainly from bulked continuous filament (BCF) nylon yarns since in the USA, at present, all car carpets are tufted mainly from BCF nylon [16].

2. CASE STUDY- FORD MOTOR COMPANY

2.1. Ford Motor Company Bussines

Henry Ford did not invent the car, but the motor industry did not really take off until he produced an automobile that was within the economic reach of the average. Out of his determination came in 1908 at Detroit the mass-production assembly line, and in 1913 at Old Trafford, Manchesterhe his Model T Ford and - two innovations that revolutionized American society and molded the world we live in today.

Ford Motor Company, a global automotive industry leader based in Dearborn, Mich., manufactures or distributes automobiles across six continents. With about *201,000* employees and about 62 plants worldwide, the company's core business includes designing, manufacturing, marketing, and servicing a full line of Ford cars, trucks, and SUVs, as well as Lincoln luxury vehicles. The company provides financial services through Ford Motor Credit Company.[18]

2.2. Ford Motor Company Sustainability

Ford Motor Company has been a leader in the use of recycled materials, starting in 2008 with the upholstery in the Ford Escape hybrid. The company has been working for many years to increase the use of recycled and renewable materials and to reduce the use of unwanted materials. Vehicles in the USA are composed of 20-25% post-consumer recycled material by weight, for the most part due to the extensive use of metals with recycled content.

With each global vehicle program, Ford has been able to increase its use of sustainable fabrics by researching new technologies and identifying suppliers that share its commitment to sustainability. At the beginning Ford had to go outside the auto industry to find a textile manufacturer capable of producing recycled fabric. Now, Ford have teamed up with one of the world's largest and leading organisations involved in sustainable textile solutions, Unifi Inc.[19]

Since 2011, Unifi Company launched its „textile take-back" program in which it obtine fabric scraps from textile manufacturers and using them in REPREVE, a polyester fiber containing recycled materials that have the same look, feel, and performance of virgin polyester fibers. Five major apparel customers — Eddie Bauer, Quiksilver, North Face, Patagonia and Polartec — sell outdoor and sportswear featuring REPREVE. Wal-Mart Stores Inc., Haggar, Sears and Cintas are working with Unifi on Repreve apparel programs but Ford is the only automanufacturer to use this material in its vehicles.

Through their global materials strategy, Ford are increasingly using materials that are more sustainable from a total life cycle perspective, including recycled, renewable and recyclable materials, and working to decrease or eliminate less sustainable materials.

Since the 2009 model year, the seat fabrics in most of new or redesigned Ford vehicles have been made from at least 25 percent post-industrial or post-consumer recycled content. Fifty different fabrics meeting the requirements have been developed and incorporated into 12 Ford vehicles. In addition, many of the non-woven headliner fabrics now contain 50 percent to 75 percent recycled yarns, depending on the color.[20]

Besides Unifi Company, Ford is also working with other innovative companies like Sage Automotive Interiors, based in Greenville, S.C., and Unifi, in Greensboro, N.C., to accelerate development of recycled fabrics. Other recycled items in the Modell Fusion 2013 include soy-based foam in seat cushions; plastic underbody panels made from recycled car battery casings, and sound-absorption materials made from old denim [21]. F-Series trucks used eco-friendly materials like soybeans to make seat cushions, seat backs and head restraints and post-industrial recycled cotton. one 2014 Ford F-150 truck uses the equivalent of about 10 pairs of jeans, 26 bath towels or 31 T-shirts as carpet insulation or sound absorber [22].

Rice hulls are the latest sustainable material used in Ford F-150; the hulls reinforce plastic used in an electrical harness in 2014 F-150. Some F-150 trucks have cylinder head covers made with EcoLon, a nylon resin produced from 100 percent post-consumer recycled carpet**.** A thermoplastic material made from recycled tires and post-consumer recycled polypropylene is used to make shields and some underbody covers on F-150.

While it's a good green message to get out, Ford also happens to save, by its own calculations, approximately 4.5 million USD by recycling materials.

3. CONCLUSIONS

Car manufacturing is a material-intensive process that is impacted by growing resource scarcity and the increasing prices of critical materials.

It is a challange for textile supplier to work with the automotive industry, with its higly complex development process. Appart of the aesthetic requirmetnt, there are many technical regulations and demands: the material should exude quality and harmony, should look the same after tree-four years, will age in a homogeneus way, be easy to clean, whitout smell etc. Aditionally the materials have to fulfil the EPS (Environmental Priority Strategy) and the materials and chemicals containing substances listed in the Restricted Substance Management Standard must not be used.

Ford is currently using REPREVE, a 100% recycled polyester yarn made from both post-consumer and post-industrial waste, in five vehicles around the world, making it a truly global material. It represents Ford's larger commitment to reduce, reuse and recycle as part of the company's global sustainability strategy to lessen its environmental footprint.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

BRIEF CONSIDERATIONS ON THE RIGHTS AND WORKING CONDITIONS OF EMPLOYEES IN THE TEXTILE AND CLOTHING INDUSTRY GLOBALLY AND IN ROMANIA

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Abstract: *It is well known that the textile and clothing industry plays an extremely important role in the global context, being one of the most powerful industries, which is capable of generating a turnover of billions of EUR. A fundamental part of the manufacturing process is represented by the employees that have an essential place in each step of the value chain, from fibre to fabric to ready-to-use product. The majority of the companies in this domain use the "lohn" system, which means that, first of all, that they redirect their attention to the countries which offer a cheap manpower. As a consequence, countries such as Romania lose their own identity regarding their own brands, becoming just a so considered minor player in the textile and clothing industry, but having the significant role of producing for the big companies of the world.*
The aim of this paper is to point out the great importance of the people who work in this industry, from the unqualified personnel to the qualified one, because each of one has a specific role in the manufacturing process, and also to emphasize that companies should not minimize this fact; on the contrary, besides worrying only about the profit, attention should be focused primarily on employees, in order to create optimal working conditions, to respect the fundamental human rights and to provide wages proportionally with the work-hours.

Key words: *wages, sweatshop conditions, long working hours, overtime practices, safety*.

1. INTRODUCTION

The textile and clothing industry worldwide shows that it has enormous potential and important amounts of money are involved in it. Globally, there are million of people who work in this area, but many of them work in bad conditions and are not paid as they should really be, this phenomenon prevailing in countries where the "lohn" system has developed and where the wages are very low.

In 2015, at the European level, the overall size of the Textile & Clothing industry in the EU-28 reflected a turnover of 169 billion € and also investments of around 4 billion €. When talking about the number of employees, thanks to the revival of the EU activity, the approximately 174,000 companies still employ over 1.7 million workers [1].

For the last 25 years now, the Romanian textile industry struggles to remain balanced, but local producers have not managed to perform with any brand, the market being flooded with foreign retailers which require their own brands.

After 1990, the textile industry in Romania has somehow lost its identity. Even if during the communist era, Romania was known as one of the most popular destinations of production for major brands, nowadays many factories went bankrupt or were swallowed by the big foreign producers.

2. CHALLENGES FACED BY THE WORKERS IN THE TEXTILE INDUSTRY WORLDWIDE

From the very beginning, we can state that the working conditions in the textile industry are not the easiest ones, and employees have to face a series of serious problems, such as:

- long working hours, exceeding the normal schedule;
- low or even very low wages;
- non-compliance with the workers' legal rights;
- the lack of individual labor contracts.

When the working environment is difficult or even dangerous for the employees, we talk about sweatshop (or sweat factory), to express the fact that workers have to stay more hours at their jobs, which, of course, is very unpleasant as these extra hours are either not paid at all or are being paid inappropriately.

So, the main problems are:

- poor working conditions, the so called "sweatshop" conditions, defined in long working hours every day, having to stay overtime at job and the income is not sufficient according to the hours of work; moreover, there are cases when people work even in the nights or in the weekends, without having enough time to rest;
- poor working conditions from the point of view of infrastructure; the bigger and bigger demand on the market of textiles and clothing has led to finding new places/buildings to work in, many of which were not designed for this type of activity. Also, often the machinery used is not as safe as it should be because in many cases is very old and has not been replaced for years. There are also cases when workers do not use the appropriate protective equipment and do not have the possibility to air the places in which they work, which, of course, is very dangerous for their health;
- low or very low wages, not according to the time of work and usually workers are paid by piece;

In other cases, the following have been pointed out:

- discrimination when it comes to genders (females are preferred);
- discrimination between females, for example, unmarried women are preferred; also, there are cases when women are obliged to sign an agreement not to get pregnant as long as they work at the factory. Moreover, there can be situations when pregnant workers suffer verbal abuse, higher production rates, longer work hours and more difficult tasks such as standing instead sitting or working in a hotter area;
- the forced labor;
- the lack of the freedom to associate; in some cases, employers even use physical violence against employees in order to stop them from starting riots or strikes;
- the child labor.

The worst global problem that has been reported is the one from Asia, where the working conditions are so burdensome, that the job in the textile industry is usually seen as "slave labor".

In many countries which suffer from poverty, the textile and clothing industries are considered a loophole, a helping hand for the poor people who at least have the possibility to earn a certain income, even it often is a small one, but first of all, the great benefit is the one of detaining a job as safe as possible. Unfortunately, from this situation of need which characterizes the population, arise the benefits for the companies, which take advantage of the fact that people in need accept any

type of working conditions and of wages only to gain something. The purpose of the companies is to make manufacturers lower their production costs and to produce goods as quickly as possible.

Let's take, for example, Bangladesh, where the textile and clothing industry is the most important of the country, with approximately 86% of all exports; here, the wages are extremely low, but exactly this lead to the flourishing of this industry. Also, Bangladesh is world's second-largest garment exporter after China, with 60% of its clothes going to Europe and 23% to the US [2]. In Bangladesh, as in other countries as well, there are many people who work from home, the Bangladesh Home Workers' Association estimated that there are millions of home-based garment workers, because entire rural families are involved in the traditional embroidery work [3].

Because of the availability of raw materials and a large market, the textile and clothing industry in India has become the second largest provider of employment in this country; Pakistan is the fourth largest producer of cotton in the world; in the meanwhile the textile, leather products and footwear sectors - all combined - represented the fourth largest contributor to the manufacturing industry in Indonesia, with a market share of 7.8% for the quarter ending December 2013 [2].

In Europe, the textile and clothing industries still play an important role for the economy of the states, the European Union being the world's largest second exporter

Exact and recent data about the rate of employment in textile industry is very hard to find, as there are so many small and medium companies in this domain, and they do not always report the real number of employees, as they are in continuous change at this level.

Table 1: *Employment in the textile and clothing industry [4].*

Country	**Employment in textiles industry**	**Employment in clothing industry**	**Total employment in textiles and clothing industries**	**Year**
China	6 700 000	4 501 100	11 201 100	2010
India	1 379 264	862 689	2 241 953	2009
Vietnam	195 551	844 069	1 039 620	2010
Brazil	308 155	671 356	979 511	2010
Indonesia	498 005	464 777	962 782	2009
Thailand	311 554	345 835	657 389	2006
Turkey	265 957	329 584	595 541	2009
Pakistan	438 657	62 388	501 045	2006
United States	290 804	130 340	421 144	2008
Italy	182 177	199 001	381 178	2008–09
Sri Lanka	35 264	260 308	295 572	2010
Japan	137 772	137 665	275 437	2010
Mexico	83 674	163 118	246 792	2010
Egypt	130 815	103 268	234 083	2010
Taiwan (China)	114 253	87 261	201 514	2006
Romania	27 763	154 547	182 310	2010
Republic of Korea	87 868	76 701	164 569	2008
Morocco	34 026	129 508	163 534	2010
Poland	49 688	109 253	158 941	2009
Portugal	47 463	97 516	144 979	2009
Philippines	16 853	105 875	122 728	2008
Germany	76 676	43 775	120 451	2009
Bulgaria	11 631	99 998	111 629	2010
Spain	43 948	62 181	106 129	2009

France	49 002	48 701	97 703	2009
Malaysia	29 982	54 512	84 494	2010
United Kingdom	55 250	28 056	83 306	2009
Jordan	3 797	33 683	37 480	2010

Source: UNIDO: International Yearbook of Industrial Statistics, Vienna, 2013.

3. INTERNATIONAL LEGAL ASPECTS REGARDING WAGES IN THE TEXTILE AND CLOTHING INDUSTRY

The International Labor Organization (ILC) adopted the following Conventions and Recommendations, which reffer to the textile and clothing industry [4]:

- Protection of Wages Convention, 1949 (No. 95) and Recommendation, 1949 (No. 85)
- Minimum Wage Fixing Convention, 1970 (No. 131) and Recommendation, 1970 (No. 135)
- Protection of Workers' Claims (Employer's Insolvency) Convention, 1992 (No. 173) and Recommendation 1992 (No. 180)

The first one, the Convention No. 95 and its accompanying Recommendation No. 85 on the protection of wages point out the “forms and manners (where, when, how) of the payment of wages, to provide the fullest possible protection to workers”, while Convention No. 173 and its accompanying Recommendation No. 180 include “provisions on wage protection in cases of the insolvency or closing down of an enterprise” [4].

The second one, the Convention No. 131, requires states “to establish a system of minimum wages which covers all groups of wage earners whose terms of employment are such that coverage would be appropriate”. In taking this action, states have to take into consideration “the needs of workers and their families, taking into account the general level of wages in the country, the cost of living, social security benefits, and the relative living standards of other social groups”, as well as “economic factors, including the requirements of economic development, levels of productivity and the desirability of attaining and maintaining a high level of employment”. To ensure the application of the minimum wages provisions, “appropriate measures, such as adequate inspection reinforced by other measures” are being imposed [4]. The role of the Recommendation No. 135 is to supplement the provisions of the Convention mentioned before, by presenting some mechanisms that can be used to set minimum wage rates.

4. THE WORKERS’ SITUATION IN ROMANIA

Romania’s textile and clothing industry is one of the most important in our country, being a real support for the national economy.

Romania is the second largest employer in textile and fashion sector in the European Union, a sector which includes mainly small and medium enterprises and in general women are more preffered than men [5].

The peak was reached in 2004, when the statistics show that there were 450,000 employees in Romania [6].

Wages in the textile industry were located on a slightly upward trend, increasing gradually in recent years, but this was due to the increase in the minimum wage and less labor market developments, although production of lohn garments gain magnitude increasingly. Although the minimum wage changed from 1 February 2017 to 1,450 lei, small wage increases are expected in the textile industry

The 9,700 companies in Romanian textile industry have more than 250,000 employees. And 70% of production is under the lohn system, according to industry employers' federation, cited by

Wall-Street.ro. Zara, H & M, Louis Vuitton, Armani are just some of the fashion companies working with factories in Romania.

In Romania, the lohn production is represented by foreign companies that choose to open production places and make garments locally and later export them for marketing abroad. This process has gradually led to the decrease of the domestic production, which had suffered from the disappearance of Romanian suppliers of raw materials.

In other words, in the field of the textile and clothing, Romania has declined in recent years, and the only sector that was developed was that of the lohn production, which is characterized primarily by cheap and unqualified personnel.

The most commom salary in a manufacturing textile factory is the minimum wage. Sometimes, performance bonuses are added, depending on the number of products shipped, overtime and bonuses for night or weekend. Employees can benefit from meal tickets or transportation provided. Depending on this, employees can achieve a net salary of between 1,100 and 1,700 lei, but not many are those who come to collect at the end more than 1,200 lei.

Regarding the wage of skilled workers, technicians can earn up to 2,100 lei monthly and the salary of the operators who work with numerical control (CNC) may also be 2,500 lei. Currently, all companies in the textile focus on application of the minimum wage, but there are pressures on the cost of labor for those working in the lohn system, that restricts salary increases, while maintaining a competitive price.

If referring to the working conditions, Romanian employees complain about:

- low wages, not sufficient for a decent living;
- illegal overtime practices, the overtime is not organised officially and is not paid at the legally rate;
- the working conditions are not healthy, by the contrary, they are dangerous for the employees;
- the lack of strong unions that would have the possibility to pretend increases of wages;
- short-time labor contracts.

The rights and obligations concerning the employment relationship between the employer and the employee are established by law through negotiations under collective agreements and individual employment contracts.

According to article 39 of the Romanian Labor Code, employees' rights are [7]:

- the right to remuneration for their work;
- right to daily and weekly rest;
- the right to annual leave;
- the right to equal opportunities and treatment;
- the right to dignity at work;
- the right to safety and health at work;
- right of access to vocational training;
- right to information and consultation;
- right to take part in the determination and improvement of working conditions and working environment;
- the right to protection in case of dismissal;
- the right to collective bargaining;
- the right to participate in collective actions;
- the right to form or join a union;
- other rights provided by law or collective agreements.

5. CONCLUSIONS

The global textile and clothing industry is one of the most important sectors of the global economy that creates jobs for million of people all over the world. The reality of this industry is that many employees work long hours under poor conditions for low wages. There exist many unacceptable working conditions, like long working hours and forced overtime. Employees normally have to work between 10 to 12 hours, sometimes 16 to 18 hours a day, but when a factory faces order deadlines, working hours get longer. Also, workers worry about their health and safety at the workplace, as they have to work in inadequate places. What is extremely important is the changing of all these, which can only be obtained by employers' awareness of these issues and also the existence of stable legal provisions is compulsory.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A CRITICAL AND COMPARATIVE ANALYSIS OF THE INDUSTRIAL CORPORATIONS IN THEIR EVOLUTIONARY DYNAMIC

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Abstract: *Since the 2000s, a series of mergers and acquisitions of brand at industrial corporations' level has been observed in the global industry landscape, and an even more pronounced dynamism was manifested in Europe. The wave of mergers and acquisitions continues nowadays, when the concentration of the dominant "actors" on the industrial stage is followed by a similar process of creating enterprises able to compete with the first ones, either by the size of production or financial strength, or by innovativeness and introduction of new and competitive products. The existence of the Common Market and the EU on our continent has contributed enormously to the process of restructuring the "old" Europe.*
In the first phase of the European construction, the stage where national markets were still dominant, but there could be noticed a serious growth of competition, in Europe there has been produced a huge wave of mergers, for many surprising. Once with the consolidation of the European Community, a new phase begins, in which enterprises begin to adopt "continental" strategies and policies, reasoning according to the logic of a market area. Through international mergers means, is implemented a strategy that adapts the minimization of costs and simultaneously an insurance policy against a future possible currency devaluation. Today we are witnessing the third stage, with rules that tend quickly towards a complete unification and a single currency. The agreements between the European enterprises can be considered favorable because they often lead to high levels of efficiency without decreasing elements that make them competitive.

Key words: *system production, competitiveness, merge, enterprise, market.*

1. INTRODUCTION

With the strengthening of the new economic Europe and the start of harmonizing the administrative-economic rules and the discipline competition, begins a new phase in which companies adopt a continental strategy and they are beginning to act according to a unique market logic. International mergers are realized, and enterprises implement strategies in order to minimize costs and simultaneously are heading a policy of insurance against the risks of currency depreciation.

The current industrial reorganization is primarily due to a strong activism of the major groups. The fundamental critique resource of all these corporations is defined by their ability to respond to competitive market dynamics by adapting their continuous production systems and technologies used and also by an efficient management of human resources and leadership. The textile and clothing sector is one of the most important of areas in the European manufacturing

industry. At the level of the European Union, approximately 1.7 million people are working in this particular field, fact which has the ability to generate a turnover of EUR 166 billion [1].

2. A CRITICAL COMPARATIVE ANALYSIS OF INDUSTRIAL CORPORATIONS

The critical comparative analysis of the industrial corporations is based on the following criteria:

- The performance of the production system adopted by the corporation,
- The anthropocentric orientation of the corporate management,
- The flexibility of the organizational model adopted by the corporate management,
- The control system adopted by the corporate management.

2.1. The comparative analysis of the production systems by specific characteristics

The comparative approach of the usual five production systems that characterize the industrial corporations is presented in Table.1., which summarizes, on a number of common features, six different levels for each type of production system.

Table 1: *Comparing different production systems adopted in corporations*

Characteristic features	**Corporate production systems**				
	Manufacturing (MF)	Pure fordist (FP)	Neofordist (NF)	Economical (E)	Neomanufacturing (NM)
Division of labour	Reduced	High, by managers	High, by managers	High, by team-work	Reduced
Duties area	Large	Narrow	Narrow	Moderate	Large
Team-work	Moderate	Reduced	Reduced	Extended	Extended
Size of stocks	Big	Moderate	Big	Small	Small
Buffer facilities	Big	Reduced	Big	Reduced	Reduced
Area of fixes	Integrated	Small	Big	Very small	Very small, integrated

By comparison, it appears that the pure Fordist system (FP) is similar to the economic system (E), while differences between the Fordist and the neofordist systems are much obvious. If we represent the distribution of the four types of production systems under a matrix form, according to the degree of adaptability to the changing offer and depending on the volume of production which makes an efficient system, is obtained: [2]

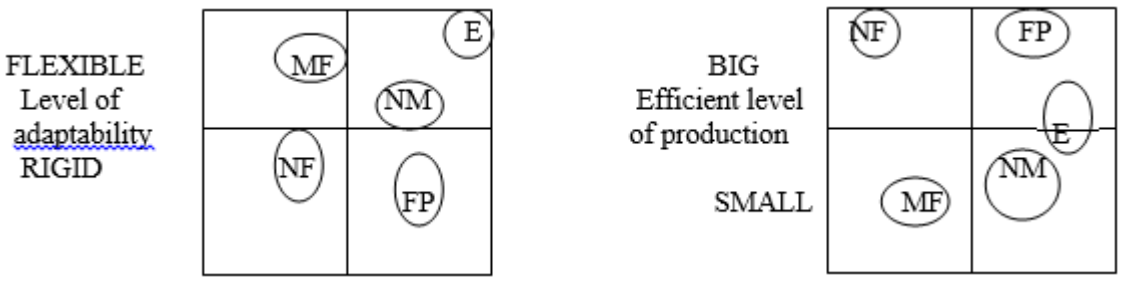

Fig. 1: *Comparison of the efficiency of the production system types*
(Krafick adaption)

The figure shows that, in terms of adaptability, the most flexible, and thus the most adaptable are the manufacturing system (MF), the neomanufacturing system (NM) and the economical system (E), while the systems pure Fordist (FP) and neofordist (NF) are characterized by rigidity, so they have a low adaptability level. Therefore, Krafcik used two types of production systems, those of "buffer" (neofordist and manufacturing) and type "Economy" (pure Fordist, economical).

2.2. A comparative approach of the production systems in terms of industrial corporations' anthropocentrism

The anthropological approach of the evolution that has been experienced by the influence of the industrial techniques on manufacturing systems adopted by corporations belongs to Alain Touraine, who, while performing a deeper analysis, has managed to identify a complex transformation, structured in three phases, which do not follow perfect in time in terms of evolution, and that can coexist in different proportions in enterprises nowadays.

The first phase "A" represents the old labor system, in which independent worker action prevails. Also, the company is characterized by the coexistence of two worlds: one of the production, where the qualified worker is autonomous, and the other world, of the management, where the top manager has the full initiative.

Phase "B" appears and develops when the economic and technical conditions are relatively stable and predictable. The techniques can be scientifically studied and work organization is centralized. This phase is characterized by the predominance of the organization on execution, maintaining direct labor execution, and so the idea of human performance. Meanwhile, the priority of organization on execution provides some autonomy from technique.

Phase "C" begins with the advent of automation of manufacture. The worker turns into a supervisor of the technical system, which is inserted in a communication network.

Although aspects of the production system itself are not explicit, we can consider that the phases identified by Touraine are found in their evolution [3]. Thus, the phase "A" corresponds to the first form of production system, the manufacturing. Phase "B" corresponds to the system of mass production, Fordist, the production process having a manual-mechanized character. The third phase, "C" relates to the system of mass production, but which reached the stage where technical progress, on one hand, made possible the execution of performant and reliable production equipment, and on the other hand, the increase of the annual volume of production allowed the economic efficiency of the use of such equipment in the production process.

2.3. The "organizational" comparative approach of the industrial corporations. The flexibility and agility of the corporate's structure.

In the specialty literature is shown that many organizations, being under pressure environment, are moving towards new technologies such as flexible manufacturing systems, integrated manufacturing by computer, robots. The main reason for this happening is that new technologies promise to have the ability to operate in a flexible manner, in real time and at a much lower cost than the previous ones. However, current organizational models are not in line with technology, the motivation being of managerial nature, and there is no reason to have flexible systems if the company itself is inflexible and unable to respond quickly to changing needs of its customers [4]. Flexible systems and manufacture integrated by computer mean contextual changes in concepts related to manufacturing rather than simple steps in the development process and therefore the proposal that is made is a completely new form of organization to be developed so that the potential for them to be achieved [5].

Kakati shows that the process of development of manufacturing concepts can be identified in four stages shown in Table 2. [6].

Table 2: *Stages of the process of development of the concepts in organizing the production in industrial corporations*

Stage	Concepts of manufacturing	Variables of success-objectives that the organizational model must include	The properties of the organizational mode
Stage 1	The traditional manufacturing system: production workshop, batch, mass production	- efficiency	- a functional organization with high fragmentation of tasks, - the existence of many management functions, - generating a high degree of specialization.
Stage 2	Just–in–time (JIT): a manufacturing system based on the use of cards (Kanban)	-efficiency, -quality, -the reduction in the operating time (the duration of the production process)	- structuring JIT by overlapping functions, - the allocation of functional responsibility at the point of origin, - eliminating the unnecessary processes, - reducing the top management functions.
Stage 3	Reprogrammable automation DNC, CNC, SFF, CAD-CAM, Robots	-efficiency and efficacy, - quality, - flexibility, - reducing the duration of production	- vertical and horizontal integration of functions and tasks, - removal of both the processes and the support functions, - coexistence of opposite business elements, - a multiple rate structure type.
Stage 4	CIM, computer integrated manufacturing, integration of the functions of design, production, information and of the logistic technology with the marketing function and the other functions	-efficiency and efficacy, - quality, - flexibility, - reducing the production duration, - innovation, - mass customer (product adaptation to the individual customer needs)	- very high degree of integration of tasks and functions, - complete elimination of functions and processes within the senior management, - coexistence of some opposite business elements, - a multi-beam type of structure.

2.4. A comparative approach of the production systems in terms of "process control" made by the management of the industrial corporations.

Jaikumar identifies six stages of production, which are considered process control. This system of periodization of the evolution of manufacturing systems is based on the consideration of

12 quantitative and qualitative characteristics that define various aspects of how the control process was conducted in the companies and how performance parameters were recorded [7], [8].

***Table 3**: Comparison of the corporate management systems from the "control process" point of view.*

Characteristics	**The British manufacturing system**	**The American manufacturing system**	**The Scientific Management (taylorism)**	**The improvement of the process (statistical process control)**	**Numeric control**	**Computer-integrated manufacturing**
Number of machines	3	50	150	150	50	30
Optimal size(number of employees)	40	150	300	300	100	30
Indirect labour – direct labour ratio	0:40	20:130	60:240	100:200	50:50	20:10
The growth of the labour productivity as against the previous period	4:1	3:1	3:1	3:1	3:1	3:1
Rejects as a share of the overall labour	0,8	0,5	0,25	0,08	0,02	0,005
Number of products	No limits	3	10	15	100	No limits
The target of the design	Mechanical	Production	Industrial	Quality	Systems	Knowledge
The purpose of the technology	Precision	Repeatability	Reproducibility	Stability	Adaptability	Versatility
The purpose of the control	The product functionality	Conformance	The conformance of the process	The capability of the technological process	Product-process integration	The existing technological processes
Organizational change	The guild destruction	Separation of the hierarchic and functional staff	Functional specialization	Teams of problems solving	Control at cell level	Functional integration
Work philosophy	"perfect"	"satisfying"	"reproduction"	"monitoring"	"control"	"develop"
Necessary abilities	Mechanical job	Repetitive sub-abilities	Sub-abilities	Diagnostic skills	Experimentation	Learning, generalization and abstracting

Data in the report presented show that, with the advent of the computer technology, changes have occurred in understanding the scope of technology, in terms of methods and forms of organization, which caused the substantial downsizing of the optimal production unit from the number of employees' point of view. Simultaneously, the labor productivity continued to grow

considerably, the scrap reduced to insignificant odds in the total labor, and the indirect / direct labor ratio decreased permanently [9].

3. CONCLUSIONS

The economy manufacturing system is the one that combines the flexibility of adaptation with obtaining high efficiencies for low volume production, a situation characteristic for a growing number of industries, including the branch of textiles and leatherwork, faced with the need to meet the consumer demands, by diversifying the ranges of products.

The "computer-integrated manufacturing" phase requires learning, generalization and abstraction skills, which is correlated with the general trend of increasing the companies' flexibility. People must become more flexible in terms of professional knowledge and the best solution is continuous learning. The same problem is a priority for the companies, and that is considered as the optimal solution is the creation and maintenance of a "learning organization" by the managers of the business.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE ROLE OF THE UNIVERSITY IN FOSTERING ENTREPRENEURIAL INTENTION AMONG STUDENTS

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Abstract: *Entrepreneurial intention among university students may be conditioned by following training activities related to entrepreneurship during the course of their degree studies. There has clearly been an increase in the number of university graduates who become entrepreneurs, so it is necessary to determine the services that should be offered by the university as a platform to support university entrepreneurship. This research examines this issue through the use of statistical analyses. The main objective of this research is to determine the different types of entrepreneurial training offered to students and the services they think the university should establish as a platform to support entrepreneurship, thereby enabling a comparison of current and desired practices. The study determines whether access to training activities conditions the entrepreneurial intention of university students. Descriptive statistics have been used to conveniently present the information and to identify behavioral patterns of the variables analyzed. Data have thus been examined using frequency analysis, contingency tables and independence tests. The variables used in this survey are designed to represent the role of the university in fostering entrepreneurial culture and the intention among the university comminity to start their own business, having first extensively analyzed the concept of an entrepreneurial university*

Key words: *Entrepreneur, entrepreneurial profile, , entrepreneurial training, business creation.*

1. INTRODUCTION

This article is structured into three parts and contains a description of the methodology, a discussion of results and ends with conclusions relating to the intention among university students to engage in activities related to entrepreneurship during their undergraduate studies.

2. EMPIRICAL STUDY

2.1 Methodology

The main objective of this research is to determine the different types of entrepreneurial training offered to students and the services they think the university should establish as a platform to support entrepreneurship, thereby enabling a comparison of current and desired practices. The study determines whether access to training activities conditions the entrepreneurial intention.

To this end, we propose the following hypotheses: The intention to start a business among university students is related to their participation in entrepreneurial training activities during the course of their studies. For this purpose, it is necessary to determine: (H1) whether the students have

participated in entrepreneurship activities and if the nature of these activities is university or non university-related and, (H2) what are the services that students think should be offered by the university during the different stages of the entrepreneurial value chain

We then went on to identify the target population and carry out the subsequent data collection, conducting the questionnaire with students from the 6 degree courses offered at the Campus d'Alcoi of the Universitat Politècnica de València.

Statistical analysis of the data was performed using the IBM® SPSS® Statistics 20 program. The data were subsequently analyzed using frequency analysis, contingency tables and independence tests [1].

2.2 Measurement variables

Variables related to the role of the university in entrepreneurial intention: The sample was differentiated into two categories of first and fourth year students of each degree, since it is the fourth year students who may have been influenced most by the services provided at the university during the course of their studies in the intention to start a business (H).

Intention of students to start up their own business: this categorical item is composed of two concepts, the first concerns whether they consider themselves to be entrepreneurs and the second relates to the intention to create a business.

Table 1: *Measurement variables*

Items	Measurement scale
DEGREE COURSE	Categorical Variable: 6 Subcategories relating to the 6 different degree courses.
INTENTION TO START UP A BUSINESS	Dichotomous Variable. Yes/No
	Likert scale from 1 to 5, where 1 = never and 5 = yes, I firmly intend to start my own business
NO INFLUENCE EXISTS ON THE PART OF THE UNIVERSITY (FIRST AND FOURTH YEAR UNDERGRUADUATE STUDENTS: 630 interviewees)	Dichotomousvariable. Yes/No
	Categorical variable: 12 Subcategorías sin límite en la elección correspondientes a plataformas de apoyo a la persona emprendedora.
	Dichotomous variable. Yes/No
THE UNIVERSITY INFLUENCES THE INTENTION TO CREATE MY OWN BUSINESS (FOURTH YEAR UNDERGRADUATES: 274 interviewees)	Dichotomous variable. Yes/No
	Likert scale from 1 to 5, where 1 = totally disagree and 5 = entirely agree
	Dichotomous variable. Yes/No
	Categorical variable: 37 Subcategories corresponding to the services that they include: 0. DECISION TO START UP A BUSINESS (5 sº) 1. BUSINESS IDEA DEVELOPMENT (6 sº) 2. PROJECT DEVELOPMENT (8 sº) 3. BUSINESS CREATION (8 sº) 4. BUSINESS CONSOLIDATION (10 sº)

Source: Original material

3. RESULTS

3.1. Analysis of the results

We identified the subjects with the highest number of students by degree and year (first and fourth years), by either core or compulsory subjects, and conducting the questionnaire interviews

face-to-face, after receiving authorization from the relevant professor, with a total of 630 students, who represent 72.83% of the total enrolled in these subjects (865 students enrolled).

Hence, using the sample obtained and through the use of frequency analysis, we can observe that 69.2% consider themselves to be entrepreneurs and 80.5% indicate that they have seriously considered creating their own business. An analysis of the results from interviews with first and fourth year students indicate that:

- 25.2% of enrolled students have attended and / or participated in some kind of activity that promotes an entrepreneurial culture.
- They mainly attend activities that foster an entrepreneurial culture organized by UNIVERSITY SERVICES (27.55%), followed by those organized by BUSINESS ASSOCIATIONS AND TRADE UNIONS (11.70%) and those organized by SCIENTIFIC AND TECHNOLOGICAL PARKS (11.32%), .
- 66.3% consider that they do not possess the knowledge and skills necessary to set up their own business compared to 33.7% who state that they do.

With regard to the data we analyzed from fourth year students on the role that the university plays in their entrepreneurial vocation, we can draw the following conclusions:

- Half of the students (51.5%) think that "university training equips them with the necessary knowledge and skills and provides the required tools to develop their business".
- 15.5% agree with the statement "the training that students receive from the university is oriented towards constituting their own business".
- The vast majority of students (89.4%) did not participate in any activity that encourages entrepreneurship organized by the university.

An analysis of the entrepreneurial value chain according to the services demanded by the final year university students indicates that those in most demand are related to the links 0. EMPLOYMENT DECISION, 1. IDEA DEVELOPMENT 2. PROJECT DEVELOPMENT and 3. BUSINESS CREATION. The first service requested corresponds to the last stage (4). BUSINESS CONSOLIDATION, which appears in 14th place with the service "Consultancy services (HR, legal-mercantile, financial, commercial, subsidies)."

It should be noted that, in this study, 2 possible scenarios are generated from the general hypothesis H. HA establishes a scenario that analyzes the relationship between those considered to be entrepreneurs (B2P1) and entrepreneurship promotion activities (B2P2), and HB proposes a scenario where there is a relationship between those who want to create their own business (B3P19) and participating in activities that promote an entrepreneurial culture (B2P2). Similarly, we carried out an analysis of the variable (B2P2) of the students who answered both items affirmatively (B2P1 and B3P19), obtaining 384 affirmative answers for both items, which represents 61.0% of the total number of surveys. As a partial conclusion from the data obtained in this analysis of contingency tables, the following characteristics can be established:

- Of the students who considered themselves to be entrepreneurs, only 29.1% have participated in activities that foster an entrepreneurial culture.
- Of the students who have thought seriously about setting up their own business, only 26.8% have participated in activities that foster an entrepreneurial culture.
- Of the students who considered themselves entrepreneurs and also seriously intend to start up their own business, 12.9% have attended activities that foster an entrepreneurial culture.

3.2. Independence test between variables

Table 2 shows the data obtained from the chi square analysis of the two questions B2P1 and B3P19 versus the B2P2 variable.

Table 2: *Dependence between the items*

SUB-HYPOTHESES	Chi SQUARE VALUE	Type of dependence
1A. vs B2P2	0,001	Dependent
1B. vs B2P2	0,063	Uncertain
1A&B. vs B2P2	0,214	Independent

4. CONCLUSIONS

There is limited information on education in university entrepreneurship], while it should be noted that 73.42% of Spanish universities undertake non-curricular entrepreneurship training, but no data are available on what services are offered or should be offered from the view of the entrepreneurial value chain [3]. The university is seen a platform to support the creation of companies by their students and / or graduates under the paradigm of innovation agent and engine of economic growth of their regional environments areas in fulfilling the so-called "third mission" [4,5]. The rise of the enrollment of university graduates in the RETA is the basis for establishing the hypotheses proposed in the present research, in order to focus on the educational role in entrepreneurship that the university has and must have.

It has been verified that there is a clear relation in this study between participating in activities that foster the entrepreneurial culture and university students who consider themselves entrepreneurs, although a very low percentage has participated in activities of this nature. The services most demanded are those related to the decision to start a business and the development of the business idea, compared to the results obtained in other studies

Thus, as a final conclusion, it can be stated that universities should carry out an analysis of the services currently offered as platforms to support an entrepreneurial culture, based on the data obtained in the present study in order to provide better services that encourage the creation of businesses within the university context.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

LEGISLATIVE ASPECTS CONCERNING THE LEATHER WASTES

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Abstract: *This paper underlines the current legislation and compliance issues leather waste in different waste groups according to relevant legislation and shows that, although seemingly harmless waste of skin sometimes contain dangerous compounds. As presented risks to human health were some restricted substances in leather. Since 2001 Romania had preoccupation in national legislation on waste management, but some categories, such as leather waste are not framed to this category. Also, another goal is implementing the EU management/storage strategy of industrial waste. Unfortunately, Romania imports huge quantities of used clothing and shoes. Transport, storage and use of them are poor, and many of these are subsequently stored waste by the fact that it is even sometimes improperly discarded.*
The paper also shows the statistics on waste management in the Bihor County by activity of national economy and by activity of industry at level of CANE REV.2 Section.
Analyzing the postings on Internet regarding the sale and purchase of leather wastes in Romania, it was found that there are the following 'categories' of wastes: leather goods, leather from coats, leather from footwear industry, suede, leather, leather resulting from the production of upholstery. It was found that most car buyers use waste leather upholstery. It is recommended that production companies to highlight more transparent their inventory textile and leather waste on types for those interested (including online) can access/capitalize them.

Key words: *tanning sector, legislation, codes, management, convention*

1. INTRODUCTION

Based on the definition in 2001 [1], stating that "waste - any substance or product in the categories set out in Annex no.1, one that the owner is no longer using or having the intention or obligation to stop using it "(Emergency Ordinance no. 16/2001), the concept has evolved through the implementation of Directive 2008/98/CE [2] in national law. Thus, according to Law 211/2011 [3] wastes are "substances or objects which the holder discards them or intends to discard them or he is required to discard".

As for the classification of wastes with reference to the classification of leather wastes, it is remembered:

• According to Law no. 211/2011, provenience → C. Production wastes resulting from industrial or agricultural technological processes → C1 industrial wastes stock that European norms classify them in Class 1 as hazardous industrial wastes, but nontoxic; Class 2 as hazardous industrial and toxic wastes;

• According to Directive 2006/12/CE [4] → Q1 Production or consumption residues not otherwise specified below; Q14 Products which are no further useful to the holder; Q16 Any materials, substances or products which are not included in the above categories;

• According to the European Wastes Catalogue EWC (The European Waste Catalogue (EWC) [5] and HG. 856/2002 [6] – Categories of waste: 04. Waste from leather, fur and textiles categories. Subcategory: 04 01 leather and fur waste industries (with 10 subcategories).

2. RAW MATERIALS AND LEATHER INDUSTRY

In the production of leather, leather goods and footwear, Europeans have a long tradition and the raw materials of the tanning industry are hides and skins of which over 99% are derived from domestic animals.

Leather is a constituent material, and, in Europe, the first destination use of leather is the production of leather for uppers for the footwear sector (41% on total). Other destinations are: furniture upholstery 17%, upholstery for cars 13%, Leather goods 19%, garments 8%, aircraft, boats etc. 2% [7].

According to The First Social & Environmental Report of the European Leather Industry [7], in 2013, the EU leather industries are composed of nearly 24.000 companies and 400.000 employees. The total yearly turnover is reported to be more than 31 billion Euros, comprised of the following markets: 3.8% EU member States' sales in their domestic market, 60.7% intra-EU trade, 35.5% extra-EU exports.

3. ARE LEATHER WASTES HAZARDOUS?

Although seemingly harmless, some types of leather waste can be dangerous. Thus, Law no. 265 of May 15th, 2002 [8] to accept amendments to the Basel Convention (1989) on the Control of Transboundary Movements of Hazardous Wastes and their Disposal [9], include as hazardous waste in List A at A3 category Wastes containing principally organic constituents, which may contain metals and inorganic → A 3100 scraps and wastes of leather or synthetic leather, which are not suitable for the production of leather articles containing hexavalent chromium compounds or biocides; A 3110 fur waste containing hexavalent chromium compounds or biocides or infectious substances.

From this perspective, the Research Institute for Leather and Footwear in Romania through Research Department of Leather aims, as special activity regarding fundamental research, to optimize alternative technologies "that remove chromium by studying the behavior of other chemicals tanning agents and their chemical modification so as to ensure the effect of tanning".

Regarding legislation on transport of hazardous and non-hazardous waste in Romania is regulated by HG 1061/2008 [10]: "(2) The procedure for regulation and control of shipments of waste is applied to hazardous and non-hazardous waste listed in Annex. 2 to the Government Decision no. 856/2002 relating to waste management records and for the approval of the list of wastes, including hazardous wastes, with subsequent"; "(4) It is forbidden to carry any kind of waste from the place of production to that of the collection/temporary storage/treatment/recovery/disposal, without compliance with this decision."

Regulation (CE) No. 1907/2006 provides that if a Member State considers that the

manufacture, marketing or use of a substance such as a mixture or in an article presents a risk to human health or environment, risk that is not adequately controlled and must be addressed, it must prepare a file after notifying its intention to the European Chemicals Agency [11]. On this basis, in 2011, France showed that the substance dimethyl fumarate (DMF - a biocide used for preventing molds that may damage furniture or leather shoes during storage or transportation in a humid climate) contained in articles or parts thereof, in concentrations greater than 0,1 mg/kg, presents a risk to human health and it was proposed the restriction of this substance.

Other substances have been restricted in the leather industry according to Regulation (CE) No. 552/2009 of June 22nd, 2009 of Amending Commission of Regulation (CE) No. 1907/2006 of the European Parliament and of the Council concerning the registration, evaluation, authorization and restriction of chemicals (REACH) as regards Annex XVII, for example [12]:

- Cadmium - the use has been prohibited for determining the following mixtures or articles manufactured from polymers or copolymers of vinyl chloride: synthetic leather [Code 4202];

- azo dyes and azo substances – the use has been prohibited in textile and leather articles in concentrations above 30 mg/kg (0.003% by weight).

4. LEATHER WASTE MANAGEMENT IN ROMANIA AND BIHOR COUNTY

Thus, according to Romanian Statistical Yearbook 2015 and 2016 Civil employment, by Activity - Water supply; sewerage, waste management and decontamination activities (CANE Rev.2 Sections) was 123 thou persons in 2012, 2013 and 126 thou persons in 2014, 2015 (end of year).

The following provides some statistics on waste management in the Bihor County by activity of national economy and by activity of industry at level of CANE REV.2 Section:

Table 1: *Employment, average number of employees and number of employees by activity of national economy (Bihor County Statistical Yearbook, 2016)*

ACTIVITY OF NATIONAL ECONOMY AT LEVEL OF CANE REV.2 SECTION (end of year)	***End of year…***				
	2011	**2012**	**2013**	**2014**	**2015**
1. EMPLOYMENT *(thou persons)*					
Economy total	263.0	268.3	266.4	264.8	262.8
Industry	66.6	66.8	67.7	68.8	72.1
- Water supply; sewerage, ***waste management*** *and decontamination activities*	2.8	2.9	3.0	3.0	3.1
2. EMPLOYMENT STRUCTURE (*percentage*)					
Economy total	100.0	100.0	100.0	100.0	100.0
Industry	25.4	24.9	25.4	26.0	27.4
- Water supply; sewerage, ***waste management*** *and decontamination activities*	1.1	1.1	1.1	1.1	1.2
3. AVERAGE NUMBER OF EMPLOYEES *(persons)*					
Economy total	144,475	143,590	145,910	150,333	153,529
Industry	52,838	53,706	54,101	57,039	57,804
- Water supply; sewerage, ***waste management*** *and decontamination*	2,305	2,448	2,326	2,385	2,500

activities					
4. NUMBER OF EMPLOYEES BY ACTIVITY *(persons)*					
Economy total	152,032	155,084	155,833	159,700	166,685
Industry	56,312	56,986	57,033	59,320	61,167
- Water supply; sewerage, ***waste management*** *and decontamination activities*	2,474	2,634	2,623	2,611	2,686

Table 2 *Average number of employees and number of employees by activity of industry at level of CANE REV.2 DIVISION* (*Bihor County Statistical Yearbook, 2016*)

ACTIVITY OF INDUSTRY AT LEVEL OF CANE REV.2 DIVISION	***End of year…***				
	2011	**2012**	**2013**	**2014**	**2015**
1. AVERAGE NUMBER OF EMPLOYEES (*persons*)					
INDUSTRY - TOTAL	263.0	268.3	266.4	264.8	262.8
MANUFACTURING	66.6	66.8	67.7	68.8	72.1
- Tanning and dressing of leather; manufacture of travel and leather goods, harness	16,413	16,684	16,420	17,434	16,987
2. ***NUMBER OF EMPLOYEES, BY GENDER*** *(total persons/women)*					
INDUSTRY - TOTAL	56312/ 28749	56986/ 28595	57033/ 27956	59320/ 29039	61167/ 30411
MANUFACTURING	49948/ 27633	50226/ 27392	50566/ 26844	52942/ 27967	55088/ 29360
- Tanning and dressing of leather; manufacture of travel and leather goods harness	17791/ 12111	18642/ 12506	18073/ 12267	17758/ 12083	17184/ 11430

However, in Romania there are few centralized data on waste leather or statistics as there is in Europe. For example, in The First Social & Environmental Report of the European Leather Industry [7] shows that European tanneries produce on average 2.14 kilograms of waste for every square metre produced (in Figure 1).

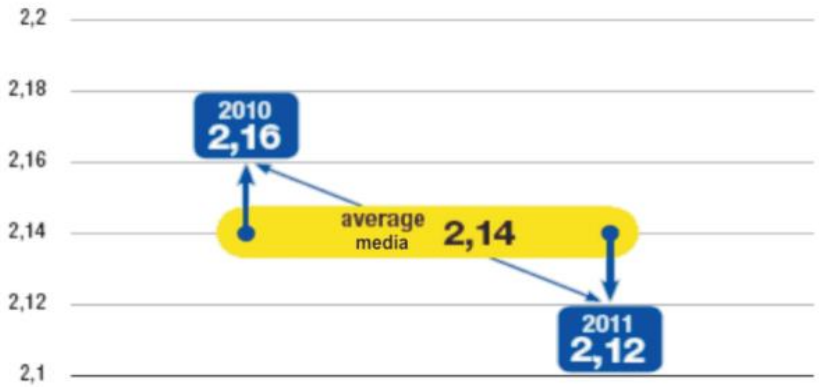

Fig. 1: *Waste production per product unit 2010-2011 (kg/m)*

5. CONCLUSIONS AND CONCERNS

The Environmental principles of EU tanning sector are mentioned in the Framework Agreements and Joint Statements done by COTANCE and IndustriAll. The leather industry, in Europe, tanning wastewater quality is a priority and is monitored. The Europe's tanneries consume today less water and energy and they have substituted dangerous chemicals, because the good water management represent almost 60% of total environmental costs [7].

With regard to leather wastes are recyclable or not, we can see that Romania since 2001 has no legislative concerns through OU no 16 from January 26th, 2001 on waste management which provides in Article 2 groups of recyclable industrial waste according to Annex 1. Such textile wastes occur in recycled industrial waste group (with metal, glass, paper, plastic products and rubber) but not the leather ones. As textile waste, leather waste are generated both from own production and exports and imports of shoddy second-hand goods that convert into waste in a short time.

For at least 20 years in Romania have been entering huge amounts of second-hand clothes and shoes. Their transport, storage and capitalization are unsatisfactory. Many of them even if they are brought in a good shape, later they become waste because they are improperly stored and sometimes even abandoned. In the Shoe and Leather Research Institute (ICPI) one of the main objectives of the Research Department Leather is: Promoting the concept of "clean production" and new cleaning systems through [15] "replacing harmful chemicals with products with low toxicity; recovery/recycling of wastes resulting from technological process; recovery/reuse of useful substances resulting from processing; wastewater treatment by modern methods in order to provide advanced pollution". Also, another goal is implementing the EU management/storage strategy of industrial waste.

Analyzing the postings on Internet regarding the sale and purchase of leather wastes in Romania, it was found that there are the following 'categories' of wastes: leather goods, leather from coats, leather from footwear industry, suede, leather, leather resulting from the production of upholstery. It was found that most car buyers use waste leather upholstery. It is recommended that production companies to highlight more transparent their inventory textile and leather waste on types for those interested (including online) can access/capitalize them.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

COMPARATIVE ADVANTAGE OF CLOTHING SECTOR IN THE EU-28 MARKET

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Abstract: *The study presented here is aimed at analyzing the comparative advantages in the European clothing sector with the focus on Balkan states. The dynamics of change over a 15-year period following economic reforms are revealed. For all Balkan countries export plays an important role in promoting economic growth and development and the clothing industries play a significant role and continue to contribute to the economic prosperity in this countries. The evolution of the RCA index for garment industry is decreasing for all countries in the Balkans. The evolution of the Lafay index is also decreasing in the most Balkan countries (except Greece, Montenegro and Slovenia) but still the values for Lafay index is positive what indicating that in these countries the sale of garments contribute positively to balance the trade balance of countries analyzed. Negative value of the Lafay index may be due to the fact that the garment industry is one of the key industries in the economy of that country and also because the earnings from garment industry in these countries is high. When the producers of the Balkan countries will create products with higher added value in garment industry the competitiveness of these countries will decrease. Also rising wages in this industry, as a result of trade union pressure or government policy, will lead to decreasing competitiveness of these products on the EU market and implicitly to the decrease of exports of garments from these countries.*

Key words: *comparative advantage, clothing, Balassa index, Lafay index*

1. INTRODUCTION

The textile industry is a vital to the economic development for a many country because has provided both products and jobs needed by humans around the world. So in every developing nation, the textile industry has been the stepping stone for economic development, relying on textile and clothing exports to produce income. Globalization affects the economies of most of the world's countries, as capital is free flowing over the world, seeking a host country where the costs are as low as possible. So, the international context in trade of clothing has changed dramatically in the last few years and will probably continue to do so under the impact of the global crisis, liberalization and globalization, which resulted in a relocation of production and capital, a greater mobility of production factors. Consequently, intense competition grew, as most countries produced textile wares for the same markets in more wealthy countries.

The EU personality has proved to be an exceptional one, because with the EU signing of international agreements there has been no economic disaster. The European Union is based on five principles of good governance: openness, participation, accountability, efficiency and coherence. [1]

For all Balkan countries export plays an important role in promoting economic growth and development. These country confronted with problems such as restructuring of economic system, changing trade markets and patterns, reduction of competitive ability, narrow export base, and lower economies of scale. In these context, we considered opportune to analyses the current situation from Balkan countries (Albania, Bulgaria, Bosnia and Herzegovina, Croatia, Greece, Montenegro, Serbia, Slovenia, Republic of Macedonia and Turkey) in the clothing's European market. With respect to the object of this study, the clothing industry as an individual sector, we have decided in favor of a result-oriented indicator like revealed comparative advantage (RCA). The RCA is analyzed by two indices: the Balassa index (BI) and the Lafay Index (LFI).

Scope and objective of the research

The main aim of this paper is to examine and analyze Balkans countries' comparative advantages of the clothing industry and to compare its trade vis-à-vis the EU-28. We present the analysis of indices which reveal comparative advantage of Balkan State clothing industry during 2000–2015.

Methodology and methods

Methods of the scientific research that have been employed in the paper are scientific analysis and summarizing of literature, mathematic calculations, comparative analysis of statistic indexes.

To analyze the trade patterns and changes in the mentioned countries in the European Union (UE 28) clothing markets we used the Revealed Comparative Advantage Index (RCA) of Balassa (1965) and Lafay index LFI.

The paper is organized as follows: the first part present the theoretical foundations for the analysis of the RCA and LFI. The results of the selected indices are presented in the second part where we calculated and analyzed the RCA and LFI of the Balkan States. The final part draws some conclusions based on the findings.

2. REVEALED COMPARATIVE ADVANTAGE

The concept of comparative advantages has the foundation in conventional trade theory and is widely used in modern economic literature to evaluate the patterns of trade and specialization of countries in commodities which have a competitive advantage.[2] One of the most widely used methods involves the concept of "revealed comparative advantage" developed by Balassa (1965). The Balassa index basically measures normalized export shares, with respect to the exports of the same industry in a group of reference countries.[3] RCA is the ratio between the export share of a given commodity or sector in a country and the export share of that commodity or industry in the global market, as shown in next equation:

$$RCAij = (Xij / Xit) / (Xnj / Xnt) \quad \textbf{(1)}$$

where X is exports, i is the country, j is the commodity/industry, n is the world or a set of countries, and t is all product groups.

When the RCA index exceeds unity, a comparative advantage is 'revealed' for the country in that particular sector. There is some criticism of this method. The RCA has been criticized for taking only the exports into consideration while ignoring the imports. Another objection is the fact

that if the country has a “comparative disadvantage” the index ranges from zero to one, whereas if it has a “comparative advantage”, the index ranges from one to infinity. [4]

Although pros and cons of the Balassa index are still debated in the literature, it stands as the most widely used revealed comparative advantage index. [5]

Several attempts have been made in the literature to overcome the former empirical weakness of the pure Balassa index. One of this is Lafay index who combines together trade and production variables.[6] The Lafay index shows with respect to alternative measures of specialization, especially that of taking into account both exports and imports flows, which is a quite important fact due the increasing role of intra-industry trade all over the world. The LFI index enables to analyze the position of every specific product within the foreign trade structure of every specific analyzed country or a group of countries.[7]

Lafay index LFI [8] defined as where:

$$LFI_j = 100\left(\frac{x_j - m_j}{x_j + m_j} - \frac{\sum_{j=1}^{N}(x_j - m_j)}{\sum_{j=1}^{N}(x_j + m_j)}\right)\frac{x_j + m_j}{\sum_{j=1}^{N}(x_j + m_j)} \quad \textbf{(2)}$$

where:

x and m represent exports and imports of “j” product realized by country or a group of countries with respect to the rest of the world or with respect to a selected business partner (partner country). “N“ is the number of analyzed items.

Country is considered to have a comparative advantage (disadvantage) in a given commodity when the balance in relation to GDP (Gross Domestic Product) exceeds (is less than) the attributed balance, i.e. exceeds (is less than) zero. The comparative advantage neutral point is thus when the net exports marks zero, i.e. .

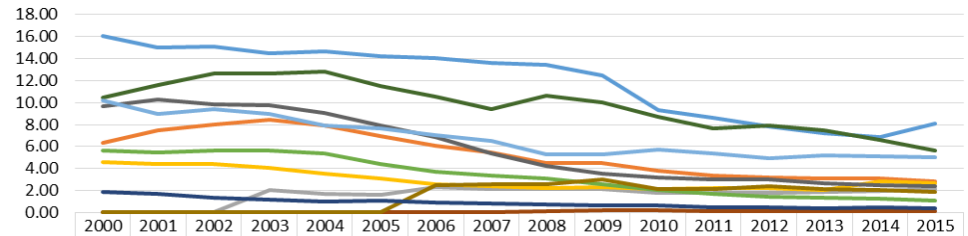
3. MEASURING REVEALED COMPARATIVE ADVANTAGE OF CLOTHING SECTOR: BALKAN COUNTRIES VIS-À-VIS THE EU-28

We calculated the Revealed Comparative Advantage Index (RCA) of Balassa (1965) to analyze the trade patterns and changes in the Balcanic States, in the European Union (UE 28) clothing markets during the period of 2000-2015.

In the Figure 1, the most remarkable changes of the Balassa indexes are presented.

The evolution of RCA for the clothing industry for the Balkan countries is presented in the figures 1. As can be seen from this evolution, the RCA is decreasing for all countries in the Balkans, whether they have or not the status of EU member.

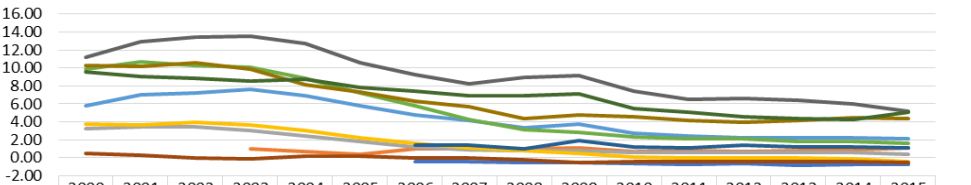
In 2015, countries with the highest Revealed Comparative Advantage Index (RCA) at garment industry on the EU market are Albania (8.07), Republic of Macedonia (5.64) and Turkey (5.04).



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Albania	16.05	15.05	15.11	14.50	14.69	14.21	14.05	13.57	13.39	12.48	9.35	8.65	7.86	7.19	6.83	8.07
Bulgaria	6.30	7.52	8.00	8.43	7.93	6.98	6.04	5.46	4.50	4.52	3.85	3.34	3.20	3.08	3.07	2.88
Bosnia and Herzegovina				2.05	1.72	1.62	2.28	2.15	2.14	2.18	1.81	1.81	1.82	1.87	1.96	2.12
Croatia	4.59	4.43	4.39	4.07	3.53	3.07	2.59	2.39	2.21	2.28	2.13	2.25	2.21	2.09	2.82	2.64
Greece	5.67	5.44	5.62	5.65	5.34	4.39	3.71	3.38	3.12	2.57	2.01	1.73	1.42	1.35	1.27	1.13
Montenegro							0.05	0.07	0.12	0.21	0.18	0.09	0.15	0.11	0.17	0.14
Romania	9.71	10.28	9.88	9.78	9.02	7.89	6.83	5.41	4.25	3.52	3.20	3.00	3.06	2.68	2.53	2.37
Serbia							2.47	2.55	2.60	2.98	2.14	2.12	2.38	2.11	2.06	1.90
Slovenia	1.92	1.71	1.33	1.14	1.05	1.06	0.92	0.84	0.72	0.63	0.61	0.49	0.45	0.43	0.45	0.41
Republic of Macedonia	10.41	11.61	12.62	12.68	12.81	11.55	10.56	9.44	10.65	10.06	8.67	7.63	7.94	7.44	6.60	5.64
Turkey	10.19	8.95	9.41	8.93	7.96	7.62	7.03	6.54	5.32	5.28	5.77	5.36	4.96	5.20	5.15	5.04

***Fig. 1**: Evolution of Balcanic states, (Balassa index) for clothing in the period 2000-2015. Calculated by the author according to the WTO dates.*

We calculated the LFI index to analyze the position of every specific product within the foreign trade structure of every specific analyzed country. Country is considered to have a comparative advantage in a given commodity when the balance in relation to GDP exceeds the attributed balance, i.e. exceeds zero. As can be seen from figure 2, in the most Balkan countries (except Greece, Montenegro and Slovenia), in 2015, Lafay index has positive values who indicating that in these countries the sale of garments contribute positively to balancing the trade balance of the countries surveyed.



	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
Bulgaria	5.77	6.97	7.25	7.60	6.88	5.81	4.77	4.17	3.31	3.70	2.75	2.42	2.27	2.20	2.26	2.09
Bosnia and Herzegovina				0.98	0.71	0.40	1.02	0.97	0.97	1.14	0.73	0.79	0.74	0.80	0.89	1.06
Croatia	3.25	3.45	3.48	3.08	2.45	1.84	1.22	0.90	0.77	0.82	0.58	0.57	0.57	0.58	0.56	0.42
Greece	3.77	3.64	3.96	3.69	3.06	2.18	1.58	1.08	0.82	0.49	0.12	0.03	-0.01	-0.06	-0.15	-0.42
Montenegro							-0.40	-0.44	-0.49	-0.53	-0.62	-0.76	-0.67	-0.81	-0.74	-0.71
Romania	9.84	10.69	10.27	10.10	8.81	7.19	5.80	4.30	3.13	2.82	2.33	2.13	2.10	1.85	1.80	1.64
Serbia							1.43	1.39	0.95	1.96	1.19	1.12	1.36	1.22	1.20	1.13
Slovenia	0.46	0.31	-0.02	-0.09	0.15	0.18	0.02	-0.07	-0.24	-0.51	-0.41	-0.47	-0.41	-0.40	-0.47	-0.48
Republic of Macedonia	11.17	12.94	13.46	13.56	12.77	10.56	9.29	8.21	8.99	9.11	7.38	6.54	6.62	6.41	6.01	5.15
Turkey	10.30	10.14	10.56	9.87	8.14	7.32	6.27	5.70	4.40	4.77	4.56	4.13	3.93	4.17	4.42	4.38
Albania	9.60	9.07	8.82	8.59	8.71	7.83	7.40	6.94	6.93	7.09	5.48	5.07	4.61	4.33	4.30	5.12

***Fig.2**: Evolution of Balcanic states, (Lafay index) for clothing in the period 2000-2015. Calculated by the author according to the WTO dates.*

LFI negative value index registered in Montenegro may be because the garment industry is one of the key industries in the country's economy - exports of garments representing 0.3% of total exports of this country. LFI negative index for Slovenia and Greece have been influenced by the earnings from the garment industry in these countries, which led to lower levels continuously in recent years the importance of clothing in the export structure of these countries. As can be seen in figure 3 of these countries wages in the garment industry are the largest - Slovenia 10.02 EURO / hour and Greece 8.51 EURO / hour.

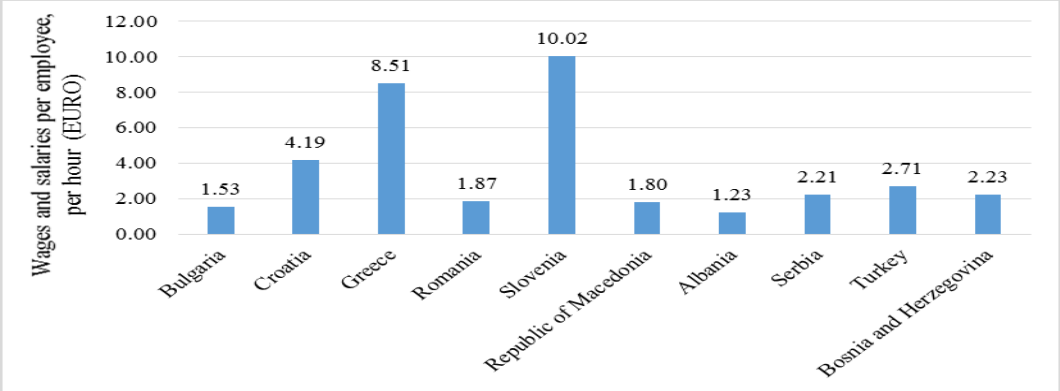


Fig. 3: *Wages and salaries per employee in full-time equivalents, per hour in manufacture of wearing apparel, in EURO.*

4. CONCLUSIONS

Based on the present analysis several conclusions can be drawn with respect to the comparative advantages of Balkan countries. The evolution of the RCA index for garment industry is decreasing for all countries in the Balkans. In 2015, countries with the highest Revealed Comparative Advantage Index (RCA) at garment industry on the EU market are Albania (8.07), Republic of Macedonia (5.64) and Turkey (5.04). At the opposite pole are Montenegro (0.14) and Slovenia (0.41).

The evolution of the Lafay index is also decreasing in the most Balkan countries (except Greece, Montenegro and Slovenia) but still the values for Lafay index is positive what indicating that in these countries the sale of garments contribute positively to balance the trade balance of countries analyzed.

Negative value of the Lafay index may be due to the fact that the garment industry is one of the key industries in the economy of that country and also because the earnings from garment industry in these countries is high.

The main factors that influence the level of level of competitiveness of textile products from the Balkans country are the gross value added per employee and wages. When the producers of the Balkan countries will create products with higher added value in garment industry the competitiveness of these countries will decrease. Also rising wages in this industry, as a result of trade union pressure or government policy, will lead to decreasing competitiveness of these products on the EU market and implicitly to the decrease of exports of garments from these countries.

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ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CAREER DEVELOPMENT OF TEXTILE INDUSTRY EMPLOYEES

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Abstract: *Textile industry is a very important industrial branch because it produces clothes for nearly seven billion people and textile materials for technical usage. It employs a huge number of competitive and qualified, mostly female work force. It is also technologically and technically challenging. Thus, it is vital to employ qualified and well trained employees with certain competences, knowledge and skills in order to respond to rapid technological and market changes. Here, we will consider the influence of the career development on doing business in the textile industry while acquiring the competitive advantage. Career development is a lifelong process and it is includes knowledge management. The term career has several meanings while nowadays it can mean advancement. The career usually reflects the professional development path of an individual during his or her working career. The career is that concept which connects and unifies most strongly and explicitly individual and organizational interests and needs. The theoretical part explains terms such as career development, importance and improvement of employees for an organization, the possibility for career development within the textile industry. The second part of the paper deals with research conducted among the employees of the textile sector in Leskovac, the town in Serbia with a long-lasting textile tradition.*

Key words: *textile industry, career development, employees, human resources, Leskovac*

1. INTRODUCTION

The main pillars of each and every organization are their employees who perform certain tasks directed towards organizational goals. Thus, human resources determine the success of every organization. There is a trend which shades light on the human resources and it is also becoming present in Serbia, but insufficiently. Human resource management is very important in those workforce intensive industrial branches, such as the textile industry. The textile industry should base its development and competitive advancement on the human resources, as a key element and factor of its success. Today, almost every organization worldwide, especially human resource departments, deal with career and career development. A lot of owners and managers now know that the success does not only depend on the workload itself and the potential of employees, but also on their involvement based on the process of gaining knowledge, career management, motivation and evaluation of their work [1].

In the textile companies, human resource management is a subsystem of general management where the selection of high quality employees is an imperative, which results in

creating employees who are "tailored" for the textile industry. The basic role of the general management is the recognition of the current and future needs of the production process, the capacities for the workforce at hand, and thus, to create the education plan and foresee all of the potential problems in the organization. Qualified workers of the textile industry are those who constantly improve their education and are prone to lifelong learning and innovating their knowledge and skills. In such a way, certain preconditions are being created needed for successful technology management which is vital for the development and growth of these companies and the industrial branch [2].

For a person to be successful professionally or at work, a continuous professional development is required which is embedded in the lifelong learning. Individual career development directly influences the change of the general management and the organization. The career is such that it is quickly and easily being changed due to changes in the working environment, personal interests, abilities and individual values. Career development consists of career planning, development of possible career paths, trainings and development. A career is an interrelated network of activities and tasks, and the working experience growth due to changes as the career develops. Therefore, the need for career development is very important both for the individual and employees and the organization.

There is a common problem in regard to employees lacking adequate knowledge and skills in the textile industry in Serbia. They are not properly suited to perform the tasks at hand; the socialization process is quite long; they are not prone to teamwork; they lack entrepreneurial and business skills and knowledge; they lack communication and problem solving skills; incongruity between the theoretical and practical knowledge and skills; unfamiliar with new technologies; unfamiliar with the quality system, etc. [3]. This requires changes when searching for human resources and employing highly skilled workers, who would be familiar with new technologies and new work places through additional trainings and by acquiring certain competences and skills.

This paper considers the career development of workers employed in the textile industry and their advancement within the organization. In the era of knowledge, the career development of employees in regard to acquiring new knowledge and skills is becoming more and more important as the link between an individual and the organization. The organization, in order to reach its goals and development, has to turn more to individual goals and interests of its employees. Thus, it should create, plan and reach its advancement through the development of its employees. The key concepts of the career development are: adopting knowledge, applying knowledge and providing results so that the organization can profit [4]. The goal of this research is the analysis of the career development of those who are employed in the textile industry and their role in doing business and reaching the competitive advancement, while the organizational strategy supports this goal by matching the organizational interests with employees' interests. It is important to point out that the research has been done in the town of Leskovac which has a long-lasting textile tradition and the production of textile products, where the first textile factory was built in 1884. This factory represented the beginning of the textile industry both in Leskovac and in Serbia. Traditionally having the textile industry, the town nicknamed the Serbian Manchester, the town of Leskovac is trying to revive this industrial branch. Today, there is a primary production of various treads, but also of end products (knitting, socks, fabrics and ready-to-wear clothes) [5].

2. CAREER PHENOMENON AND PERCEPTION OF CAREER IN THEORY

Modern comprehension of career is quite different than it used to be 20 years ago [1] and according to Donald Super, one of the most known career development theorists, the term "career

development" did not even exist 40 years ago [6]. Hierarchical advancement within a company is not enough any more for those who consider to have a career. Traditional ladders for career development no longer exist. Careers became complex labyrinths, and the employees should set their goals and the means to success. In order to develop one's career, he or she should be familiar with the basic career management principles and career influencing factors. An employee has to set up a relation with the organization in such a way that so that he or she could get timely and adequate support for the career development and thus, make himself or herself possibilities or chances for advancement.

Leković and Štangl Šušnjar [7] state that career usually means getting a job, changing jobs and posts. We can regard career as keeping one's position in the organization or as a characteristic of an employee. Also, every career consists of different tasks, positions and experiences. Today, career could be defined as a chain of different work roles. Traditionally this term was only related to those who were managers or professionals, but now it is being use more and more in general in order to describe the work roles of employees [8]. The career can be defined as an individual development path of working experience which is defined by posts in the organization [9].

The difference between a job and a career is best explained though a statement that a job is something a person does at his or her work in order to bring home the bacon, while the career refers to a fruitful activity which brings satisfaction [10]. Career can also be defined as the development of an individual learning and work through life. Therefore, career can be defined more widely as "development of an individual learning and advancement through life", and then it also relates to volunteering and other life experiences [8].

Dessler [11] considers employees as capital which should be encouraged, guided, provided with the opportunities for development and he stresses that work based training is the most popular means of management development. Torrington and associates [8] think that employees have to manage their own career in line with the career goals which relate to the perception of their own individual talents, values and needs. Schein [12] studied the career development through connecting individual and organizational needs.

Career development can be regarded as the process of permanent education and constant change of employment. Goldsten and Ford consider training [13] systematic approach towards learning and development in order to achieve individual, collective and organizational efficiency. On the other hand, development is related to activities which result in acquiring new knowledge and skills for personal development. Barber [14] concludes according to his research that training and education at work resulted in the increased innovation and the development of tacit skills. Tacit skills are related to non-formal learning and they improve the performance and efficiency which lead to better organizational performance.

The primal goal of career development is to achieve the current and future organizational and individual needs at work, but also the improvement of employment opportunities or the development of employment skills. The general use of career development for an organization:

- Organization is attractive for potential workers,
- Strengthens the image of the organization by acknowledging employees'' needs,
- Increases the dedication of employees,
- Increases the motivation of employees,
- Influences the recognition of the workforce potential.

New concept of career is often called *flexible career*. That is a frequently changing career based on the change of personal interests, abilities and values and changes in the working environment. It occurs when an individual changes careers through time by taking personal responsibility for personal development [15]. The main role of the management of the textile

company is the recognition of current and future needs of the production process, as well as the workforce capacities, based on which the employee education plan should be created, and to be able to assess the efforts and to detect problems in time. Within a textile company employee development programs should be created and integrated within the general development strategy. Factors which influence the development tendency are skilled workers, open management to innovate knowledge, open environment, existence of qualified edukacitional institutions, financial resources, teamwork, etc. [16].

3. RESEARCH AND RESEARCH RESULTS

The goal of this paper, both on the basis of theoretical and empirical research, is the analysis of the nature of the connection between the career development of workers employed in the textile industry through individual employee career development, on the one hand, and the development goals of the organization, on another, and discover the factors which would improve the career development and employee advancement in the textile industry.

There were 113 questionnaires handed out, out of which 94 were correctly filled in. Both genders participated, of various age and education backgrounds. This research was based on the descriptive statistical method, and the results were processes by SPSS 20 program. In order to prove the set goals, the research was carried out in textile companies for producing fabrics and textile products in the town of Leskovac. The survey was based on the questionnaire which was filled in by employees expressing their level of agreement by the Likert scale, which represents a scale of agreement with certain statements. There is a total disagreement, then neutral and total agreement for each statement. The questionnaire consists of 16 questions, out of which 6 are related to demography, while 10 questions are related to the career and advancement of employees in the textile industry. Based on the research, we found out how important the career was for the employees and what it takes in order for an employee to advance in the textile company.

According to the first group of questions, related to demography, one can conclude that the majority of questionees are women (69,1%), which is in line with the state in the textile industry which traditionally employs women more. Most of the employees are middle aged people with considerable working experience (31,9%), so we conclude that according to their working experience those 31,9% of employees have a developed career and are in the phase of maintaining their career. This is the phase when the employee has a stable career and a good professional status one should desire to keep. The education level of the questionees who participated in the survey, employed in the textile industry, is a high school degree (36,2%), but there are also quite a number of people with a university degree. Out of all of the questionees there are textile engineers the most 53, then 18 weavers, 7 seamsters, 5 preparation workers, 3 tailors, and 4 directors and sales manager.

The second group of questions is related to the career development and advancement of employees in the textile industry. In table 1 we can see the results of the second group of questions related to the employee development and advancement in the textile industry. Marks 1-5 represent the level of agreement, or disagreement with the questions. The marks have the following meanings: 1-total disagreement, 2-partial disagreement; 3-neutral; 4-partial agreement, 5-agreement. After the analysis of the results one can conclude that the majority of employees in the textile company have set goals they would like to achieve throughout their career. This also includes finding possibilities and means to improve and develop as stated by the questionees. When considering education of employees in the textile industry, 43,6% agree that they are in need of further education. Most of the questionees agree that they lack certain types of knowledge because they think that those types of knowledge acquired through additional trainings such as seminars, fairs and scientific gatherings, can influence their career advancement.

Table 1: *Replies to the second group of questions related to the career development and advancement of employees in the textile industry*

Career development and advancement of employees in the textile industry	Percentage				
	1	2	3	4	5
1. In order to develop their career, further education is needed for the employees in the textile sector.	7,4	9,6	17,0	22,3	43,6
2. For personal advancement of employees in the textile industry retraining, specialization, master or doctoral studies are required.	7,4	4,3	18,1	54,3	16,0
3. Educational programs (conferences, scientific gatherings, fair) improve the advancement of the employees in the textile industry.	2,1	19,1	21,3	30,9	26,6
4. There is a lack of certain knowledge for successful execution of professional roles in textile companies.	5,3	5,3	22,3	29,8	37,2
5. Change of job provides better opportunity for advancement in the textile companies.	24,5	31,9	18,1	10,6	14,9
6. Managers and superiors are important for career development of employees in the textile companies.	11,7	17,0	23,4	22,3	25,5
7. Personal traits influence individual development and career development of employees in textile companies.	6,4	11,7	21,3	36,2	24,5
8. Abilities, skills and education are important factors for career development of employees in the textile industry.	2,1	5,3	14,9	29,8	47,9
9. Good social and economic conditions provide opportunities for career development of employees in the textile industry.	4,3	11,7	23,4	28,7	31,9
10. Motivation has an important impact on career development of employees in the textile industry.	4,3	11,7	13,8	25,5	47,9

The questionees totally disagree (24,5%) that change of job provides better chances for advancing within the textile company. Most of the questionees partially agree (54,3%) that retraining, specialization, master or doctoral studies are required for personal improvement of employees working in the textile industry. Questionees agree 47,9% that personal abilities, skills and education can enable career development, while 2,1% of the questionees completely disagree. Survival on the market and improvement of the market position is possible only if the employees have the knowledge, experience and skills which can enable them to solve all problems quickly and adequately both dealing with technical and organizational issues. By analyzing the last question we can conclude that motivation has a major influence on career development, to which a majority of questionees agree 47,9%. It is known that the motivation of organization members is very important for the final business result of the company. Motivation within a company urges members of the system to perform their activities in the best way and therefore, fulfill the organizational goals and personal goals.

4. CONCLUSION

According to our research we concluded how important the career is for employees and what it takes for employees to advance in the textile companies. It is very important for a textile company to keep track of what other competitors are doing in regard to innovation, improvement or maintaining quality levels, in order to make adequate decisions concerning their own quality of products by comparing it with the competitors'. The competitive advantage of the textile industry of

Serbian has to be embedded in innovation, quality, technological improvement, improved human resources. Moreover, the biggest potential, which would result in a rapid economic development of textile industry, represent educated and skilled workers. The research results showed the importance of taking initiative and active participation towards career development of employees in order for textile companies to successfully acquire favorable market positions and business results. One can conclude that an organization has a more important role than personal traits in regard to career development, and is therefore an important factor for career development of employees working in the textile sector. Those organizations which support their employees to advance and develop their careers, can expect growth and success on the market, which is very important for textile companies.

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