ANNALS
OF THE
UNIVERSITY OF ORADEA

FASCICLE OF TEXTILES, LEATHERWORK

VOLUME XVII, 2016

No. 1

ISSN 1843 – 813X

ANNALS
OF THE
UNIVERSITY OF ORADEA

FASCICLE OF TEXTILES, LEATHERWORK

VOLUME XVII, 2016

No. 1

This volume includes papers presented at International Scientific Conference "Innovative solutions for sustainable development of textiles and leather industry", 27th-28th of May 2016, Oradea, Romania

Contact and Editors' Address:
Liliana INDRIE,
UNIVERSITATEA DIN ORADEA,
FACULTATEA DE INGINERIE ENERGETICĂ ŞI MANAGEMENT INDUSTRIAL
DEPARTAMENTUL: TEXTILE- PIELĂRIE ŞI MANAGEMENT INDUSTRIAL
Str. B.St.Delavrancea nr. 4,
Oradea, 410058, Romania,
Tel.: 00-40-259-408448
E-mail : lindrie@uoradea.ro

Published by
Editura Universităţii din Oradea
Universitatea din Oradea, Str. Universităţii Nr. 1, 410087, Oradea, Bihor, Romania
P-ISSN 1843 – 813X
E- ISSN 2457-4880
CD- ISSN 2068 – 1070

Indexed in:
Index Copernicus
EBSCO-Textile Technology Complete
Ulrich's Update - Periodicals Directory
Directory of Open Access Journals (DOAJ)
Directory of Research Journals Indexing (DRJI)
InnoSpace - SJIF Scientific Journal Impact Factor
International Impact Factor Services
SCIPIO

CNCSIS ACCREDITATION since 2007 "Clasa B"

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CONTENTS

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

INVESTIGATION OF COLOR PARAMETERS AND FASTNESS PROPERTIES ON DIFFERENT KNITTED FABRIC STRUCTURES DYED WITH REACTIVE DYES

ALAM Md Shamim[1], HAQUE Mr.Emdadul[2]

[1,]South East University,, Lecturer, Department of Textile Engineering, 251/A & 252 Tejgaon I/A, 1208 Dhaka, Bangladesh, E-Mail: shamim100486@gmail.com

[2]Ahsanullah University of Science and Technology, Assistant professor, Department of Textile Engineering, 141 & 142 Love Road Tejgaon I/A, 1208 Dhaka, Bangladesh, E-Mail: emdad.haque@aust.edu

Corresponding author: Haque, Mr. Emdadul, E-mail: emdad.haque@aust.edu

Abstract: *The main objective of this paper was to analyze various color parameters and measure the fastness properties on different fabric structure like as plain single jersey, single lacoste, Terry fleece and heavy single jersey. Color has a semantic content which touching directly our sentimental world. It has a significant influence on the aesthetic properties of textiles. Color is the result of dyeing a textile material depends on the chemical structure of the dyes and the physical and chemical properties. In this research work the author use spectrophotometer to find out the color parameters among different fabric structures that were dyed with the same recipe. For this study dyeing was carried out on different fabric structures for light, medium, dark and extra dark shade. Remazol Yellow RR, Remazol Red RR, Remazol Blue RR reactive dye was used for dyeing. Heavy jersey Fabric was taken as a standard and different color parameters like as DL*, Da*, Db* and DL*, Dc*, Dh* were measured. Before measuring the color parameters different fastness properties were tested also. This study comparatively discusses on the different colour parameters and fastness properties of plain single jersey, single lacoste, Terry fleece and heavy single jersey made from 100% cotton fibre. As colour parameters are important term in wet processing and dyeing quality depends on this parameters. In this research work the Author analysis the colour parameters among different fabric structure. Standard recipe for light, Medium, Deep & extra deep Shade was used for this study.*

Key words: *Spectrophotometer, aesthetic properties, Remazol Dye, Terry fleece and heavy single jersey.*

1. INTRODUCTION

The use of knitted fabric has been rapidly increasing in world wide. Both men & women feel comfortable wearing knitted fabric for their shape fitting properties, softer handle, bulkier nature and high extension at low tension compared to woven fabric [1].Samples showed evidence of more redness and yellowness than the standard. Saturation level of dye also influenced positively in most cases i.e more intensive in higher dye concentration and fabric GSM.

Cotton today is the most used textile fiber in the world. Its current market share is 56% for all fibers used for apparel and home furnishings and sold in the U.S. Another contribution is attributed to nonwoven textiles and personal care items. Current estimates for world productions are about 25 million tones or 110 million bales annually, accounting for 2.5% of the world's arable land. China is the world's largest producer of cotton, but most of this is used domestically. The United States has been the largest exporter for many years [2].

In recent years, reactive dyes have been most commonly used the reactive dyes are the best for cotton for its wide range of application and better fastness properties [3]. There for 50% of cellulosic fibers are dyed with reactive dyes. Share of reactive dyes among all textile dyes is 29%. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics [4]. In Bangladeshi wet processing industries, reactive dyes are extremely used. The reactive site of the dyes reacts with functional group on fiber under influence of heat and alkali [6]. Fiber reactive dyes react with the cellulosic fiber in the presence of alkali to form a strong covalent chemical bond between a carbon atom of the dye molecule and an oxygen atom of the hydroxyl group in the cellulose. Reactive dyes are popular in textile manufacturing due to their fastness properties[7].

In this research Work we use cotton weft knitted (plain single jersey, single lacoste, fleece and heavy single jersey) fabric & reactive dyes. All of the samples were dyed by reactive dyes with different amount of shade% with the help of Remazol Red RR, Remazol blue RR and Remazol yellow RR. After completing dyeing different parameters like as DL*, Da*, Db*, DC* and DH* were observed.

2. MATERIAL AND METHOD:

2.1. Instruments: following are the instruments that were used during research work:
Electric Balance, Scissor, Beaker, Sample dyeing Machine, Hot wash Machine, Pipette, squeezer Machine, Dryer and Spectrophotometer with colour I match software etc.

2.2. Dye Stuff and Chemicals: The chemicals and dye stuff were collected from N.A.Z Ltd. Reactive Dye (Remazol Red RR, Remazol Blue RR, Remazol Yellow RR), Electrolyte (Gluber salt Na_2SO4. 10 H_2O), Alkali: (Soda ash-Na_2CO_3 and coustic soda NaOH), Soaping agent (SW CONE), Acetic Acid (100%), Wetting agent and Sequestering agent etc were used.

2.3 Sample preparation: In this research work I have used various weft knitted fabric samples that were prepared from N.A.Z LTD . Four types of samples were prepared including plain single jersey, single lacoste, fleece and heavy single jersey. These fabrics were made from cotton yarn,

2.2: Methodology:

2.2.1: Preparation of 0.5% stock solution: 0.5% stock solution(0.5 gm each dye mixed with 100 ml water.) was prepared for Remazol Yellow RR, Remazol Red RR, Remazol Blue RR.

2.2.2: Dyeing of Samples with Reactive Dyes: In this research work, four types of weft knitted fabric were dyed with different depth of shade%. These are:

Table 1*: Different shade% applied on weft knitted fabric*

Fabric structure	**Shade% (red 0.056+yellow 0.26+blue 0.125)**	**Shade% (red 0.11+ yellow 0.54+blue 0.262)**	**Shade% (red 0.19+ yellow 0.97+blue 0.47)**	**Shade% (red 0.24+ yellow 1.26+blue 0.61)**
plain single jersey	0.44%	0.91%	1.63%	2.11%
single lacoste	0.44%	0.91%	1.63%	2.11%
Terry fleece	0.44%	0.91%	1.63%	2.11%
heavy single jersey	0.44%	0.91%	1.63%	2.11%

The different weft knitted fabric were dyed by batch process with the help of lab dyeing machine keeping material to liquor ratio 1:10 for the above mentioned shade percentage. During dyeing standard method were followed as per prescribes by the manufacturers. At first we marked 16(4*4) dyeing pot for the 4 samples and 4 shade. The pH of the dye bath was adjusted by soda ash. Set the bath with substrate at room temperature 40°c and add sample, dyes, soda ash, Sequestering Agent, Wetting Agent, Anti Creasing Agent, Leveling Agent and salt. Then raise the temperature at 60°c at 1°/minute. Run the dyeing for 60 minutes at as same temperature 60°c. Decrease the temperature from 60°c to room temperature. After this dropped the samples from bath and rinsed and then carried on after treatment process. After dyeing the samples were washed by hot water, detergent & finally rinsed. Then the samples washed with cold water & neutralized by 1g/l acetic acid (100%) for 10 minutes. Dry the sample by incubator (dryer). Then take the spectrophotometer reading for different color parameters.

2.2.3: Color Fastness Measurement:

In this research work, three types of fastness properties were measured [8-10] like as Color fastness to wash (ISO 105 C04 B2S), Color fastness to water (ISO 105 E01) and Color fastness to rubbing (ISO 105 X12)

2.2.4: Color parameters measurement:

Color iMatch was used for taking different color parameter (CIE L*a*b* and CIE L*C*h°) under the D65 and 10 degree Observer.

3. RESULTS AND DISCUSSION:

3.1: Analysis of Fastness Properties: different color fastness properties like as color fastness to wash, water and rubbing were measured according to ISO standard. The results are as follows:

Table 2: *Color fastness to wash for different knitted samples dyed with different shade%*

Fabric	Shade%	Color Staining						Color
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
plain single jersey	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4-5
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4	4	4	4
single lacoste	0.44%	4-5	4	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4-5
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4	4	4	4
Terry fleece	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4-5
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4	4	4	4
heavy single jersey	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4-5
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4	4	4	4

From the table, the results of Color fastness to wash of cotton knitted fabric for different dept of shade have been showed. Wash fastness of cotton knitted fabric decrease with the increases of shade. Here for color staining cotton and wool show considerable color change but Acetate, Nylon, polyester, Acrylic are almost same.

Table 3: *Color fastness to water for different knitted samples dyed with different shade%*

Fabric	Shade%	Color Staining						Color
		Acetate	Cotton	Nylon	Polyester	Acrylic	Wool	
plain single jersey	0.44%	4-5	4	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4-5	4	4	4
single lacoste	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4-5	4	4	4
Terry fleece	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4-5	4	4	4
heavy single jersey	0.44%	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	0.91%	4-5	4	4-5	4-5	4-5	4	4
	1.63%	4-5	4	4	4-5	4	4	4
	2.11%	4	4	4	4-5	4	4	4

It is seen from the above result of Color fastness to water of cotton knitted fabric for different shade%. Water fastness of cotton knitted fabric decrease with the increases of shade%.

Table 4: *Color fastness to rubbing for different knitted samples dyed with different shade%*

Fabric structure	Shade%	Dry Rubbing	Wet Rubbing
Plain single jersey	0.44%	4-5	4
	0.91%	4-5	4
	1.63%	4-5	4
	2.11%	4	3-4
Single lacoste	0.44%	4-5	4-5
	0.91%	4-5	4
	1.63%	4	4
	2.11%	4	4
Terry fleece	0.44%	4-5	4-5
	0.91%	4-5	4
	1.63%	4	4
	2.11%	4	4
Heavy single jersey	0.44%	4-5	4-5
	0.91%	4-5	4-5
	1.63%	4	4
	2.11%	4	4

It is seen from the above result of Color fastness to rubbing (dry & wet) of cotton knitted fabric for different shade are observed and fastness properties decrease with the increases of shade%.

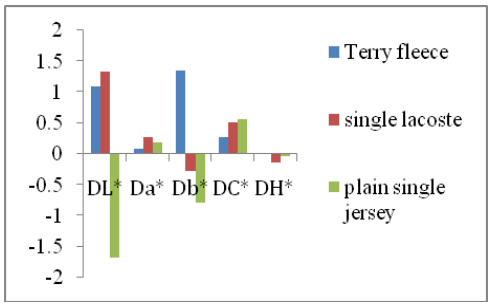


***Fig. 1**: Effect of color parameters on different fabric Structure dyed with 0.44% shade*

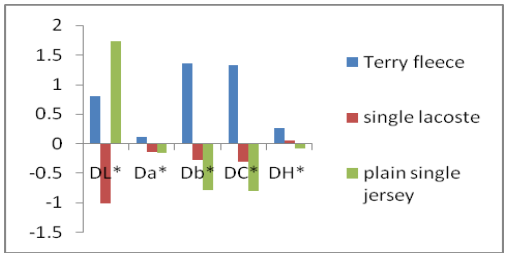


***Fig. 2**: Effect of color parameters on different fabric Structure dyed with* 0.91% shade

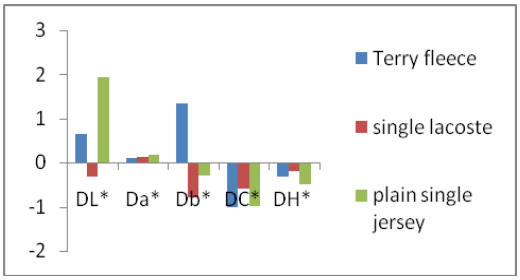


***Fig. 3**: Effect of color parameters on different fabric Structure dyed with* 1.63% shade

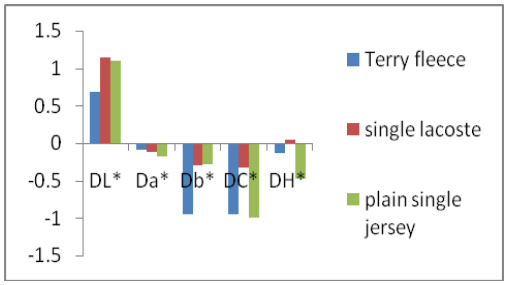


***Fig. 4**: Effect of color parameters on different fabric Structure dyed with* 2.11% shade

It is seen from the above graph that the effect of different color parameters varies from fabric to fabric. It is also observed from the graph DL* (lightness or darkness), Da*(reddish or greenish), Db*(yellowish or bluish), DC* (Chroma or saturation) and DH*(Hue) varies with the fabric structure and shade%.

4. CONCLUSIONS

In this research work, it was observed that, with the increase of shade% for different fabric structures, Color fastness properties of weft knitted fabric are affected. Again it was also observed With the increase of shade% of cotton knitted fabric a considerable change were found for different color parameters (CIE L*a*b* and CIE L*C*h°).At last we can say that, there is a considerable Effect of knitted structure were investigated for different color parameters and color fastness to washing, color fastness to rubbing and color fastness to water when cotton knitted fabric were dyed with different shade% i.e 0.44%, 0.91%, 1.63% and 2.11%.

REFERENCES

[1] V. A. Shenai (1993),*Technology of Textile processing,* Sevak Publications, Bombay, Vol-II, 557.

[2] Arthur D Broadbent (2001), *Basic principles of Textile Coloration,* Society of Dyers and colourists, 346-347.

[3] Deane B. Judd (1940), *Hue, saturation and lightness of surface colors with chromatic illumination,* Journal of the Optical Society of America, Volume 24, March 1940, 1-32, ISSN 2277 – 4106.

[4] Md. Rahman, A.K.M. A.H. Asif, Md. A.B. Siddique, Md. Rokonuzzaman(2014), *Effect of shade percentage on various properties of cotton knitted fabric dyed with reactive dyes*, International Journal of Research in Engineering and Technology, Vol.3(2),.339-343., ISSN: 2319-1163.

[5] A. N. M. A. Haque (2014), *Influence of electrolyte and liquor ratio on exhaustion and color coordinates of cotton fabric dyed with monofunctional and bi-functional reactive dyes, Borneo Science,* 34, 27-33.

[6] R. B. Rangulam, J. Amirbayat and I. Porat(1993), *"The Objective Assessment of Fabric Pilling Part 1: Methodology,"* Journal of Textile Institute, 84, pp. 221-226, ISSN: 2212-1185

[7] Ahmed Asif, , Moshiur Rahman, , Farial Islam Farha(2015), *Effect of Knitted Structure on the Properties of Knitted Fabric,* International Journal of Science and Research (IJSR), Volume 4 Issue 1, January 2015, ISSN (Online): 2319-7064,

[8] ISO 105-C04:1989; Textiles -- *Tests for colour fastness* -- Part C04: Color fastness to washing: Test 4

[9] ISO 105-E01:1994; Textiles -- *Tests for color fastness* -- Part E01: Color fastness to water

[10] ISO 105-X12:2001; Textiles -- *Tests for color fastness* -- Part X12: Color fastness to rubbing

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FE-SEM COMPARATIVE STUDY ON SURFACE MODIFICATION OF WOOL FIBER AFTER DIFFERENT CHEMICAL TREATMENTS

BONET-ARACIL Marilés[1], BOU-BELDA Eva[1], DIAZ Pablo[1], RUIZ-CALLEJA Tamara[1]

[1] Universitat Politècnica de València, Textile and Paper Department, Plaza Ferrándiz y Carbonell s/n, 03801, Alcoy, Spain.

Corresponding author: Bonet-Aracil, M. E-mail: maboar@txp.upv.es

Abstract: *Wool surface comprehends numerous scales which are responsible of certain undesirable behavior of this fiber during its use and maintenance. One of the most significant issues is related to shrinkage, caused during washing, as a consequence of friction between the fibers. Chemical modification of wool is considered a useful option to avoid these kind of circumstances. During the last years, multiple alternatives for chemical modification of wool have been studied, comprising enzymes or acids amongst others. In this case of study, three different treatments were carried out in order to evaluate wool morphological appearance. The first treatment was an oxidative procedure, containing Basolan DC and sodium acetate as the main components. The second treatment was accomplished using Lanaperm VPO, a commercial finishing agent for wool fiber that claims to soften its surface. The third finishing process was performed employing Siligen FA, a commercial agent intended to act as an antimigrant for dye baths and also provide a smoother and regular surface. After said treatments, microphotographs of all treated and untreated fibers were taken so that a comparison between final appearance could be done. Analyzing results and conclusions, it can be stated that chemical modification of fiber does change its surface appearance and, consequently, its behaviour.*

Key words: *Oxidation, Lanaperm, Siligen, wool cuticle, scales*

1. INTRODUCTION

Natural protein fibers are formed by animal sources through condensation of α-amino acids to produce repeating polyamide units with various substituents on the α-carbon atom. The sequence and type of amino acids making up individual protein chains contribute to the overall properties of the resultant fiber. Wool is a protein fiber chiefly composed of keratin. It is a natural, highly crimped protein hair fiber derived from different breeds of sheep such as Merino, Lincoln, and Sussex, amongst others [1]. Despite the fact that wool can be used not only for cloths but for upholstery or technical textiles, it is estimated that two thirds of the wool production are focused on the manufacture of garments. Wool is widely known by its properties mailt thermal insulation and moisture retention what makes it to be a fibre which does not retain static electricity. Fineness of wool determines the final use. There is a vast range of fibres fineness. It can vary from 16 microns to 40 micros from the coarse fibres. Fineness is a parameter which will influence the touch of the fabric made of wool. Due to its properties wool has been used for cloths market ans anciently was considered the most resitant to fire. However, synthetic fibres imporved their behavior regarding falmability and wool has been used mainly in garments.

Among all the advantages wool can confer to products made of it, there is a special characteristic of this fibre, the scales. The scales are overlapped on the fibre surface and are observed on every animal fibre including animal hair. They are responsible of the users´sking stinging when wearing that kind of gaments on the skin. If the scales are adhered to the fibre surface they should not confer any side effect on peoples´skin. On the other hand, when scales are slightly opened the user can notice it depending on the skin sensibility. Scales are also respoible of felting. Whe the scales slip over one onether the scales interlock and prevent the fibre from coming back to the original position and offere a felt. Felting can be cosndiered a desired effect for some fabrics and felts can be used in shoues hats and many other goods. Felting shrinkage is a typical property of wool when washed and must be controlled to achieve a washable wool product [2]. Due to the configuration of the cuticle scales on the surface of wool fiber, the mechanical action of aqueous washing causes the progressive entanglement of wool fibers leading to irreversible shrinkage of wool fabric [3]. Smoothing or eroding the cuticle scales lowers the friction between the fibers and therefore can prevent shrinkage. Shrink-resist finishing processes often consist of an oxidation/reduction step to degrade the cuticle scales and/or an additive polymer process to mask the scales [4-6].

It is not conceivable to develop a garment with wool and not having to wash it. Soaps usually confer an alkaline pH to water. Alcaline pH is harmful for proteinic fibres, however, it is not the only one, many oxidative products are used on laundry nowadays. Since oxidative treatment can damage the fiber, plenty of alternative treatments are being tested in order to smoothen wool's surface as well as attempting to avoid shinkragee, causing as less degradation to the fiber as possible. Thus, this comparative study highlights the differences between three different treatments, including oxidative process and two other finishing products comprising Lanaperm VPO and Siligen FA

2. MATERIALS AND METHODS

2.1 Fabric

Wool fabric used was supplied by SDC ENTERPRISES LIMITED according to BS EN ISO 105 F01 standard.

2.2 Oxidative treatment

Oxidative treatment was carried out to degrade the wool scales in order to avoid fabric feltering. It consists of a treatment using the sodium salt of dichloroisocyanuric acid, Basolan DC (Basf, Germany).

Table 1: *Oxidative treatment parameters*

Wetting agent	1% owf
Sodium acetate	1g/l
Acetic acid	0.5 g/l
Basolan DC	5% owf
pH	3-4
Fibre weight	0,20 g
Temperature	Room temperature
Liquor ratio	1:80
Time	Samples were extracted 9 hours

2.3 Lanaperm treatment

Lanaperm VPO (Archroma) is a chlorine-free pretreatment agent for antifelt finishing of textiles made of wool and wool blends, supplied by Archroma. The treatment with this product is supposed to cause a light, superificial attack on the wool fibre. Spreading of the wool scales is said to be reduced which would result in a certain reduction of felting.

Table 2: *Lanaperm treatment parameters*

Lanaperm VPO	5% owf
Fibre weight	0,50 g
Temperature	Room temperature
Liquor ratio	1:80
Time	Samples were extracted after 24 hours

2.4 Siligen treatment

Siligen FA (BASF) is a finishing agent which performs as an antimigrant for pigment pad dye and one-bath pigment dyeing and also claims to impart a softer hand of the fabric.

Table 3: *Siligen treatment parameters*

Siligen FA	5 g/l
Fibre weight	0,50 g
Temperature	Room temperature
Liquor ratio	1:80
Time	Samples were extracted after 24 hours

2.5 Characterization of samples

A Field emission scanning electron microscope (FESEM) ULTRA 55 (ZEISS) was used for observation of surface morphology at direct magnification ranging. Samples were tested at 1 kV. Prior the analysis, samples were gold/paladio coated using Sputter Coater EMITECH mod. SC7620 (Quorum Technologies Ltd.).

3. RESULTS AND DISCUSSIONS

After haveind used fifferent productos on the fibre, in ordet to determine the scales shape or effect some observation was conducted. SEM images of the morphological structure of wool fibers were taken in order to make a visual comparison between different treatments achievements

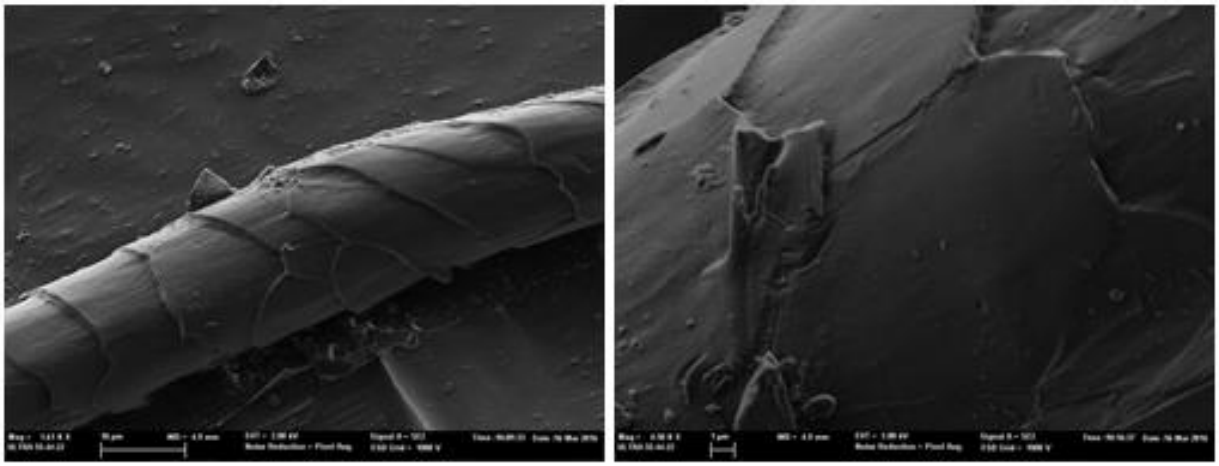


***Fig. 1 and 2**: FE-SEM images of untreated wool fiber*

As explained before, wool is composed of numerous scales, sharp and pointed as seen in the images above (fugures 1 and 2) , which are responsible for wool shrinkage due to friction between them when washing.

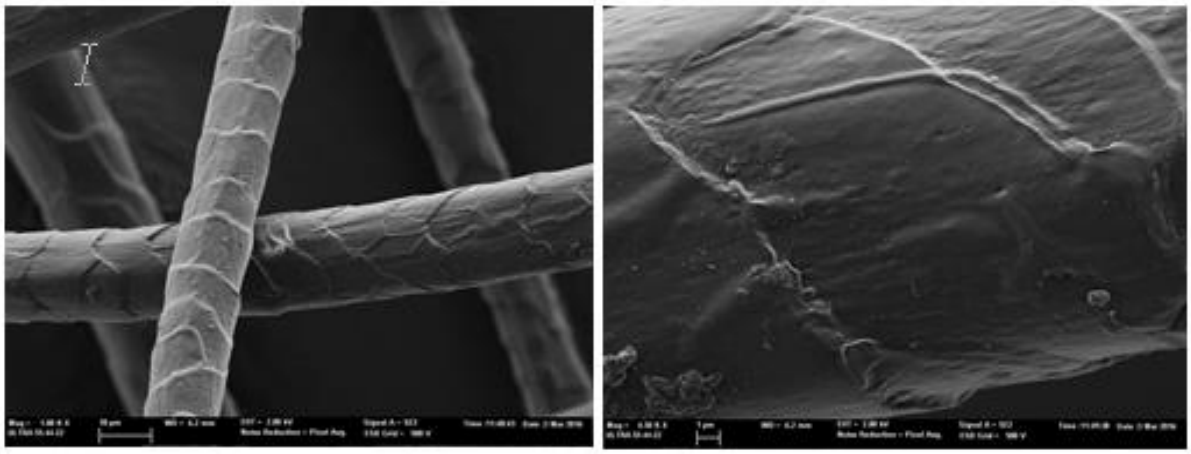


***Fig. 3 and 4**: FE-SEM images of wool fiber after 9 hours of oxidative treatment*

Figures 3 anf 4 show wool fibres at different magnifications range when they have been exposed to an oxidative treatment for a period of time. After nine hours of oxidative treatment, images show that wool surface has been softened, reducing scales' edges. However, this fact would involve a modification in fibre´s properties sucha as weight loss, weakening the fiber etc.

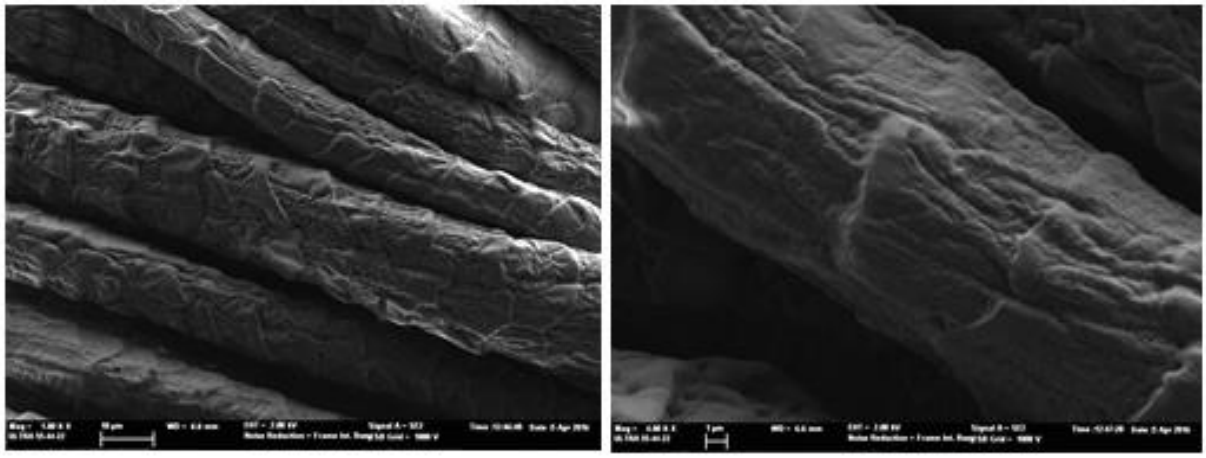


***Fig. 5 and 6**: FE-SEM images of wool fiber after 24 hours of Lanaperm treatment*

Lanaperm does not smoothen surface, but acts by coating it, achieving a soft and wavy surface of a sharpie one. This would mean a reduction of friction while washing, so shrinkage would decrease.

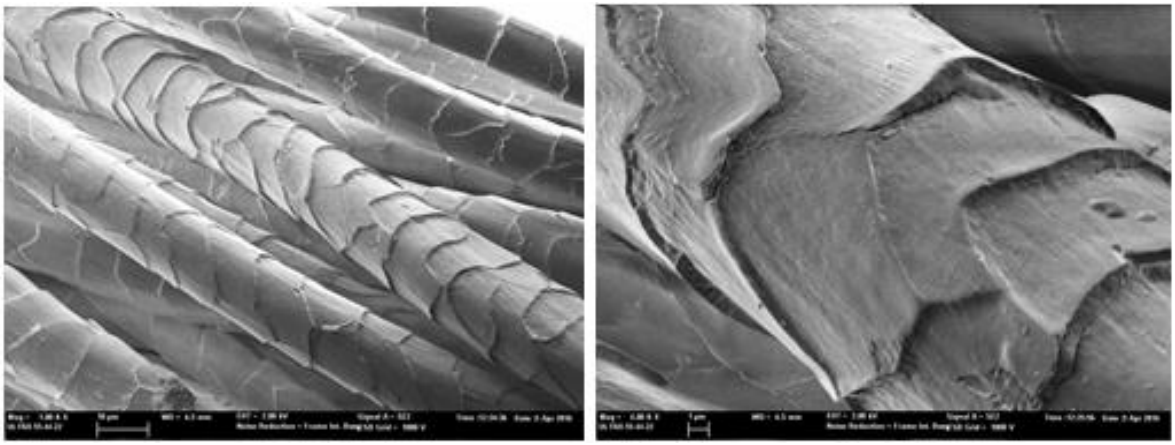


***Fig. 7 and 8**: FE-SEM images of wool fiber after 24 hours of Siligen treatment*

Apparently, from FE-SEM images observation, wool fibers after Siligen treatment do not seem to have had a relevant change, as scales remain almost the same as untreated wool, with certain polishing although not really pronounced. More tests appart from FE-SEM should be conducted to determine its effect.

4. CONCLUSIONS

After the comparative study of these three different wool finishing treatments, it can be said that oxidative treatment is the one that achieves highest degradation of scales, although it is really aggressive to the fiber so its use will not always be suitable for all kind of purposes. On the other hand, Siligen treatment did not make any significant change onto fiber surface, as scales are slightly softened but still noticeable and sharpened, perhaps more concentration was recquired. However, Lanaperm treatment demonstrates a favorable behavior, filling scales edges and smoothing wool's

surface, providing a soft hand and thus avoiding friction. Future studies would be carried out in order to analyse the fibre response and determine the chemicals effect.

AKNOWLEDGEMENTS

Authors would like to aknowledge to Electron Microscopy Service of the UPV for their support during the analysis of the wool surface and to Archroma and BASF Companies for supplying chemicals.

REFERENCES

[1] K. M. Babu, Natural Textile Fibres: *"Animal and silk fibres".* Elsevier Ltd. 2015.

[2] Hurren, C., Cookson, P., & Wang, X. *"The effects of ultrasonic agitation in laundering on the properties of wool fabrics"*. Ultrasonics sonochemistry, 2008, 15(6), pp.1069-1074.

[3] Shen, J. Smith, E. *"Enzymatic treatments for sustainable textile processing. Sustainable Apparel: Production"*, Processing and Recycling, 2015, 119.

[4] J. Lewis, *"Superwash wool part 1: a review of the development of superwash technology",* Wool Sci. Rev, 1977, 54, pp. 2 -29

[5] J. Lewis, *"Superwash wool part 2: continuous shrinkproofing processes*", Wool Sci. Rev, 1978, 55, pp. 23 -42.

[6] E. Smith, J. Shen, "*Surface modification of wool with protease extracted polypeptides*". Journal of Biotechnology, 156(2), 134–140. 2011

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A REVIEW OF COLOR MEASURMENTS IN THE TEXTILE INDUSTRY

BRAD Raluca

Lucian Blaga University of Sibiu, Faculty of Engineering, Industrial Machinery and Equipments Department,
B-dul Victoriei 10, 550024 Sibiu, Romania, E-Mail: raluca.brad@ulbsibiu.ro

Abstract: *Color is an important factor in the evaluation of aesthetic appearance and functionality of many products, but especially of textile industry ones. In textiles production process, color can be assessed in different stages: the selection of raw materials, the incoming item tests, the preparation of dyeing ingredients, the crocking resistance testing, the color fastness and in all stages, the quality control. Color evaluation can be done visually or using specialized test instruments such as colorimeters or spectrometers, therefore a high accuracy of measurements must be achieved. Standards describe different procedures and testing techniques depending on the product type and the quality level required by the customer. The paper presents the most common systems of color representation and communication, measurement methods and techniques, and standards that define them. The CIE color representation systems have been reviewed, together with the measurement methods offering the repeatability of the process. Most of the standards have been issued in US, but several European and International are stating the color assessment process. We have also conducted a review of latest published papers in the topic of color measurement, comparison and match. Several image processing applications algorithms offers new opportunities for computer assisted evaluation and control of textile color properties.*

Key words: *color measurement, measurement technique, quality control, CIE Lab, spectrophotometer.*

1. INTRODUCTION

Like any other artistic feature, color was a subjective issue in textile industry. A century after the beginning of industrialization, subjective matters started to become standards and measurable attributes. In this respect, the science of color originate almost at the above mentioned date and followed the nowadays quality assurance systems. Color measurement has important application in the selection of raw materials, the preparation of dyeing ingredients, the crocking resistance, ensuring the repeatability of production process, quality control and many others. Early systematic approaches on color matching and color control have been reported by [1], with a method for color quality improvement in dyeing of synthetic and natural fibers.

The quality of the measurement can be determined by the analysis of uncertainty. The quantification of measurement uncertainty is allowing textile manufacturers to maintain under control the quality of products [2]. Also, a comparison between the CIE Lab difference equation and a large group of observers in view of practical validation was carried out in [3]. The paper presents some important conclusions regarding accurate color matching in textile industry. The problems of cotton color measurement was investigated in [4], with a comparison of the classer and HVI color grading, using cotton samples of non-U.S. origin. The authors could replace the organoleptic assessment used for years with the spectrophotometry for grading the quality of cotton.

The paper presents a review on standardized color representation and measurement techniques for the use of textile industry. It also examines the most important papers published in the field, emphasizing their practical application.

2. COLOR REPRESENTATION

Color, as we perceive it, can be characterized by three measures: hue, chroma and lightness, which uniquely identify it and could be used to make the distinction between it and any other. Hue is used to describe the fundamental color, as we can observe, represented on the color wheel. Chroma represents the saturation of the color, as it fades to gray or vivid to the pure hue. The light intensity in a color is measured by lightness, as it varies from white to black at the extremes, as shown in figure 1.

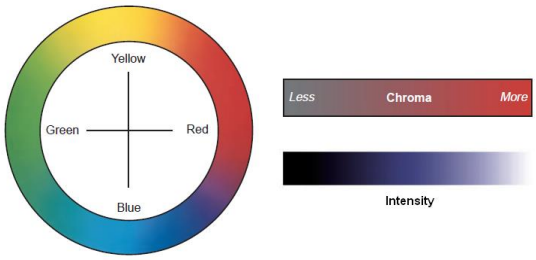


***Fig. 1**: Perceived color components [15]*

Several color spaces have been standardized over the years, with different industrial or scientific applications: Munsell, CIE Lab, CIE Lch, CIE XYZ, Hunter Lab [5]. Albert Munsell proposed in 1905 a human perception based color scale still in use today and known as the Munsell System of Color. It assigns numerical values to the three properties of color: hue, chroma and lightness, and therefore it was the first to represent colors in 3D space. The Munsell Color System was also the base for the more up-to-date representation spaces as CIELab.

Due to the fact that in the formation of visual color, three elements are required, as a light source, the object and the observer, in 1931 the Commission Internationale de l'Eclairage (CIE) has standardized a color system by specifying the light source, the observer and the methodology employed to extract the measures for color description. There are three spaces proposed by CIE, in which a color can be localized by the means of three values: CIE XYZ, CIE Lab and CIE Lch [8].

The first system introduced in 1931 by CIE, was based on tristimulus values XYZ, which unfortunately will have limited use because of a low correlation with visual attributes. If the *Y* value refers to lightness, the two others have no relation with hue and chroma. Therefore it was recommended to use the chromaticity coordinates xyz, as in figure 2. The notation Yxy specifies colors by identifying lightness *Y* and the color in the chromaticity diagram (*x*,*y*). In order to surmount the difficulties using the diagram, CIE standardized two uniform scale spaces in 1976, the Lab and Lch, still in use today.

In the Lab space, *L* represents the lightness, while *a* and *b* represents the chromaticity values, as in figure 2. In the presented diagram, *a* and *b* designate color directions: +*a* is in the red direction, -*a* is in the green direction, +*b* shifts towards yellow and -*b* shift in the blue direction. The center of the diagram located in a vertical axis that is achromatic; as *a* and *b* values moves from the center, color saturation increases. If the CIE Lab uses Cartesian coordinates which represent a color, the CIE Lch employs polar coordinates. The Lch color space uses the same diagram but with cylindrical coordinates as an alternative to the rectangular coordinates, with *L* representing lightness, *c* the chroma value, and *h* the hue angle. The chroma values start from 0 in the center and increases

with distance, while hue as an angle, starts at 0 degrees for red, pass through 90° for yellow, 180° for green and 270° for blue (figure 2).

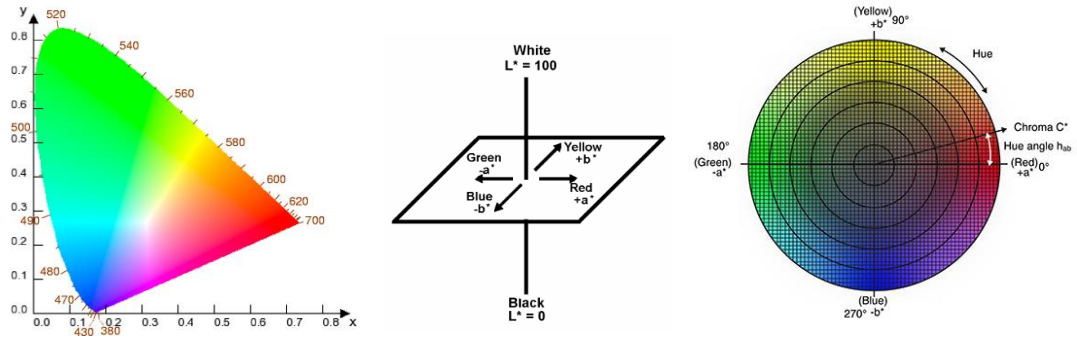


***Fig. 2**: CIE XYZ diagram, CIE Lab and CIE Lch color space[5], [6]*

3. COLOR MEASUREMENT

The observed difference between textile materials colors of different batches is inevitable and it is impossible to completely eliminate even if originates from the same dyeing process. It is very important that the client and manufacturer agree about acceptable and not acceptable products. This can be determined objectively using a color measuring instruments as colorimeter or spectrophotometer. This procedure will replace the subjective human errors, giving quantitative measurements for identifying, specifying and matching colors.

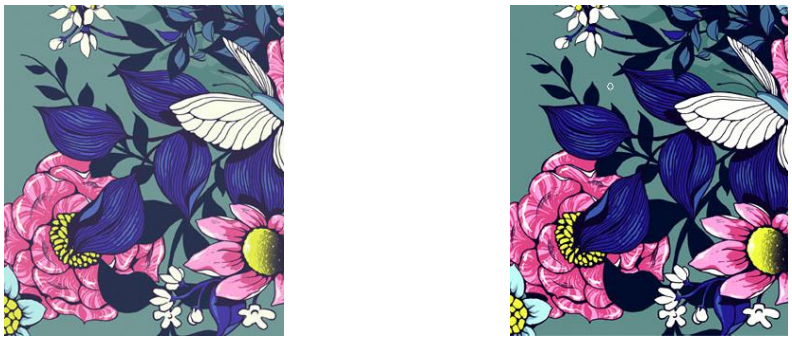


***Fig. 3**: Comparison of two printed weft materials in CIE Lab space*

The differences between the two samples of the material in the CIE Lab space is assessed as a color difference (delta), noted with ΔL, Δa, Δb. The total difference or distance ΔE, can be computed as single value using the following formula:

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

If we compare the two printed textile samples in figure 3, for the color in the white circle depicted in the right image, the Lab values are L=56, a=-12, b=-1, while for the same coordinates in the left image L=60, a=-15, b=-3. In this case, the differences will be with ΔL=4, Δa=-3, Δb=-2 and ΔE=5.38, indicating that in the right image, the color values are greener and bluer (figure 2).

A successful quality control and color measurement stands on the accurate assessment of measured samples and the repeatability of the process in standardized appropriate conditions. As a number of spectrophotometers are available on the market, most of them are configured to meet measurement requirements depending on the type of material. The sample is positioned relative to

the light source and the observer/instrument and forms what it's called geometry. The diffuse/8 and 45/0 are the most used methods for color measurements with spectrophotometers.

A spectrophotometer with the diffuse/8 geometry, uses a sphere illuminated by a D65 filtered light, reflects on the surface of the sphere and the reach the sample forming a uniform illumination, as in figure 4. The reflected light is measured by the sensor within an angle of 8° from the normal to the specimen. The advantage of the system is that it minimizes the irregularities of the sample surface. Special applications of the system are in shade matching or dyeing production.

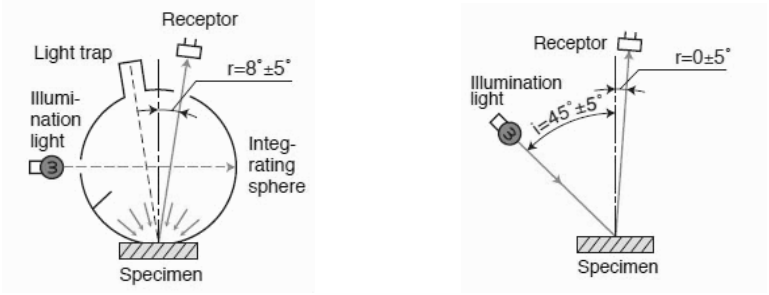


***Fig. 4**: Diffuse/8 and 45/0 system geometry[7]*

In the case of the 45/0 spectrophotometer, a light source illuminates the sample in an angle of 45°, while the sensor is placed at 0° in order to measure the sum of reflections from the specimen surface. This type of measurement system is more sensitive to surface irregularities; therefore it also measures the appearance of the sample. Consequently, the 45/0 system is used in quality control applications where the observed differences in texture and finish are important.

4. MEASUREMENT TECHNIQUES

For the quality control program it is important to provide methods ensuring the repeatability of the color measurements. In order to acquire and store valuable measures, samples must be measured multiple times in the same conditions of temperature and humidity. The thickness is also an important factor, as two to four layers are required for knits or woven materials in order to prevent the undesired reflection of light on the background. An opaque material layer will lead to a correct measured value, but thin or light textiles could require more layers. In some cases, a single layer on top of a white tile could be used for comparison purposes, as the reflectance component can be ignored.

Textile materials have an important directional feature, due to the positions of yarns or loops, therefore in order to reduce measurement variability the sample is rotated in four to eight directions. Each time, precaution must be exercised for correct leveling the material and avoid contaminations. The control technique is repeatable if the specimen is removed from the spectrophotometer and when re-measured, the differences are less than 0.15 DE(CMC) units. A common method employed for producing a correct measure is to rotate and reposition eight times the specimen and average the result [7]. The influence of the instrument geometry and the texture of samples were investigated in [8], describing the fact that the difference between D/8 and 45/0 doesn't depend on the texture and color of samples, but on the color center. The authors concluded that the D/8 produce lighter *L* component values. The most common International, European and US standards establishing the conditions, procedures and measuring instruments are presented in table 1.

In a study report [9], the use of CCD cameras instead of specific instrumentation was considered. It has been shown that on printed CMYK textiles, the RGB CCD camera obtained the

best results, and with the use of a calibrated matrix, it allows color detection with higher accuracy then a default matrix. The same comparison in view of an instrument development was presented in [10], were a tri-stimulus camera together with specific software was completed. In the same direction of replacing dedicated instrumentation, the authors in [11] have investigated the possibility of using a flat-bed scanner to assess fabric color with different texture. It was shown that the texture has a strong influence on the measurements performance; the scanner resolution has no influence on the error, but the quantization depth could decrease that influence.

Table 1: *A list of most common standards and their description [7]*

Standard	Description
AATCC Evaluation Procedure 6 Instrumental Color Measurement	a reference document covering instrumental reflectance measurement, related calculations, sample handling techniques
AATCC Test Method 173 CMC: Calculation of Small Color Differences for Acceptability	how to calculate and use the dE CMC color difference scale.
AATCC Test Method 182 Relative Color Strength of Dyes in Solution	determination of color strength of a dye spectrophotometrically by comparing its transmission measurements to reference dye
ASTM E1164 Standard Practice for Obtaining Spectrophotometric Data for Object-Color Evaluation	instrumental measurement requirements for spectrophotometers and colorimeters
ASTM E1345 Standard Practice for Reducing the Effect of Variability of Color Measurement by Use of Multiple Measurements	averaging as a technique for minimizing sample variation
ASTM E1347 Standard Test Method for Color and Color-Difference Measurement by Tristim. Colorimetry	color measurement using tristimulus colorimeters of either 45°/0° or diffuse geometry
ASTM E1349 Standard Test Method for Reflectance Factor and Color by Spectrophotometry Using Bidirectional Geometry	color measurement of opaque samples using a spectrophotometer with a 45°/0° or 0°/45° geometry
ASTM E1767 Practice for Specifying the Geometries of Observation and Measurement to Characterize the Appearance of Materials	different geometries of instruments that measure appearance
ASTM E179 Standard Guide for Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials	appropriate instrument types and measurement scales for evaluating appearance characteristics such as color, glossiness, and opacity
ASTM E2022 Standard Practice for Calculation of Weighting Factors for Tristimulus Integration	how to establish tables of weighting factors that are to be used in calculating tristimulus values from spectral reflectance or transmittance data
ASTM E275 Standard Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near-Infrared Spectrophotometers	the requirements of spectrophotometric performance for ASTM methods and explains how to test an instrument
ASTM E284 Standard Terminology of Appearance	terms used in describing appearance, as color and opacity
ASTM E308 Standard Practice for Computing the Colors of Objects by Using the CIE System	the calculation of CIE XYZ and other color scales from spectral reflectance and transmittance values and defines the CIE illuminants and standard observers
ASTM E313 Standard Practice for Calculating Yellowness and Whiteness Indices from Instrumentally Measured Color	the whiteness and yellowness indices
ASTM E805 Standard Practice for Identification of Instrumental Methods of Color or Color - Difference Measurement of Materials	how to effectively communicate color values and all the parameters that affect them
DIN 5033 Colorimetry	visual and instrumental color analysis, color concepts
DIN 6174 Colorimetric Evaluation of Colour Differences of Surface Colours According to the CIELAB Formula	measuring dL*, da*, and db* using an instrument.
ISO 105-J01, J02, J03 Textiles - Tests for colour fastness	general concepts and problems of reflectance color measurement, calculation of the color difference between two samples and allows for the specification of tolerances
ISO 7724-1, 2, 3 Paints and varnishes - Colorimetry	colorimetric terms and fundamental requirements for determining the color coordinates, determining of color values using a spectrophotometer or colorimeter
ISO/CIE 10526 CIE standard illuminants for colorimetry	the CIE standard illuminants
ISO/CIE 10527 CIE standard colorimetric observers	the CIE standard observers

The use of nowadays computer vision techniques in the unsupervised analysis of color and pattern in printed fabric could be found in [12]. The use of a Fuzzy C-Means clustering algorithm has been proved to be successful in the processing of digital images. In the same direction of

computer assisted inspection, other papers report on printed fabric segmentation with Mean-Shift algorithm [13] or color separation with back-propagation neural networks [14].

5. CONCLUSIONS

One of the major aspects of quality implies color measurement and control, starting from raw materials and finishing with completed products. The aesthetic appearance is one of the factors that influence client's behaviors, as natural, dyed or printed color. This feature is determined objectively using color measuring instruments and replaces the subjective human errors. Using tools like a colorimeter or spectrophotometer, both quantitative and qualitative information are obtained. Computer based image processing applications could be used in the automation of color measurement, segmentation and control.

Based on the product type, final application and process production, the color measurement technique must be selected among the standardized ones, employing the methods and instruments presented in the paper. Also, we have reviewed the literature published over the last years in this domain.

REFERENCES

[1] H. R. Davidson, H. Hemmendinger and J. L. R. Landry Jr., *"A System of Instrumental Colour Control for the Textile Industry"*, Journal of the Society of Dyers and Colourists, vol. 79, no. 12, pp. 577–590, December 1963

[2] N. Milić, D. Novaković, N. Kašiković, *"Measurement uncertainty in colour characterization of printed textile materials"*, J. Graphic Eng. and Design, vol. 2(2), pp. 16-25, 2011

[3] H. Mangine, K. Jakes, and C. Noel, *"A preliminary comparison of CIE color differences to textile color acceptability using average observers"*, Color research and application, vol. 30, no. 4, pp. 288-294, 2005

[4] M. Matusiak and A. Walawska, *"Important aspects of cotton colour measurement",* Fibres & Textiles in Eastern Europe, vol. 18, no. 3, pp. 80, 2010

[5] R.W.G. Hunt and M.R., Pointer, Measuring colour, John Wiley & Sons, 2011

[6] *, A Guide to Understanding Color Communication, X-Rite Inc., Michigan, 2007

[7] K.R. Butts, *"Keys to reliable digital color communication"*, AATCC review, vol. 4(4), pp. 15-19, 2004

[8] S.G. Kandi, *"The effect of spectrophotometer geometry on the measured colors for textile samples with different textures"*, Journal of Eng. Fibers and Fabrics, vol. 6, pp. 70-78, 2011

[9] H. Stokman T. Gevers, Color Measurement of Printed Textile using CCD Cameras, 1998

[10] M.A. Hunt, J.S. Goddard Jr, K.W. Hylton, T.P. Karnowski, R.K. Richards, M.L. Simpson, K.W. Tobin Jr., and D.A. Treece, *"Imaging tristimulus colorimeter for the evaluation of color in printed textiles"*, Electronic Imaging'99, SPIE, pp. 118-128, 1999

[11] H. Fashandi, S.H. Amirshahi, M. Amani Tehran, S.Gorji Kandi, *"Evaluation of scanner capability for measuring the color of fabrics with different textures in different setups"*, Fibers and Polymers, vol. 11, no. 5, pp. 767-774, 2010

[12] C. Kuo, C. Shih, C. Kao, and J. Lee, *"Color and Pattern Analysis of Printed Fabric by an Unsupervised Clustering Method"*, Textile Research Journal, vol. 75, pp. 9-12, January 2005

[13] P. Li, S. Wang and J. Jing, *"The segmentation in textile printing image based on mean shift"*, IEEE 10th International Conference on CAID & CD, Wenzhou, pp. 1528 -1532, 2009

[14] C. Kuo, T. Su, Y. Huang, *"Computerized color separation system for printed fabrics by using backward-propagation neural network",* Fibers and Polymers, vol. 8(5), pp. 529-536, 2007

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EFFECT OF POLIESTER POY FIBRE CROSS-SECTION ON THE YARN PROPERTIES OF AIRJET TEXTURING

CANOGLU Suat[1], YUKSELOGLU S. Muge[2]

[1]Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe Campus, 34722, Istanbul, Turkey, E-Mail: scanoglu@marmara.edu.tr

[2]Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe Campus, 34722, Istanbul, Turkey, E-Mail: myukseloglu@marmara.edu.tr

Corresponding author: Canoglu, Suat, E-mail: scanoglu@marmara.edu.tr

Abstract: *POY yarns are well know and commercialized since 1970s. On the other hand, air-jet textured yarns are very common due to their unique structure which looks like natural spun-staple yarns. In the air-jet texturing process, the yarn is textured by overfeeding into a high-pressure of air to create a looped and more natural yarn appearance and also the bulkiness level of the yarn is controlled by input speed and jet-take out speed. This process reassigns flat, continous synthetic yarns into entangled, convoluted, bulky, spun like structured yarns. They are of higher bulk, exhibits increased covering power, have a more subdued lustre and are warmer in hand. Therefore, air-jet textured yarns possess some unique properties that require investigation. Hence, in this study, first the texturing process is introduced briefly and its principle of manufacturing is illustrated, later four different types of yarns were produced with two different fibre cross-sections at the three different nozzle types and three different core yarn feeding. The produced yarn production details are given and their breaking strength, elongation and work of rupture are studied along with their morphological structures by using light microscope and SEM. The aim of this study is to investigate the effect of POY fibre cross-section on air-jet textured yarn mechanical properties. The overall results showed that coarser air-jet textured yarns with a round shape have higher breaking strength, elongation and work of rupture than the trilobal shaped yarns. On the other hand, half matted yarn which was applied TiO_2 has also presented better breaking strength and elongation.*

Key words: *Poliester, Air-jet, Textured yarn, Mechanical properties, Cross-section*

1. INTRODUCTION

Partially oriented yarn known as POY spinning technique was initially investigated in the early 1950s and was commercialized in 1970s. Today is generally are produced by spinning at speeds of 2500 to 4000m/min. On the other hand, the term “texture” defines and describes those attributes of an object that can be recognized by the human sight (visual characteristics) or touch (tactile characteristics) [1]. These attributes of an object features bulk, hand and warmth as the tactile properties, for appearance and lustre as the visual properties. Because of the growing world demand on textile goods and an alternative production methods for the natural resources, the first commercial air jet texturing machine was displayed at ITMA in 1979. The air jet texturing process transforms flat multi-filament yarns into yarns with a spun like formation.

As is already known that, warmth, handle, natural texture and appearance are considered to be enviable properties of most textile yarns. On the contrary, synthetic filament yarns do not have such qualities; however they are usually stronger and much more uniform than the natural fibre yarns. So, textile technologists tried to produce textile yarns from synthetic filaments, i.e. polyester and polyamide, to combine the desired properties of both natural and synthetic fibres. Although this task is not very easy, however certain aspects of natural textiles can be imitated by the synthetic filaments with the method of texturing which can be described as a modification process of regular structure of synthetic filaments into rather random structures. Another explanation for texturing is given by Denton[2] and that which " texturing is the means whereby permanent fine distortions, crimps, loops, coils or crinkles are introduced into the original straight filaments of synthetic yarns without destroying the continuity of the original filaments". Most of the texturing processes introduced on the yarns which are heat sensitive (thermoplastic property) however air-jet texturing process is not heat sensitive; it is a mechanical process. On the other hand, the air-jet texturing process is by far the most versatile of all the yarn texturing technique (such as thermomechanical texturing techniques and other texturing techniques i.e. bicomponent) which it can produce yarn by means of mechanics. In this method, the yarn is textured by overfeeding into a high-pressure of air to create a looped and more natural yarn appearance and also the bulkiness level of the yarn is controlled by input speed and jet-take out speed [3]. On the air-jet texturing process, any filament yarn (POY, FDY etc.), not necessarily thermoplastic, is fed through a special designed nozzle that creates highly turbulent air at a higher speed than is taken up as entanglement in the yarn core and loops/ arcs at the surface of the yarn (Figure 1). These air-jet textured yarns have a structure which is uniquely unstretchable just the same as spun-staple yarns made of natural and man-made fibres. The surface loops are firmly fixed into the well-entangled core of the yarn and produce a voluminous bulky structure which gives natural warmth to the material.

Thus, the air-jet texturing process re-assigns flat, continuous synthetic yarns into entangled, convoluted, bulky, spun-like structured yarns. And this is achieved by the multi filament feeding of the core/effect yarn which has a higher speed inside the nozzle and hence principally can be overfed. (Figures 2-3). Additionally, a slight intermingling can be given to the flat yarn after spinning and drawing processes and also as an alternative for the twisting intermingling can be done at the texturing process (IMG)[4] as seen in Figure 4.

The aim of this research is to study the effects of POY cross-section on the breaking strength and elongation of some air-jet textured yarns.

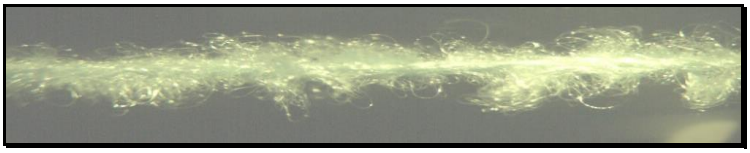


Fig.1: *Air-jet yarn*

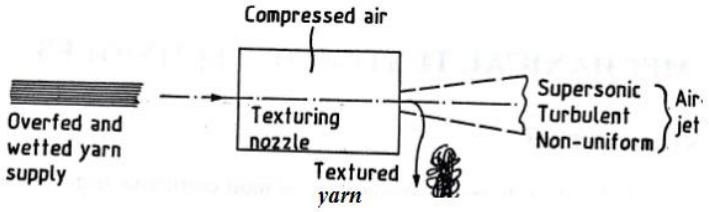


Fig.2: *Principle of air-jet texturing [1]*

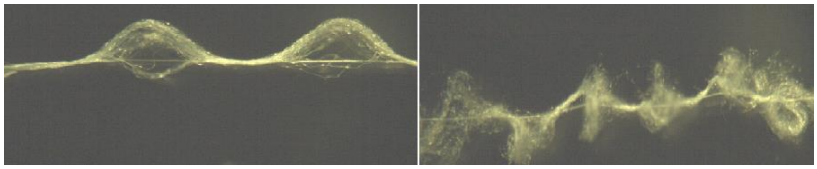


Fig.3: *Intermingled yarn (IMG) (yarn nips)*

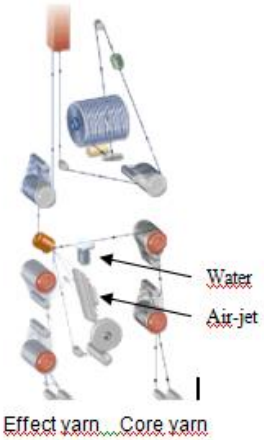


Fig.4: *Schematic diagram of air-jet textured yarn manufacturing*

2. MATERIAL AND METHOD

The aim of the work is, to study some of the effects of air-jet textured yarn production parameters on the yarn properties. Also, the cross-section of POY will be correlated on the yarn breaking strength and elongation.

2.1 Materials

In the study, to be able to observe the effect of POY cross-section on the yarn breaking strength and elongation, polyester POY yarns were produced in four different parameters: 150 f 72 dtex half matt, 150 f 72 dtex shiny, 167 f 72x2 dtex shiny and 167 f 72x2 dtex half matt appearance textured yarns.

2.2 Machinery and Instruments

The machinery and the test instruments used in the study are presented in Table 1**.**

Table 1: *Machines and the instruments used in the study*

Machines and Instruments	Purpose of the use
SSM AT01 Air-jet texturing machine	Air-jet textured yarn production
TEKTECHNO STATIMAT ME	Breaking strength and elongation
JEOL JSM-5910 LV Scanning Electron Microscope (SEM)	Surface and cross-section of yarn images
PROJECTINA 4002 microscope	Surface and cross-section of yarn images

2.3 Yarn Production Details and Yarn Properties

Yarn production details and the produced yarn properties are given in Table 2 and 3.

Table 2: *Yarn production details*

Materials and production details	**Codes for yarn types**			
	Yarn (A)	**Yarn (B)**	**Yarn (C)**	**Yarn (D)**
Material	**PET**	**PET**	**PET**	**PET**
Core yarn (dtex)	150/72 dtex half matt appearance	150/72 dtex coloured appearance	167/72x2 shiny appearance	167/72x2 half matt appearance
Effect yarn (dtex)	-	-	167/72x2 shiny	167/72x2 half matt
Nozzle type	LBO2 S3 15K2	T351	EO52-V220 K144	EO52-V220 K144
Core yarn feeding (%)	30	25	14	14
Effect yarn feeding (%)	-	-	150	150
Yarn linear density (dtex)	200	195	1310	1285
Cross-section	Round shape	Trilobal shape	Trilobal shape	Trilobal shape

Table 3: *Yarn properties*

Yarn types	**Yarn linear density (dtex)**	**Breaking strength (cN)**	**Breaking elongation (%)**	**Work of rupture (cN.cm)**	**Breaking time (s)**
A	200	569.23	30.88	6213.20	17.67
B	195	524.61	28.99	5055.20	15.51
C	1310	1229.18	22.45	10244.50	14.20
D	1285	1280.87	26.44	11904.15	15.64

2.4 Images of Produced Yarns

PROJECTINA 4002 light microscope and JEOL JSM- 5910 LV scanning electron microscope was used to observe the cross-section of the produced yarns and their surface morphologies with regarding to highlight their breaking strengths and elongations. The morphology images of the produced samples are given in Figures 5-8.

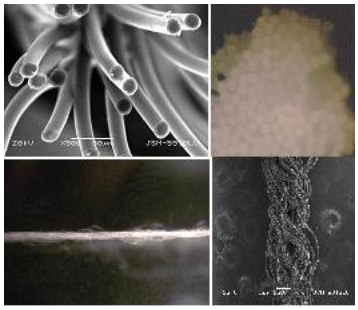


Fig. 5: *Morphology of A coded yarn (200 dtex, round shape cross-section)*

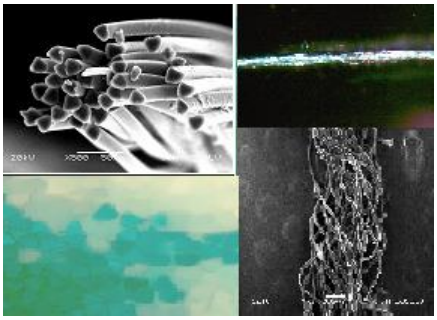


Fig. 6: *Morphology of B coded yarn (195 dtex, trilobal shape cross-section)*

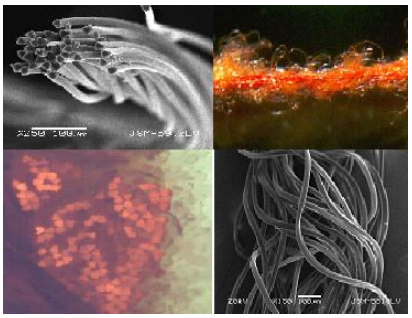


Fig. 7: *Morphology of C coded yarn (1310 dtex, trilobal shape cross-section)*

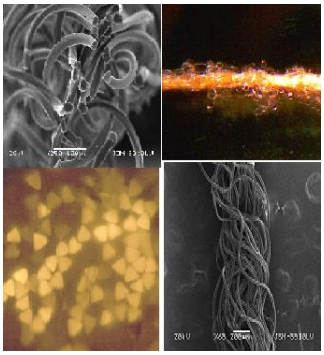


Fig. 8: *Morphology of D coded yarn (1285 dtex, trilobal* shape *cross-section)*

3. RESULTS AND DISCUSSION

1. In the study, although core yarn feeding ratio and its final yarn linear density of the A coded yarn (200 dtex, round shape cross-section) is coarser than the B coded yarn (195 dtex, trilobal shape cross-section); it confered higher breaking strength and elongation than the B coded air-jet textured yarn. In fact, the expectation for the A coded air-jet textured yarn was low breaking strength and elongation values, because of the A coded samples' core yarn feeding ratio is higher than the B coded sample. This is because of the increment in feeding ratio of a yarn causes more loosely and disordered fibre placement and hence resulting less parallel fibres at the yarn structure. As it is mentioned already, an opposite outcome occurred rather than the expected one: the reason for this might be that much more parallel fibre placements of the round shaped fibres within POY yarns (as

seen in Figure 5) taken place at the nozzle of an air-jet textured machine; consequently it is thought that this may helped to improve breaking strength of the yarns.

2. Trilobal cross-section yarns, which are C and D coded samples, have same effect and core yarn linear densities beside same feeding ratios to the machine. However, the D coded yarn has shown higher breaking strength and elongation than the C coded yarn. This may be due to the TiO_2 which is used as a delustrant on the D coded yarns.

4. CONCLUSION

This study reveals the effect of the polyester POY yarn cross-section of the air-jet textured yarn on its mechanical properties i.e. breaking strength, elongation and work of rupture. The comparison is accomplished by using tenacity instrument and morphological appearances (e.g. by using light microscope and SEM) of the produced yarns. The following conclusions can be drawn on the basis of the study:

- Coarser air-jet textured yarn, which is also a round shaped, has shown higher breaking strength, elongation and work of rupture than the trilobal shaped yarn.
- D coded half matt yarn, although it has same cross section with C coded sample, has presented higher breaking strength and elongation than the shiny trilobal cross-sectioned yarn.
- Generally it can be said that, rather than over feeding of the core yarn (A and B codded yarns), the fibre cross-section has much more effect on the air-jet textured yarn mechanical properties.

REFERENCES

[1] A. Demir and H.M. Behery, *"Synthetic Filament Yarn Texturing Technology",* Prentice-Hall Inc., ISBN 0-13-440025-9, pp.40, 1997**.**

[2] M. J. Denton, *"Texturing of Continuous Filament Synthetic Yarns"* The Journal (Bradford Textile Society), pp. 51-56, 1987.

[3] M. Acar, R. K. Turton and G. R. Wray, *"Loop Formation Mechanism in the Air-Jet Texturing Process"*, International Textile Bulletin, 3, 1983.

[4] W. E. Morton and J.W.S. Hearle, *" Physical Properties of Textile Fibers",* Heinemann, London, 1993.

[5] J. E. Mclntyre, *" The Chemistry of Fibers",* Edward Arnold, London, 1971.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

APPLICATIONS OF SPACERS MADE WITH DOUBLE BAR RASCHEL MACHINE

DÍAZ-GARCÍA Pablo, BONET-ARACIL Mariles, BOU-BELDA Eva, MONTAVA Ignacio

[1] Universitat Politécnica de Valencia., Textile and Paper Department, Ferrándiz y Carbonell s/n, 03801, Alcoy, Spain.

Corresponding author: Díaz-García, Pablo. E-mail: pdiazga@txp.upv.es

Abstract: *Nowadays, textile technologies develop to adapt their different techniques for creating new products for the different sectors of application every day.*
Particularly, warp knitted fabrics and warp-knitting technology have applications in all different groups of technical textiles. It could be the most applied technique, the most versatile technology to develop new textile products for the new textile market. Warp knitted fabrics play the most important role among the technical textile fabrics.
This technology is used in different product groups such as mobile textiles (car seat covers, dashboard cover), industrial textiles (composites), medical textiles (anti-decubitus blankets), sports textiles and foundation garments (bra cups, pads for swimwear). This study presents some examples of the application of this technology in some markets
Within the market of technical textile, medical textile has an increasing relevance and knitted fabrics and knitting technology, at the same time, play a very important role in the fields of technical and medical textiles.
Studies have demonstrated that knitted structures possess excellent mechanical properties and can promote more effective regenerative medicine, tissue repair, ligament, tendon cartilage, reconstruction, etc.
The aim of this paper is to present different possibilities of textiles developed with this kind of structures, to present different alternatives, different examples of products obtained with this kind of textile structure combined with the correct kind of textile fiber. In this kind of techology, double-bar raschel machines used for producing three-dimensional textiles, spacers, play an important role.

Key words: *Spacer, Knitted, raschel, warp. Textile.*

1. INTRODUCTION

Importance of technical textiles is great and increasing. Experts estimate annual rising ratio of this application of textile materials is 3.8 % on average and consumption in each field of this group of applications is anticipated as growing. Roughly, one third of the quantity of the world's fibre consumption is used in production of technical textiles [1].

Warp knits have been playing a predominant role in the area of technical textiles, as recent researches point out. Concretly spacer fabrics is an important option to develop new aplications. [2]

Spacer fabric is a three-dimensional knitted fabric consisting of two separate knitted substrates which are joined together or kept apart by spacer yarns.

There are two types of spacer fabrics: warp-knitted spacer fabric and weft-knitted spacer fabric. The first type is knitted on a rib raschel machine having two needle bars while the second is knitted on a double jersey circular machine having a rotatable needle cylinder and needle dial

The aim of this paper is to present the possibilities of warp-knitted spacer. A spaceer fabric is a double-faced fabric knitted on a double needle bar machine. The distance between two surfaces is retained after compression by the resilience of the pile yarn (usually mono-filament) that passes betwenn them [3].

Double-bar raschel machines are designed for producing spacer textiles. Depending on the type of machine, to form a spacer structure, fully threaded guide bars are used to form each of the side fabrics while an additional fully threaded guide bar joins the two fabric sides by joining threads. The spacer fabric may be up to 60 mm in thickness.

Textiles produced by these machines are mainly used in the shoe and mattress sectors, but also in other sectors such as the automotive industry. Spacer textiles are also becoming increasingly popular for seats and chairs, because they allow air to circulate.

Actually spacer fabrics arewidely used in different products such as mobile textiles (car seat covers, dashboard covers), industrial textiles (composites), medical textiles (anti-decubitus blankets), sports textiles and foundation garments (bra cups, pads for swimwear).

Spacer fabric as a component material is highly breathable, thus creating a moisture free environment, which in turn reduces the chances of skin maceration. These lead to an increased level of comfort when compared to materials such as foam, neoprene and laminate fabrics. Spacer fabrics are regarded as environmentally friendly textile materials (unlike polyurethane foam), since they can be recycled [4]

2. TECHNOLOGY

We can separate these technologies into different kinds of machine due to their working width, their distance between needle beds, gauges, etc. The original tecnology starts with the machine to produce blankets. Nowadays this technology has developped other important kinds of machine, other important kinds of this type of warp knitted technology. As examples of this kind of machines, to develop specifics products we can use the following:

2.1. Double needle bed warp knitting machine (30-50 inches).

This machine works widths between 30-50 inches, distances between needle beds bedween 1 - 20 mm, for the production of a wide range of articles. This machine allow for making: Technical uses (netting for sports equipment and the food industry, high resistance ribbons in special fibres, ribbons and fabrics for applications in the geo-textile, automotive, building and industrial sectors), medical uses (tubular elastic netting, emergency bandages and dressings, disposable underwear), footwear (spacer fabrics for uppers), women's apparel (mesh stockings and pantyhose) and fashion fabrics [5].

2.2. High Distance.

Special machines for producing technical and semi-technical 3D textiles. With adjustable spacer widths of 20-35 mm, and with adjustable spacer widths of 20-65 mm. Applications in mattresses and bedding, Automotive seats, Upholstery fabrics and velour

2.3. Seamless

Double-bar raschel machines for producing seamless fabrics for the apparel and sports sectors. With piezo jacquard technology designed to produce plain and patterned tubular goods and seamless products.

3. SPACER PRODUCTS

Space fabrics are widely used in different products, for different markets. Examples about these products in the different markets are listed below.

Partly-threaded guide bars can produce open-hole structures on each surface and air circulation can occur in the different millimeter spaces between the two surfaces. An important advantage is the low weight in proportion to the large volume.

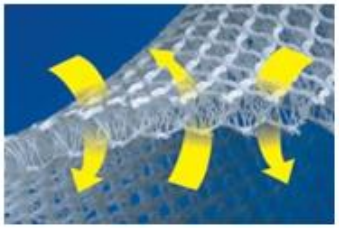


Fig. 1: *Possibility air circulation*

Spacer fabrics are used for environmental reasons, which can be used in different product groups such as mobile textiles (car seat covers, dashboard covers), industrial textiles (composites), medical textiles (anti-decubitus blankets), sports textiles and foundation garments (bra cups, pads for swimwear). This study presents some examples of the application of this technology in some markets

3.1. Mobile textiles:

Car seat covers, dashboard covers, filling seat in substitution of polyurethane foam.

These meshes, thanks to their great ductility, allow for making bodies of quite different geometry and density. It grants a good distribution of pressure. This physical and technical quality make them suitable to meet a wide range of applications.

This kind of 3D could be spacer widths of 20-65 mm. The spacer fabric incorporated herein offers an excellent seating comfort thanks to its perfect climatic behaviour.

Fig. 2: *HDR 6EL High distance Karl Mayer [6]*

3.2. Industrial Textiles:

Packaging, protective and safety nets. Nets for a wide variety of sectors – from the aerospace, medical and sports sectors to safety applications – as well as agricultural nets.

Textiles in filtration, for the separation of solids from liquids or gases by textiles made with spacer warp knitted, save energy, improve processefficiency, recover precious materials and general improvepollution control [7].

Fig. 3: *Net made with double bar raschel machine*

3.3. Sport textiles:

Sports and leisure shoes.

Warp-knitted spacer fabrics are continuing to make headway - breathable, tough and stylish, they are increasingly taking over from flat fabrics in the shoe fabric sector.

Elastic spacer fabric are used as underwear for diver's suits.

Spacer fabrics patterned with jacquard designs are products showing real growth potential. Shoe manufacturers in particular are becoming increasingly interested in spacer fabrics with their wide range of different designs. They are creating a demand that has led to textile producers investing continuously in new, innovative production machinery -

Fig. 4: *Spacer fabrics patterned with jacquard designs [8]*

3.4. Functional clothes

Knitted fabrics may be important components of functional clothes, too. For example, spacer fabrics can be used here as lining that, due to its hollow structure, enables ventilation inside the garment or, due to its elastic behaviour in thickness direction, protects against pressure or hit. This is why this fabric is a penchant for lining of motorcyclists' protective garments [9].

Innovative, warp-knitted seamless components can be produced in a single sequence, without any seams, for the toes, fingers and even the head. They can be used in functional sportswear, underwear, hosiery and fashionable outerwear.

This kind of technology produces seamless hosiery, fashion garments, lingerie, sportswear, medical garments and shape wear.

Fig. 5: *New line of unique lingerie, bodyshapers, posture garments and sportswear products based on seamless warp knitting technology - [9]*

3.5. Medical textiles

Medical textiles are a highly specialised stream of technical textiles industry with a growing range of applications. A significant advancement has been achieved in surgical products or biomedical textiles (implantable/non-implantable) with the advent of 3D textile manufacturing techniques. Cardiovascular soft tissue implants (vascular grafts) have been a field of interest over decades for use of innovative 3D tubular structures in treatment of cardiovascular diseases. In the field of soft tissue implants, knitted and woven tubular structures are being used for large diameter blood vessel replacements. Advent of electrospinning and tissue engineering techniques has been able to provide promising answers to small diameter vascular grafts. [10]

Many kinds of textiles are used in medical treatment. It is not surprising that a great part of clothing worn by doctors and nurses in hospitals and clinics is product of the knitting industry (e.g. undershirts, socks). But sometimes they are not conventional ones, they are made from yarns or with finishing that make them antibacterial against infections or against the rising of unpleasant sweaty smell. Various types of bandages (both rigid and elastic), surgical stockings, certain parts of orthopaedic equipment (ortheses) (like knee-, wrist- and elbow-braces, calf and lumbar supports, etc.) are also made by knitting technology. An important application field for spacer fabrics is the manufacturing of mattresses for beds, operating tables and wheelchairs.

Cooperation of doctors and technical experts of the textile industry can lead to development of new surgical technologies. Structure of the textiles used as implants is determined by its material composition, fibres' behaviour and features of degradation. Materials of sutures and implants having biologically good properties, designable absorption and degradability and that endure the sterilization process are continuously subjects of research. At the same time, continuous development of textile technologies and machines enables to develop newer and newer methods in surgery and medical treatment. For this mutual development textile technologists and doctors must closely cooperate, while all the administrative procedures concerning manufacturing and trading of such products must be strictly respected. [1]

Branched artificial blood arteries are produced on a fine gauge Raschel machine with 16 guide bars.

Fig. 6: *Medical Textiles: Artifitial blood vessel, [11]*

4. CONCLUSIONS

For decades, knitted technology, concretely double bar raschel machine, has been applied to manufacture home textile like blankets and velvet.

Nowadays, considerable developments have taken place for the knitting tecnologie. Concretely in double bar raschel machine different developments allow making innovative applicatios in different markets.

Spacer fabrics due to their mechanical characteristiscs could be used to produce diferent products

Spacer fabrics are used for environmental reasons, which can be used in different product groups such as mobile textiles (car seat covers, dashboard covers), industrial textiles (composites), medical textiles (anti-decubitus blankets), sports textiles and foundation garments (bra cups, pads for swimwear).

This kind of textile products have characteristics, such as air permeability, thermal conductivity and low-stress mechanical properties, stretchability, recovery, bending and compression.

These characteristics depend very much on the spacer yarn type and the spacer yarn arrangement. Bending properties are closely related to the fabric type, structure, spacer yarn type and density while stretch and recovery properties depend very much on fabric type and spacer yarn type.

Spcer fabric is a good need to develop textile products.

Thus, knits clearly prove their versatility in the various field of technical applications and therefore hold the promis to even more areas of applications in the furure

REFERENCES

[1] K. LáZáR, (2010). Application of knitted fabrics in technical and medical textiles. In Forty-fifth international congress IFKT (pp. 1-6).

[2] N., Gokarneshan, B. Varadarajan, K. Balamurugan, & Rachel, A. (2011). Engineering knits for versatile technical applications: Some insights on recent researches. Journal of Industrial Textiles, 1528083711426021.

[3] D. J. Spencer, (2001). Knitting technology: a comprehensive handbook and practical guide (Vol. 16). CRC Press.

[4] J. Yip, & S. P. Ng, (2008). Study of three-dimensional spacer fabrics:: Physical and mechanical properties. Journal of materials processing technology, 206(1), 359-364.

[5] http://www.comez.com/index.php/en/2013-04-23-16-04-21/2013-04-23-16-05-46/dnb-32

[6] http://www.karlmayer.de

[7] A. R. Horrocks, & S. C. Anand, (Eds.). (2000). Handbook of technical textiles. Elsevier.

[8] http://www.knittingindustry.com/new-doublebar-raschel-machines-for-shoe-fabric-sector/

[9] http://www.knittingindustry.com/man-on-a-seamless-mission/

[10] C. Singh, Morsi, Y., Lin, T., & Wang, X. (2011, January). 3D fibrous structures as cardiovascular implants. In Proceeding of the 3rd World Conference on 3D Fabrics and Their Applications 2011 (pp. 159-167). World Academic Union.

[11] http://www.maquet.com/us/specialities-and-therapies/vascular-surgery/

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

BINDER INFLUENCE ON KNITTING FABRICS TREATED WITH PCMs BY PADDING

DIRLIK UYSAL Çagla Dilara, BOU-BELDA Eva, BONET-ARACIL Marilés, MONTAVA Ignacio, DÍAZ-GARCÍA Pablo

[1,] *Universitat Politècnica de Valencia, Alcoy (Alicante), SPAIN*

Corresponding author: M. A. Bonet, maboar@txp.upv.es

Abstract: *Knitting fabrics are characterized by the confort they confer on the wearer. Textiles with mcirocpsules are bocoming more popular and nowadays Phase Change Materials (PCM) are used for thermal control and to avoid temperature changes to be clearly noticeable. Consequently, they can control variations in temerpature and make the user feel more confortable. Washing durability and rigidity are very important when considering fabrics treated with microencapsules. In this study we first aimed to study what influence has the resin concentration with the durability of microencapsules on the fabric after having washed it and its confort. To observe the presence of microcapsules after washing procedure the scanning electron microscopy (SEM) was used. SEM analysis showed different density of microcapsules with PCMs depending on the binder concentration used. It could be clearly noticieable that 5times washed fabric and 10times washed fabric still show microacapsules on it. On the other hand we used padding method for the application of PCMs into the fabris and this study put forth the binder effect on rigidity. We have demonstrated that when we increase the binder concentration for padding bath, after 10th laundry cycles for the same fabric, we still have microcalsules on it. On the other hand, density of binder effect negatively influences on rigidity of the fabric.*

Key words: *Microencapsulation; Phase Change Material; Functional Textiles; Rigidity; Washing Durability; SEM.*

1. INTRODUCTION

Since the end of the 1980s, functional textiles have been developed to enhance textile performances according to the consumers' demand and to include a large range of properties with a higher added value. One possibility to manufacture functional or intelligent textile products is the incorporation of microcapsules as a finishing of textile. Many substances can be encapsulated for potential textile applications [1]. One of these substances, phase change materials (PCMs), has been used to manufacture thermoregulated textiles to improve thermal comfort of the wearer [2]. One of the methods to obtain textile materials with the thermoregulating properties is the use of the microcapsules containing phase change materials (M-PCM). Microcapsules are made of polymer shell and PCM core, which bidirectionally changes physical state in the specified temperature range [3].The design and development of a functional textile providing an ability of dynamic heat regulation next to the skin have attracted more and more attention in recent years.[4] This property obtained by microencapsulated PCM in textile material and in this study microcapsules with PCM is aplicated by padding method into the fabric.

The step of encapsulation allows manufacturing textile containing microcapsules by various ways to fix the microcapsules within the fiber structure permanently, to embed them into a binder or to mixed them into foam [4,5]. They will remain thermally effective as long as the coating or the fibers stay intact [6].

2. EXPERIMENTAL

We used a 100% cotton knitted fabric because of its comfort and good flexural rigidity properties. All cotton fabric samples were impregnated with four diferent solutions containing PCM. To study the behavior of the resin, PCM particles and acrilyc binder STK-100, suministrated by Color-Center, were used. We prepared four different solutions; these are shown in the table 1.

***Table. 1**: Formulation used in each treatment.*

Samples	PCMs (g/L)	Resin (g/L)
4 JER P 50	50	0
4 JER P 50 10R	50	10
4 JER P 50 50R	50	50
4 JER P 50 100R	50	100

The samples were immersed in the aqueous solution and then were passed through squeeze rolls to give a specified pick-up, we obtained 80% in both treated samples. Treated samples were washed by following the Standard UNE EN ISO 6330 method no. 2A, during 5 cycles of washeing.

We evaluated the modification in the flexural rigidity of the treated cotton fabrics. It was measured according to UNE 40-392-79. The results obtained were the average of 10 measurements taken along the warp and weft directions and rigidity calculated according to the formulation shown below.

Flexual rigidity= 0,10 P c3 mgr. cm.

Rigidity total = (Ru x Rt)½

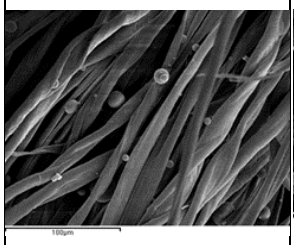
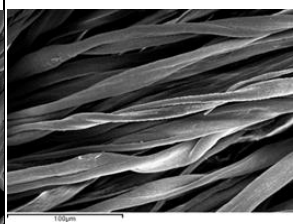
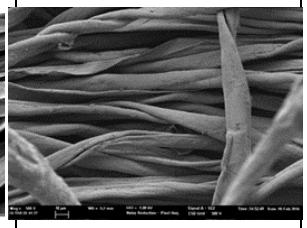
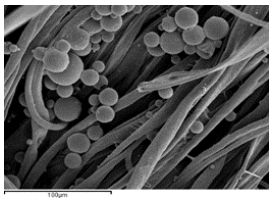
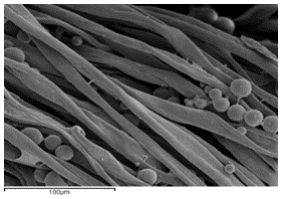
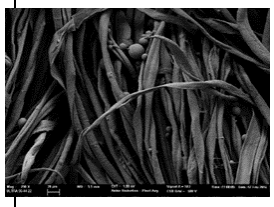
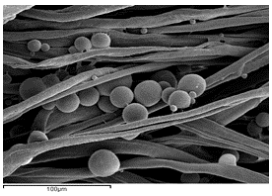
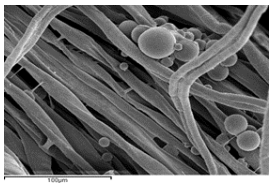
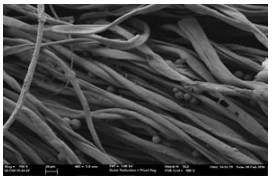
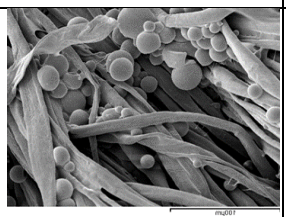
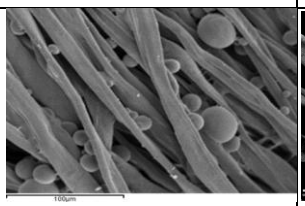
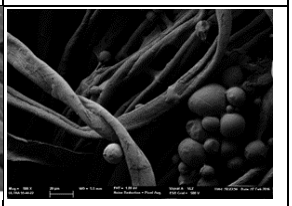
To verify the existece of silica particles on the fiber surface, treated samples were observed by a scanning electron microscope FEI model Phenom (Fei, Oregon, USA). Prior to sample observation, samples were covered with a gold–palladium alloy in a Sputter Coater EMITECHmod. SC7620 (QuorumTechnologiesLtd., EastSussex, UK). Samples were then examined with suitable accelerating voltage and magnification.

3. RESULTS

3.1. SEM RESULTS

We washed the fabric containing the micorocapsules up to 10 cycles and classified fabric three group as after 5^{th} laundy, 10^{th} cycles and without any laundry. By using SEM, we scanned all fabrics in order to monitorize the microcabsule density in fabric and we obtain below images in table 2 and its results are showns n this page.

Table. 2: *SEM images of fabrics with Mcs.*

FABRIC REFERENCE	Without laundry	5th laundry	10th laundry
4 JER P 50			
4 JER P 50 10R			
4 JER P 50 50R			
4 JER P 50 100R			

When we compare the SEM images, we can say tha when we increase the binder influence durin microencapsulation by padding, the washing durability increase. Up to 10th laundry we have still microcapsules in fabric.

3.2. FLEXUAL RIGIDITY

We evaluated the modification in the flexural rigidity and wrinkle recovery angle (WRA) from the treated cotton fabrics. It was measured according to UNE 40-392-79 and UNE EN 22313, respectively. Results showed the average of 10 measurements taken along both, the warp and weft directions.

Table 3: *Flexual rigidity of microencapsulated fabrics*

FABRIC REFERENCES	FLEXUAL RIGIDITY
4 JER P 50	22,42804209
4 JER P 50 10R	39,36339458
4 JER P 50 50R	45,46060312
4 JER P 50 100R	79,1204978

4. CONCLUSIONS

In this work we have tested the influence of binder concentration for pasting PCM on some confort paramters such as flexural rigidity. This value is directly related with the rigidity of the fabric and consequently its confort during its use. We have demonstrated that when we increase the binder concentration for padding bath, after 10^{th} laundry cycles for the same fabric, we still have microcalsules on it. On the other hand, density of binder effect negatively influences on rigidity of the fabric.

REFERENCES

[1] F. Salaüna, E. Devauxa, S. Bourbigot, P. Rumeaud, *" Thermoregulating response of cotton fabric containing microencapsulated phase change materials",* Thermochimica Acta 506 (2010) 82–93.

[2] S. Mondal, Appl. Therm. Eng. 28 (2008) 1536–1550.

[3]. Alicja Nejman, Małgorzata Cieslak, Bogumił Gajdzicki, Bogna Goetzendorf-Grabowsk, Agnieszka Karaszewska, *"Methods of PCM microcapsules application and the thermal properties of modified knitted fabric",* Thermochimica Acta 589 (2014) 158–163, June 2014

[4] . Nihal Sarier, Emel Onder, "*The manufacture of microencapsulated phase change materials suitable* for *the design of thermally enhanced fabrics*", Thermochimica Acta 452 (2007) 149–160, 22 August 2006

[5] W. Bendkowska, in: H.R. Mattila (Ed.), Intelligent Textiles and Clothing, Woodhead Publishing Ltd, Cambridge, 2006, pp. 34–62..

[6] R. Cox, Chem. Fibers Int. 48 (1998) 475–479.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

COLORING PROPERTIES OF WOOL FABRIC COLORED BY NEW DYESTUFFS - AZOMETHINES

DJORDJEVIC Dragan[1], SMELCEROVIC Miodrag[2], MICIC Aleksandra[3], AMIN Goran[4], MILIC Dragan[5]

[1, 4]University of Nis, Faculty of Technology, Textile Department, Bulevar oslobodjenja 124, 16000 Leskovac, Serbia,
E-Mail: drdrag64@yahoo.com

[2, 3]Higher Vocational School for Textile, Textile Department, Vilema Pusmana 17, 16000 Leskovac, Serbia,
E-Mail: msmelcerovic@yahoo.com

[5]Center of the Ministry of Defence Leskovac, Majora Tepica 4, 16000 Leskovac, Serbia,
E-Mail: drdrag64@gmail.com

Corresponding author: Djordjevic, Dragan, E-mail: drdrag64@yahoo.com

***Abstract*:** *The azomethines have broad applications in food and dyestuff industries, and in analytical chemistry, catalysis and also in the field of agrochemical. These have played an influential part in the improvement of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and also in optical materials. The present paper describes coloring properties of wool fabric colored by new dyestuffs - azomethines, derivate of isatin. Synthesizing of dyestuffs can often have one to six chromogen, which can be defined as the photoactive components that contain colored or uncolored absorbent components. In addition of monoazo, diazo, poly-azo, anthraquinone, xanthan and similar systems, the azomethines or imines, also includes to the chromogen groups. Azomethines, such as, isatin-3-hydrazone, isatin-3-thiosemicarbazone and isatin-3-phenylhydrazone, were synthesized and their coloring performance on wool fabric assessed. The synthesized azomethines showed very good substantively for wool fibers with good coloring performance according to CIEL*a*b* system which characterized quantitative and qualitative coloring property. Dyestuff 3 or isatin-3-phenylhydrazone bound to woolen textiles to a greater extent and greater intensity (minimum value of L). Dyestuff 2 or isatin-3-thiosemicarbazone linked to the minimum amount for textiles (the largest value of L). Although it must be noted that it is a lighter shade (yellow color) as opposed to the dyestuff 3 (red color).*

Key words: *Azomethines, Dyestuff, Coloring, Wool, CIEL*a*b*.*

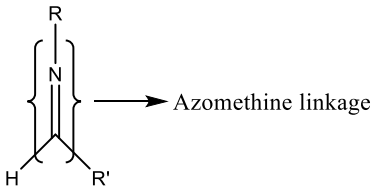
1. INTRODUCTION

Natural and synthetic dyestuffs are compounds of great interest since they play an important role in our everyday life. The broad variety of technical and industrial applications, which includes “classical” utilizations like dyeing of textiles and other consumer goods. Widely applied and interesting representatives amongst the large number of dyestuff categories are triphenylmethane, azo, anthraquinone, perylene, and indigoid dyestuffs [1].

The azomethines are the compounds having azomethine linkage (Fig. 1) and can be synthesized from an amino and a carbonyl compound. These are significant chelating ligands in co-

ordination chemistry to co-ordinate metals ions through azomethine nitrogen and have been considered broadly [2, 3].

As is known, azomethines (isatin derivatives) are reagents which are becoming increasingly important in the pharmaceutical, dyestuff and plastic industries as well as for liquid–crystal technology and mechanistic investigations of the drugs used in pharmacology, biochemistry and physiology [2-5]. Azomethines containing derivatives of salicylaldehyde and aliphatic amines have been studied for their dioxygen uptake and oxidative catalysis because of their similarities to the biological dioxygen carriers, as well as their catalysis properties for the insertion of oxygen into organic substrates [6, 7].



R = amino part
R' = aldehyde or ketonic part

Fig. 1: *General representation of the structure of an azomethines (Schiff bases)*

There are not many results in the world for azomethine application in dyeing processes of different textile materials. The aim of this work was tested synthetized azomethines as dyestuffs in treatment of wool textile fiber. It was necessary to find an adequate recipe for the the highest exhaustion of dyestuff from the baths and good color fastness on fabric.

2. EXPERIMENTAL

2.1. Materials

Equimolar amounts of isatin and amine component (hydrazine, phenylhydrazine and thiosemicarbazide) were dissolved in 95 % ethanol. The solution was heated under reflux for 1 hour. The products were filtered, washed with ethanol and dried in vacuum over $CaCl_2$ [8].

Their structure is shown in Fig. 2.

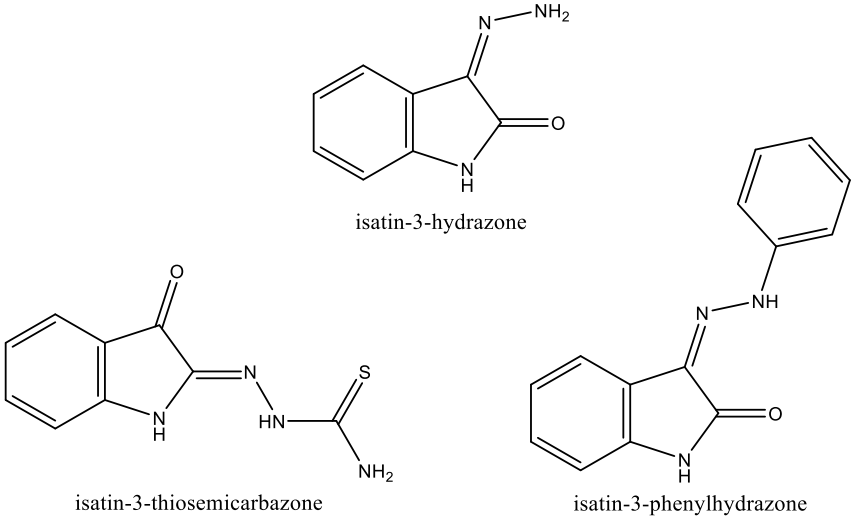


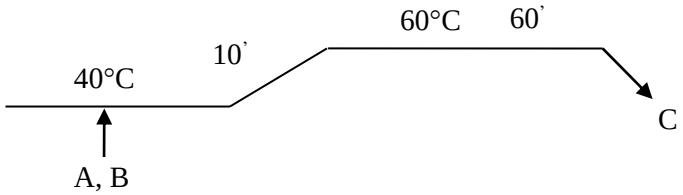
Fig. 2: *Structure of synthesized azomethines*

2.2. Dyeing procedure

The dyeing was carried out in a solution of ethanol/water (50/50 %) without additives, on 60°C for 60 min, in the presence of the new dyestuffs. The reason was the fact that the used active agents, azomethine, insoluble in water and soluble in an alcohol. Higher temperature and dispersant in pure aqueous solutions of azomethine did not give satisfactory results of wool fabrics dyeing.

Isatin-3-hydrazone (yellow powder) marked as dyestuff 1, isatin-3-thiosemicarbazone (orange powder) marked as dyestuff 2 and isatin-3-phenylhydrazone marked as dyestuff 3.

The wool fabric dyeing was performed in Linitest aparature for laboratory dyeing with temperature time regime like at scheme:



(A) - dyestuff (B) - textile (C) rinsing.

To avoid any subjective judgment when it comes to visual valuation of fiber dyeing, we used CIEL*a*b* control system of textile dyeing, considered reflection spectrophotometer, and specific computer software. In this work, we measured the reflectance (remission) of textile samples using reflection spectrophotometer Dye Eye 3000 (ICS – TEXICON) connected with personal computer and specific softer system. With this procedure, it is possible to obtain not only degree of reflection, but also Kubelka - Munk function (color strength) that express the reflection coefficient dependence on fiber color content.

3. RESULTS AND DISCUSSION

Commonly, the wool textile is colored with chromic, acid, reactive, metal-complex etc. dyestuffs. The azomethines are relatively small molecules with low water solubility and possess substantively for hydrophilic or hydrophobic fibers such as wool or polyester.

The figures from 3 to 5 show the reflection dependence on wavelength for colored samples of wool textile. Colored samples possess less reflection, i.e., the highest values for K/S (color strength), which indicates their darkness coloring compare to uncolored samples, what was expected.

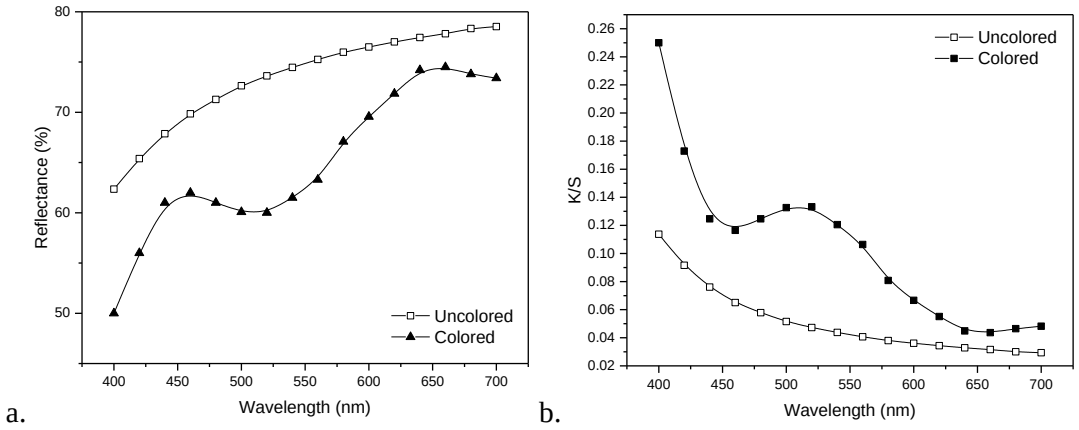
The remission on wavelength for wool (dyestuff 1) represented at Fig. 3a. It can be seen that colored textile absorbed at about 510 nm, which correspond to blue-green color of spectra, and reflects at about 650 nm, which is attributed to red (pink) color. This is actually the color of sample or color that can be seen on textile, visually.

The Fig. 3b shows the dyestuff depth indicator, i.e. the parameter K/S, dependence on wavelengths in distinct area, where the maximum of absorption can be seen. This parameter is in inverse proportion to remission of colored textile by the dyestuff. The parameter K/S increases with depth color enhancement.

The Fig. 4a and 4b represented the values of remission and K/S for samples colored by dyestuff 2. The Fig. 4a shows that the maximum of reflection is at 580-590 nm (yellow color of spectra, visible color), while the maximum absorption is at about 420 nm (blue, complementary color). The parameter, as indicator of intensity of depth dyeing, suggests that colored sample possess the higher absorption and less reflection than control, uncolored sample. Since the difference in

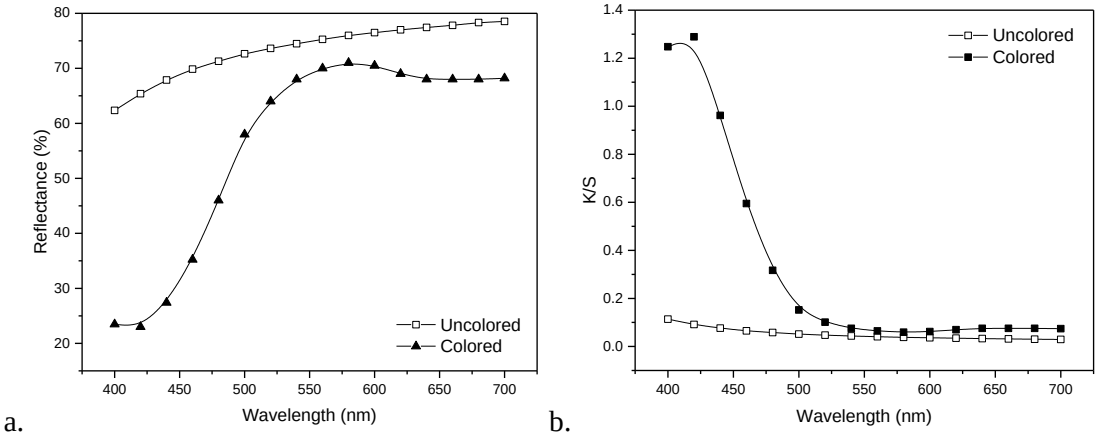
intensity of remission and K/S of colored and control sample is not such a large, it can be concluded that samples are colored in yellow and red (pink) tones by azomethine 1 and 2, respectively.

The Fig. 5a and 5b show the bigger difference in intensity of remission and color strength (K/S), which means stronger and deeper tones of sample colored by azomethine - dyestuff 3. The colored textile absorbs at 510-520 nm (blue-green color of spectra), and reflects at about 670 nm – red-pink color of spectra, which is color of sample.



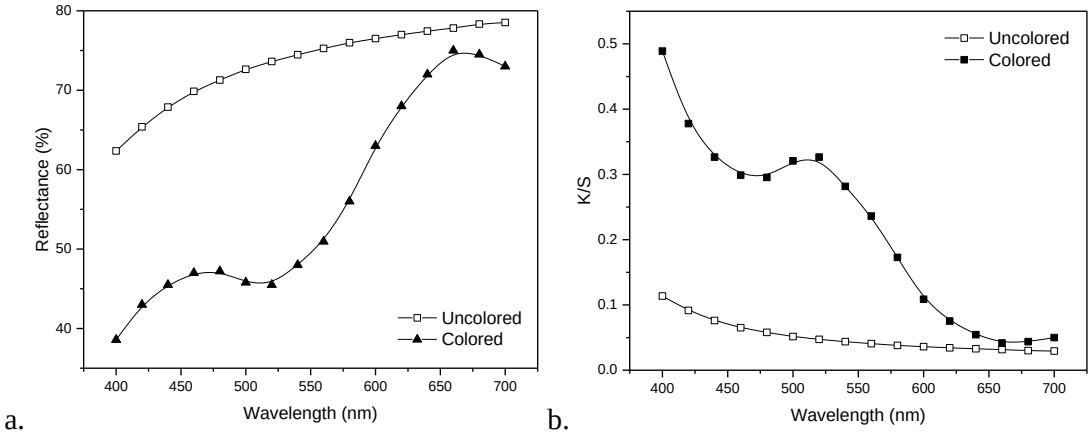
a. b.

Fig. 3: *Spectral reflectance and K/S diagram of wool textile colored by dyestuff 1*



a. b.

Fig. 4: *Spectral reflectance and K/S diagram of wool textile colored by dyestuff 2*



a. b.

Fig. 5: *Spectral reflectance and K/S diagram of wool textile colored by dyestuff 3*

Taking account, that parameter L is smaller while the sample is darker (at all samples); it is obviously that samples are colored by azomethine. It is similar with other parameters of CIEL*a*b* system speaking in favor of the existence of colored wool textile.

Parameter a* is negative at uncolored sample (indicate green), while positive is for sample colored by all the azomethines (indicate magenta). Parameter b* is positive at all colored samples (indicate yellow) and uncolored sample (light of source D65). Also, there are the difference between shades, i.e., hue of dyestuff (H*) and saturation (C*) of dyestuff on sample. h* describes the hue angle. It ranges of colored samples from about 68 to 75, i.e. it is known that, h=0° = red; and h=90° = yellow; but the uncolored sample indicates result around 92 (light of source D65).

According to the results in Table 1, colored woolen samples show higher saturation or "color purity" of non-colored sample woolen textiles, their value range from 36 to 76, while the uncolored sample has the value 12 (light of source D65).

Table 1: *Results of characteristic parameters of CIEL*a*b* system of colored wool fabric by some azomethines*

Sample	Light of source	L*	a*	b*	C*	h*
Uncolored	D65 10 Deg	81.36	-0.53	12.77	12.78	92.37
	A 10 Deg	82.14	2.83	12.83	13.14	77.54
	F2 10 Deg	81.85	-0.46	14.52	14.53	91.80
Dyestuff 1	D65 10 Deg	53.73	10.51	39.35	40.73	75.05
	A 10 Deg	56.88	16.40	42.12	45.20	68.73
	F2 10 Deg	55.34	6.53	43.75	44.24	81.52
Dyestuff 2	D65 10 Deg	62.51	28.57	71.28	76.79	68.16
	A 10 Deg	68.50	29.76	79.68	85.05	69.52
	F2 10 Deg	67.12	17.85	79.76	81.74	77.38
Dyestuff 3	D65 10 Deg	50.00	10.53	35.19	36.73	73.34
	A 10 Deg	52.98	15.82	38.09	41.24	67.44
	F2 10 Deg	51.52	6.66	39.18	39.74	80.35

5. CONCLUSIONS

The azomethines have broad applications in food and dyestuff industries, and in analytical chemistry, catalysis and also in the field of agrochemical. These have played an influential part in the improvement of modern coordination chemistry, but also they can also be found at key points in the development of inorganic biochemistry, catalysis and also in optical materials.

Azomethine derivatives, associated with the amino heterocyclic, can be used for dyeing of wool fabric. The synthesized azomethines showed very good substantively for wool fibers with good coloring performance according to CIEL*a*b* system which characterized quantitative and qualitative coloring property.

Dyestuff 3 or isatin-3-phenylhydrazone bound to woolen textiles to a greater extent and greater intensity (minimum value of L). Dyestuff 2 or isatin-3-thiosemicarbazone linked to the minimum amount for textiles (the largest value of L). Although it must be noted that it is a lighter shade (yellow color) as opposed to the dyestuff 3 (red color).

REFERENCES

[1] R. Rondao, J. S. de Melo, F. Schaberle and G. Voss, *"Excited state characterization of a polymeric indigo"* Phys. Chem. Chem. Phys., vol. 14, pp. 1778–1783, 2012.

[2] M. Sarigul, P. Deveci, M. Kose, U. Arslan, H. T. Dagi and M. Kurtoglu, *"New tridentate azo–azomethines and their copper(II) complexes: Synthesis, solvent effect on tautomerism, electrochemical and biological studies"*, J. Mol. Struct., vol. 1096, pp. 64–73, 2015.

[3] S. Eskikanbur, K. Sayin, M. Kose, H. Zengin, V. McKee and M. Kurtoglu, *"Synthesis of two new azo-azomethines; spectral characterization, crystal structures, computational and fluorescence studies"*, J. Mol. Struct., vol. 1094, pp. 183–194, 2015.

[4] N. Kurtoglu, *"Synthesis, characterization, chelation with transition metal ions, and antibacterial and antifungal studies of the 4-[(E)--phenyldiazenyl]-2-[(E)-(phenylimino)methyl]phenol dye"*, J. Serb. Chem. Soc., vol. 74, pp. 917–926, 2009.

[5] I. Anis, M. Aslam, N. Afza, A. Hussain, F. S. Ahmad, L. Iqbal, M. Lateef, M. T. Hussain and T. H. Bokhari, *"A one-pot synthesis, characterization and pharmacological investigations: schiff bases"*, IJPC, vol. 2, pp. 73-77, 2012.

[6] A. Jarrahpour, D. Khalili, E. De Clercq, C. Salmi and J. M. Brunel, *"Synthesis, Antibacterial, antifungal and antiviral activity evaluation of some new bis-Schiff bases of isatin and their derivatives"*, Molecules, vol. 12, pp. 1720-1730, 2007.

[7] M. Sarigul, A. Sari, M. Kose, V. McKee, M. Elmastas, I. Demirtas and M. Kurtoglu, *"New bio-active azo-azomethine based Cu(II) complexes"*, Inorg. Chim. Acta, vol. 444, pp. 166–175, 2016.

[8] H. J. Vashi and K. R. Desai, *"Syntheses and dyeing performance of azo disperse dyes based on schiffs base system"*, Indian J. Fibre Text., vol. 21, pp. 225-227, 1996.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PHOTOCATALYTIC EFFICIENCY OF N-TIO$_2$ APPLIED ON COTTON KNIT – PART 1

DUMITRESCU Iuliana[1], VARZARU Elena[1], IORDACHE George-Ovidiu[1], MITRAN Elena-Cornelia[1], CIOROBITCA Maria[2]

[1] National R&D Institute for Textiles and Leather Bucharest (INCDTP) 16 Lucretiu Patrascanu, 030508, Bucharest, Romania, E-mail: certex@ns.certex.ro

[2] S.C. Stofe Buhusi S.A., 36 Strada Libertăţii, 605100, Buhuşi, Romania, E-mail: stofebuhusi@gmail.com

Corresponding author: Dumitrescu, Iuliana, E-mail: iuliana.dumitrescu@gmail.com

Abstract: *The main aim of the research work is the development of photocatalytic textiles materials by treating them with TiO2 doped with nitrogen. Also, the research was focused on the nitrogen-doped titanium dioxide (N-TiO2) formulation as homogeneous, stable solution, immobilization of large quantities of N-TiO2 on 100% cotton knit while preserving its genuine properties, minimize the loss of nanoparticles in wastewaters and achieve a high photocatalytic fabrics effects under visible light. The photocatalytic effect was investigated by exposing the materials to ultraviolet and visible light, and the evaluation of exposed and non-exposed fabrics was performed using a spectroscopic method. By using scanning electron microscopy, we investigated the characteristic, morphology and distribution of nanoparticles covering the textile materials, and the presence of Ti and Fe on textile materials was analyzed by X-ray energy dispersive spectroscopy and FTIR spectroscopy. The results showed the relatively uniform coating of cotton fibers by particles by using initial and re-used N-TiO2 dispersions. By using additives like polyethylene glycols and wetting agents, the stability of aqueous N-TiO2 is increased. Wetting agents, together with a higher treatment temperature represent important factors contributing to the deposition of increased amount of N-TiO2 particles existing in the dispersion remained after the first treatment of the fabric.*

Key words: *nitrogen-doped TiO_2, photocatalysis, cotton fabric, nanoparticles, scanning electron microscopy*.

1. INTRODUCTION

The N-TiO_2 was intensively studied due its extended absorption in visible light, stability and enhanced photocatalytic activity [1,2]. Most of the researches investigate the physical methods to deposit N-TiO_2 on solid substrates by spin coating [3], plasma treatment [4], DC magnetron sputtering [5–7], pulsed laser deposition [8], ion implantation method [9]. Even these methods ensure a uniform deposition of very pure thin layers of TiO_2, the disadvantages such as high investment costs, high temperatures and energy consumption needed to deposit the film make them hard to be applied on textiles. Few scientific papers are dedicated to the techniques used to deposit N-TiO_2 on textiles such as impregnation of activated carbon fibers [10], wool [11], or cotton fabrics[12]. The main aim of the research work is the development of photocatalytic textile materials by coating with TiO_2 doped with nitrogen. Also, the research was focused on: N-TiO_2 formulation as homogeneous, stable solution; depositing a high quantities of N-TiO_2 on 100% cotton knit while

preserving the genuine properties of textiles and minimize the loss of nanoparticles in wastewaters; investigation of the photocatalytic effect of N-TiO_2 deposited on textile materials under visible, UV and solar light.

2. EXPERIMENTAL PART

2.1. Materials

Chemically bleached 100% knit cotton fabric 213 g/m^2, 1.08 mm thick, TiO_2 doped with nitrogen (prepared by Kumoh National Institute of Technology, South Korea), PEG 200, PEG 20000, ethanol, ITOBINDER AG (LJ Specialities, UK), NUVA 4200 liq (Clariant), Biowet PB (nonionic tensioactive, LJ Specialities, UK), distilled water.

2.2. N-TiO_2 dispersions preparation

1N: 0.5g PEG 20000 is introduced in the mixture of 24.5mL PEG 200 and 49.5mL distilled water. The mixture is magnetically stirred at 60-65^{0}C until a clear, transparent solution is formed. The solution is cooled at 30^{0}C and 25mL ITOBINDER AG are added. 0.1g N-TiO_2 is added gradually under vigorous stirring and, the dispersion is continuously stirred for 2 hours at 25-30^{0}C. A milky white solution was obtained, which remains homogeneous after 24 hours. The so prepared solution was coded 1N. For comparison and to verify the results reproducibility, two separate 1g/L N-TiO_2 aqueous dispersions (coded **2N and 3N**) were prepared.

2.3. Method to coat the textiles with photocatalysts

N-TiO_2 was applied to cotton fabric the following pad-dry methods:

1Na: the cotton knit (16x16cmxcm) was immersed in 100mL 1N dispersion for 10 minutes and then, dried in an oven at 100^{0}C for 3 hours. The fabric remains damp and waxy.

1Nb: assuming that the solution has a relatively large amount of N-TiO_2 and to increase the ability of particles to migrate on fabrics, 50 ml of distilled water were added to 50 ml of 1Na solution remained after the first treating of the cotton knit. In this solution, a new knit (16x16cm) was introduced and treated under identical conditions as 1Na.

2N & 3N: the cotton knit (21.5x21.5cmxcm) is immersed in 1000mL solution 2N and respectively 3N, it is brought to 80^{0}C in 60min and held at this temperature on ultrasonic bath for 30 minutes. The fabric is removed from the treatment bath, immersed in 1L of 50 mL/L NUVA 4200 liq. (pH 4.5) and kept under magnetic stirring for 10 minutes at 30^{0}C. The fabric is removed from the bath and is dried in oven at 100^{0}C.

2N bis: in 2N dispersion remaining after first knit treatment, 50mL absolute ethanol, 50mL PEG 200, 10mL Biowet PB, and 50mL Itobinder AG are added. A milky white emulsion was obtained, which remains stable for 24 hours at room temperature. In so prepared solution, two pieces (16x16cm each) of white knitted cotton were immersed. The temperature was raised to 75-80^{0}C in 15 minutes and the knit was maintained under magnetic stirring at this temperature for 30 minutes. The knit was removed and dried in oven at 100^{0}C.

3N bis: the method is similar to method 2Nbis except the addditon of 50mL of water instead of ethanol and the treatment temperature which was raised to 85-95^{0}C.

2.4. Characterization

The morphology, shape, size and distribution of the nanoparticles covering the textiles were investigated by scanning electron microscopy (SEM, Quanta 200, FEI, Holland). The presence of Ti and Fe on the textiles surface was analyzed by X-ray energy dispersive spectroscopy and FTIR spectroscopy (Excalibur FTS 3000, Digilab).

To evaluate the photocatalytic effect of the materials coated with N-TiO_2, the fabrics were immersed for 30minutes in 0.0064 g/L MB aqueous solution, dried under an IR lamp and exposed to UV (254 nm) and visible light (Xenotest, 1000 W xenon arc lamp, irradiance 4.5mW/cm^2 at 300-400 nm, Heraeus Industrietechnik, Hanau, Germany). The trichromatic coordinates of the exposed and non-exposed samples were measured on Hunterlab spectrophotometer, with CIELAB 1976 color space and D65-light source.

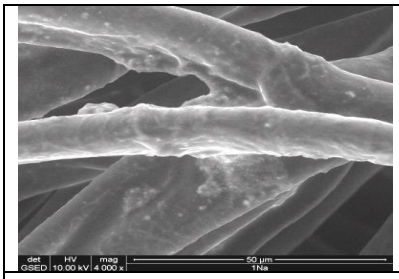
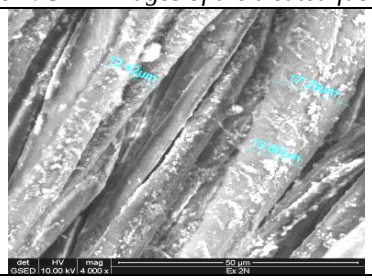
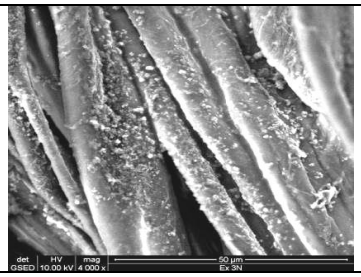
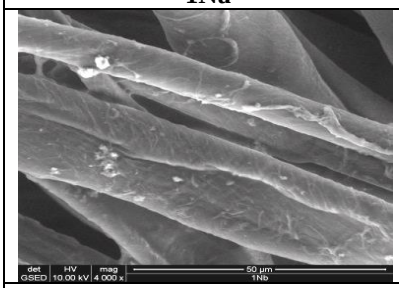
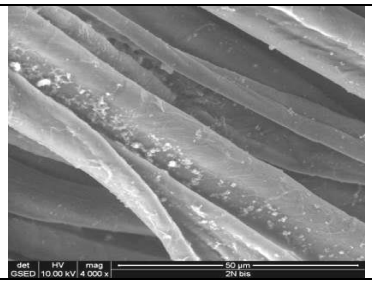
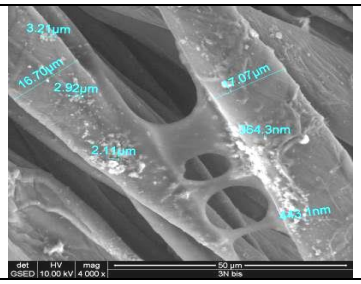
To test the particles adherence to the surface, the materials were subjected to five washing cycles under the following conditions: (5x5cmxcm) materials were washed in 100ml of distilled water containing 0.4g ECE detergent without phosphate and optical brighteners at 40^0C for 30min, then were rinsed 2 times with 100 ml water at 40^0C for 3 minutes. Washings were carried out in order to assess the adherence of N-TiO_2 particles on the fabrics surface. The remained TiO_2 particles were quantified by SEM/EDAX.

3. RESULTS

3.1. Characterization of the fabrics treated with N-TiO_2 nanoparticles by Scanning Electron Microscopy (SEM)

The SEM images of the cotton knit covered with N-TiO_2 are shown in Table 1.

***Table 1**: SEM images of the treated fabrics*

		
1Na	**2N**	**3N**
		
1Nb	**2Nbis**	**3Nbis**

Cotton fibers are coated in a polymer film, thicker for 1Na than for 1Nb fibers. Most of the particles are embedded in polymer and a small percentage in the form of relatively large agglomerations visible on fibers surface.

2N cotton fibers are coated uniformly with the N-TiO_2 particles of relatively small sizes while **2N bis** cotton fibers are enveloped in a polymer film and rare particles with different sizes (437.1nm, 804.7nm, 1.17 μm), mostly crowded, unevenly dispersed on the surface.

3N: fiber surface is covered almost entirely with particle with different sizes (the smallest being 231.8nm. 361.5nm) evenly dispersed, some of them forming small clumps.

3N bis: the deposition of the polymer and N-TiO_2 particles is demonstrated by the increased diameter (17.07- 16.70 μm) of the cotton fibers treated with 3N bis compared to the untreated fibers of 8.34- 15.17 μm. Most of the particles are deposited in the form of large clusters (364.3nm to 3.21 μm) embedded in the acrylic polymer.

3.2. EDAX elemental analysis of the fabrics treated with N-TiO_2

The energy dispersive spectroscopic (EDX) microanalysis results are shown in the Tables 2 and 3.

***Table 2**: EDAX spectra of the treated fabrics*

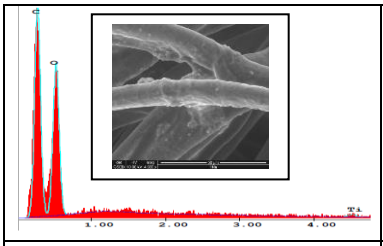
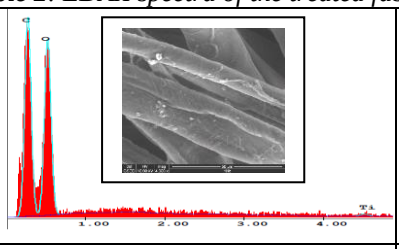
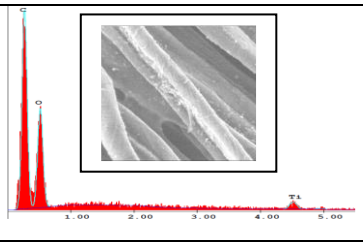
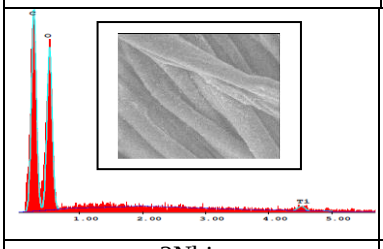
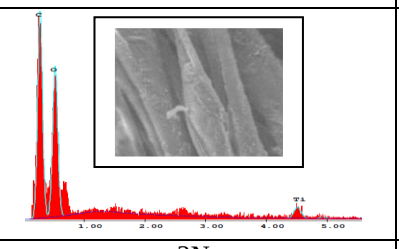
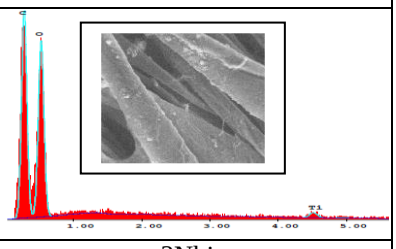
		
1Na	1Nb	2N
		
2Nbis	3N	3Nbis

***Table 3**: EDAX elemental microanalysis of N-TiO_2 deposited on knit*

Element, %Wt/ Knit	1Na	1Nb	2N	2Nbis	3N	3Nbis
C K	51.96	48.69	52.92	48.40	45.13	47.03
O K	43.96	47.58	35.39	45.18	40.89	45.92
Ti K	**4.08**	3.73	**11.69**	6.42	**13.99**	7.05

As results demonstrate the treatment with the 1Nb re-used dispersion, containing less than 0.5g/L N-TiO_2 lowers the %TiK deposited on fabric by only 8.57% compared to the treatment with 1Na dispersion containing 1 g/L N-TiO_2.

The amount of N-TiO_2 deposited on 2Nbis fabric represents more than half from the amount deposited using 2N dispersion even the TiO_2 concentration is lower than that of 2N solution due to the dilution and the use of a wetting agent (Biowet PB) which causes more intense particle wetting and cotton fabric swelling. By diluting the dispersion with ethanol and wetting agent, a higher number of particles are deposited on fabrics than by using water.

Also, the amount of TiO_2 deposited using dispersion 3Nbis represents ~ 50% of that deposited by treating the fabric with dispersion 3N and is slightly higher than that deposited by using the 2Nbis dispersion although the compositions of the 2Nbis and 3Nbis dispersions and the parameters of fabrics are basically similar. The only difference is represented by higher temperature treatment of 3Nbis fabric, which causes a more pronounced swelling of the fabric, and consequently the deposition of larger quantities of TiO_2.

The stability of aqueous N-TiO_2 dispersion is improved by addition of polyethylene glycols probably due to their absorption on particles which decreases the nanoparticles ability to agglomerate. The main disadvantage of PEG is its hydrophobicity, prolongation the time necessary for textiles drying. Also, even used in very low quantity, PEG 20000 remains on textile surface making them damp and waxy. To avoid these disadvantages, the re-used N-TiO_2 dispersions were diluted with water, organic solvents (ethanol) and wetting agents (Biowet PB). The dilution favors a better dispersion of particles which migrate much easier on the material.

Concluding, the use of a wetting agent and a higher treatment temperature favors the deposition of a higher amount of N-TiO_2 particles existing in the dispersions remained after the first treatment of the fabric.

4. CONCLUSIONS

The stability of aqueous N-TiO_2 dispersion is improved by addition of small amounts of polyethylene glycols and wetting agents. The use of a wetting agent and a higher treatment temperature favors the deposition of a higher amount of N-TiO_2 particles existing in the dispersions remained after the first treatment of the fabrics due to a better nanoparticles wetting and swelling of the cotton fabric.

Acknowledgements

The authors acknowledge the financial support from the UEFISCDI in the frame of programme PN II through the research project No. 87/2014 (CLEANTEX) and EUREKA-EUROSTARS programme through the project 334E /19.12.2013.

We thank Professor KIM SUNG JIN, Kumoh National Institute of Technology, South Korea for N-TiO_2 samples.

REFERENCES

[1] R. Asahi, T. Morikawa, H. Irie, T. Ohwaki, *"Nitrogen-Doped Titanium Dioxide as Visible-Light-Sensitive Photocatalyst: Designs, Developments, and Prospects"*, Chem. Rev., 114 (19), pp. 9824–9852, 2014.

[2] S. Sato, Chem. Phys. Lett. 123, 126, 1986.

[3] W. Mekprasart, T. Khumtong, J. Rattanarak, W. Techitdheera, W. Pecharapa, *"Effect of Nitrogen Doping on Optical and Photocatalytic Properties of TiO_2 Thin Film Prepared by Spin Coating Process"*, Energy Procedia, vol. 34, pp. 746–750, 2013; 10th Eco-Energy and Materials Science and Engineering Symposium.

[4] C. Chen, H. Bai, S. M. Chang, C. Chang, W. Den, *"Preparation of N-doped TiO2 photocatalyst by atmospheric pressure plasma process for VOCs decomposition under UV and visible light sources"*, Journal of Nanoparticle Research, vol. 9, no. 3, pp. 365–375, 2007.

[5] L. Zhu, J. Xie, X. Cui, J. Shen, X. Yang, Z. Zhang, *"Photoelectrochemical and optical properties of N-doped TiO2 thin films prepared by oxidation of sputtered TiNx films"*,Vacuum, vol. 84, no. 6, pp. 797–802, 2010.

[6] J. M. Yates, M. G. Nolan, D.W. Sheel, M. E. Pemble, *"The role of nitrogen doping on the development of visible light induced photocatalytic activity in thin TiO2 films grown on glass by chemical vapour deposition"*, Journal of Photochemistry and Photobiology A, vol. 179, no. 1-2, pp. 213–223, 2006.

[7] C. J. Tavares, S. M. Marques, T. Viseu et al., *"Enhancement of the photocatalytic nature of nitrogen-doped PVD-grown titanium dioxide thin films"*, Journal of Applied Physics, vol. 106, 2009.

[8] Y. Suda, H. Kawasaki, T. Ueda, T. Ohshima, *"Preparation of high quality nitrogen doped TiO2 thin film as a photocatalyst using a pulsed laser deposition method"*, Thin Solid Films, vol. 453-454, pp. 162–166, 2004.

[9] A.L. Stepanov, *"Applications of ion implantation for modification of TiO2: A review"*, Rev. Adv. Mater. Sci. 30, 150-165, 2012.

[10] X. Guo, J. Dai, K. Zhang, X. Wang, Z. Cui, J. Xiang, *"Fabrication of N-doped TiO_2/activated carbon fiber composites with enhanced photocatalytic activity"*, Textile Research Journal, vol. 84 no. 17, 1891-1900, 2014.

[11] A. Behzadnia, M. Montazer, A. Rashidi, M. M. Rad, *"Rapid Sonosynthesis of N-Doped Nano TiO_2 on Wool Fabric at Low Temperature: Introducing Self-cleaning, Hydrophilicity, Antibacterial/Antifungal Properties with low Alkali Solubility, Yellowness and Cytotoxicity, Photochemistry and Photobiology"*, vol. 90, Issue 6, pp.1224–1233, 2014.

[12] D. Wu, M. Long, *"Realizing Visible-Light-Induced Self-Cleaning Property of Cotton through Coating N-TiO2 Film and Loading AgI Particles"*, ACS Appl. Mater. Interfaces 3, 4770–4774, 2011.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PHOTOCATALYTIC EFFICIENCY OF N-TIO$_2$ APPLIED ON COTTON KNIT – PART 2

DUMITRESCU Iuliana[1], VARZARU Elena[1], IORDACHE George-Ovidiu[1], MITRAN Elena-Cornelia[1], CIOROBITCA Maria[2]

[1] National R&D Institute for Textiles and Leather Bucharest (INCDTP) 16 Lucretiu Patrascanu, 030508, Bucharest, Romania, E-mail: certex@ns.certex.ro

[2] S.C. Stofe Buhusi S.A., 36 Strada Libertăţii, 605100, Buhuși, Romania, E-mail: stofebuhusi@gmail.com

Corresponding author: Dumitrescu, Iuliana, E-mail: iuliana.dumitrescu@gmail.com

Abstract: *The objective of this work was to demonstrate the treatment durability at washing of N-TiO$_2$ layers applied on cotton fabrics by padding and to investigate the particle adherence and morphology of the textile surface. After 5 washing cycles, the cotton fibers are covered with a high number of particles, which demonstrate that the particle adherence to the substrate is high, most of them being present as large clusters. Also, the washing process does not affect in an important manner the polymer layer, only from place to place the cotton knit beeing disrupted. To evaluate the photocatalytic effect of the materials after washing treatment, samples were exposed to ultraviolet and visible light. The trichromatic coordinates of the exposed and non-exposed samples were measured on Hunterlab spectrophotometer. The contradictories values are determined by the non-uniformities of the materials which don't allowed a uniform dyeing of the fabrics. The obtained results showed that after 5 washings, the particles adherence to the substrate is still high and the photocatalytic effects are not significantly impaired. The photocatalytic efficiency of cotton knit treated with N-TiO$_2$ nanoparticles is higher under visible light than under UV light demonstrating the extension of the TiO$_2$ absorption in the visible range.*

Key words: *nitrogen-doped TiO$_2$, photocatalysis, textiles, washing durability, nanoparticles*

1. INTRODUCTION

Majority of the researches evaluate the photocatalytic effects of N-TiO$_2$ on the pollutants solutions [13-15] and none on the N-TiO$_2$ immobilized on textiles. Even the photodegradation efficiency in liquids is high, the results could be unreliable if the photocatalyst is fixed on solid substrates which acts as a barrier limiting the mass transport of pollutants to reduced surface of the adsorption sites. In addition, due to non-uniformity of the textile surfaces and the traditional methods used in the textile industry [16,17], the immobilized photocatalysts are randomly dispersed as clusters lowering the surface exposed to light. Our study was focused on the analysis of the photocatalytic effects of N-TiO$_2$ deposited on textile materials under visible, UV and solar light and their durability at washing.

1.1. Photocatalytic effect of the fabrics treated with N-TiO_2

The photocatalytic efficiency of the fabrics treated with N-TiO_2, stained with methylene blue (MB), and exposed to visible, UV and solar light is shown in the Tables 1 – 6.

***Table 1**: The aspect of the cotton knit exposed to UV (λ=365 nm) light*

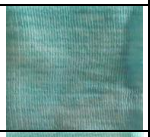
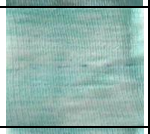
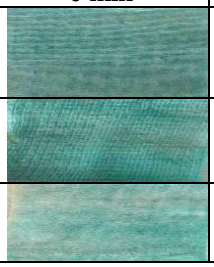
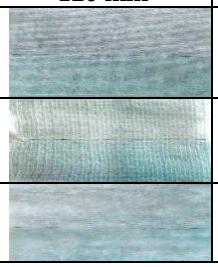
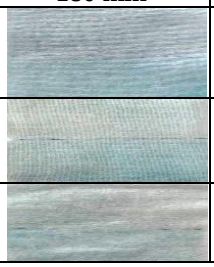
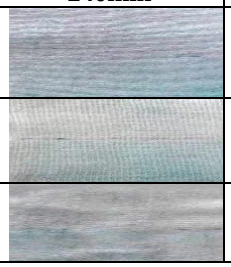
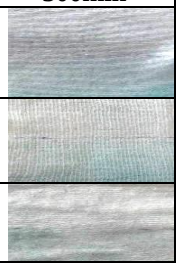
Time (min)	Blank	1Na	1 Nb	2N	2Nbis	3N bis
0						
120						
360						

***Table 2:** Trichromatic coordinates of the cotton knit treated with N-TiO_2, stained with MB and exposed at UV light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	Tone	% Strength SUM
Blank	83.33	-8.85	-8.02	1.67	3.65	3.83	5.55	-5.28	2.50	74.23
1Na	86.05	-11.86	-4.85	**3.43**	2.63	4.56	6.28	-4.47	2	66.83
1Nb	81.46	-9.62	-6.29	2.23	3.21	6.24	**7.36**	-6.44	2	79.63
2N	82.64	-7.59	-4.26	-1.90	-0.79	0.12	2.06	0.61	4	124.04
2N bis	85.15	-10.65	-3.35	2.04	3.27	5.13	6.41	-5.13	2	76.84
3N bis	84.71	-11.41	-3.63	0.55	2.80	4.67	5.47	-4.49	2.5	88.14

Under the UV light, except 2N and 3Nbis fabrics, the treated samples are more decolorized than the untreated fabric (blank) as the grades on gray scale demonstrate. The highest lightness difference (dL*, + = lighter, - = darker than blank) and the lowest % strength SUM is found on sample 1Na, proving that the methylene blue is more intense decolorized on this fabric than on the other materials after the exposure to UV light. What is important to notice is the behavior of sample 2N, which shows the shade darkening, the color being shifted to green (da* negative) and yellow (db* positive) contrary to the rest of fabrics which colors are shifted to red-yellow.

***Table 3**: Aspect of the knit cotton exposed 5hr to solar light*

Time	0 min	120 min	180 min	240min	300min
Blank					
1Na					
1 Nb					

2N					
2N bis					
3N					
3N bis					

Table 4: *Trichromatic coordinates of the materials treated with N-TiO_2 stained with MB and exposed to solar light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	85.76	-2.70	-4.15	0.69	1.34	1.51	2.14	-2.01	3.5	93.80
1Na	90.69	-3.78	1.47	3.96	3.21	4.94	7.10	-3.74	2	71.50
1Nb	87.69	-3.77	0.53	3.15	1.37	4.79	5.90	-2.87	2	80.01
2N	88.05	-3.48	-0.11	**5.23**	3.06	5.03	7.87	-4.83	2	77.73
2Nbis	89.05	-3.25	1.32	3.08	3.04	5.97	7.37	-4.31	2	88.63
3N	91.09	-2.39	2.66	4.49	3.68	4.77	7.52	-2.86	2	55.20
3Nbis	87.44	-3.66	1.31	3.43	3.03	7.33	8.64	-5.11	1.5	104.76

Sun exposure leads to faster degradation of methylene blue on treated materials than on blank sample, the difference being 1.5 tones compared to untreated material exposed to UV light. Degradative action of sunlight is more intense on 1Na on which surface a higher amount of TiO_2 (4.08 wt% TiK) exists than on 1Nb knit (3.73 wt% TiK) as demonstrated by the lightness (dL*) and color differences (dE*) values and confirmed by % Strength Sum. Also, in the case of 2N and 2N bis, 3N and 3Nbis, it is clear that higher amount of N-TiO_2 existing on the 2N material leads to a faster degradation of the dye.

Table 5: *Aspect of the cotton knit treated with2N, 2Nbis, 3N, 3Nbis exposed 4 h to visible light*

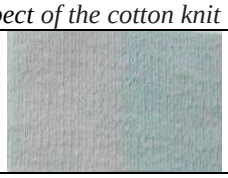
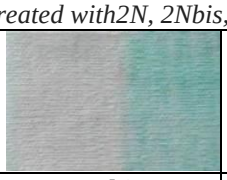
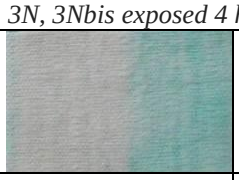
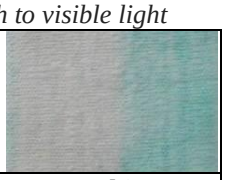
				
Blank	**2N**	**2N bis**	**3N**	**3N bis**

Table 6: *Trichromatic coordinates of the materials treated with N-TiO_2 stained with MB and exposed to 4hs visible light*

Sample	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	84.16	-3.05	-5.62	0.68	8.01	4.97	9.45	-8.92	1.5	79.95
1Na	89.13	-4.93	-0.02	10.42	14.04	15.40	23.30	-19.52	1	25.00
1Nb	85.73	-4.58	-3.95	4.18	7.28	7.36	11.16	-10.34	1.5	56.00
2N	86.48	-2.92	-0.26	1.30	5.14	4.47	6.93	-6.41	2	92.33
2Nbis	88.33	-2.53	2.05	5.68	12.63	10.90	17.63	-14.29	1	48.00
3Nbis	88.72	-3.05	2.99	5.51	9.63	10.43	15.23	-10.42	1	61.76

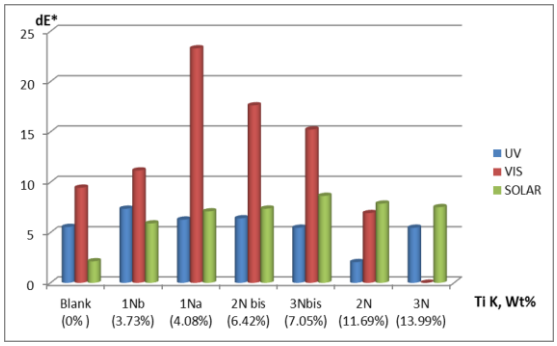


***Fig. 1**: Correlation dE* and TiK*

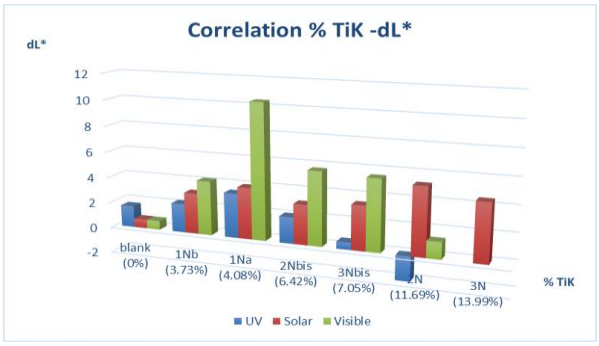


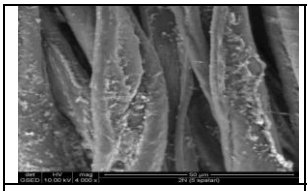
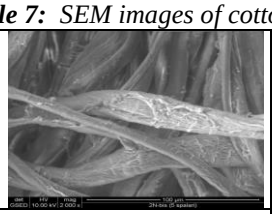
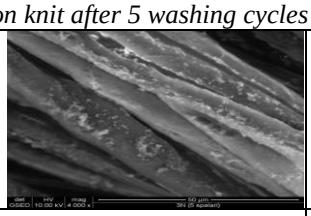
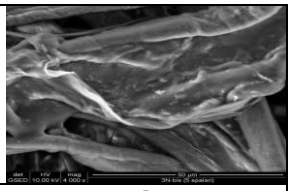
***Fig. 2**: Correlation dE* and TiK*

Under UV and visible light, comparing the values of dL*, dE* and % TiK (Fig. 1 and 2), it is obvious that, the photocatalytic efficiency increases until TiO_2 concentration reaches an optimum value (4.08 wt% TiK), than decreases as the amount of N-TiO_2 increases. Under the solar light, the photocatalytic effects are higher for high amount of TiO_2 deposited on materials.

1.2. The treatments durability (Resistance to washing)

The morphology of the textile surface (Table 7) and the amount of N-TiO_2 (Table 8) remained on the knits after 5 washing cycles were investigated to determine the treatments durability.

***Table 7:** SEM images of cotton knit after 5 washing cycles*

			
2N	**2Nbis**	**3N**	**3N bis**

After 5 washing cycles, the cotton fibers are covered with a high number of particles, most of them being present as large clusters, which dimensions vary from 145.7nm to 2µm. The polymer layers are not much affected by washing, only from place to place being disrupted.

***Table 8:** EDAX spectra of the cotton knit after 5 washing cycles*

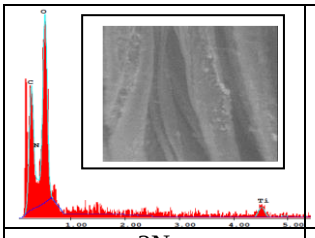
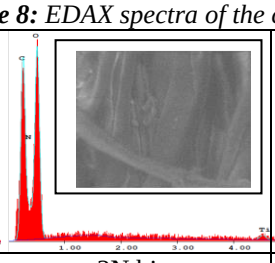
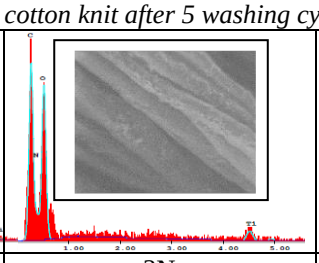
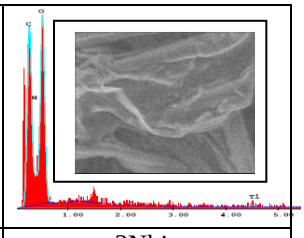
			
2N	2N bis	3N	3Nbis

***Table 9:** Elements founds on cotton knit initial and after 5 washings*

Ti K, Wt, %	2N	2N bis	3N	3N bis
Initial	**11.69**	6.42	**13.99**	7.05
After 5 washings	13.03	5.48	11.90	3.53
Removed, %	+ 10.28	14.64	14.94	49.93

Except the 3N bis cotton knit, the adherence of the particles is very high if we consider the amount found on the fabrics after 5 washings which decreases by 12.57% for 2N, 4.51-6.42% for 2N bis, and 15% for 3N in comparison with the initial fabrics. It seems that addition of Itobinder instead to improve the particle adherence to the textiles surface, remove a large part of them, especially in the case of 3N bis knit (Table 9).

1.3. Photocatalytic evaluation of the N-TiO_2 cotton knit after 5 washing cycles

Table 10: *Aspect of the cotton knit after 5 washing cycles and exposed 4 hours to visible light*

Blank	2N	2N bis	3N	3N bis

Table 11: *Trichromatic coordinates of the cotton knit after 5 washing cycles and exposed 4 hours to visible light*

Material	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	85.52	-2.94	-4.59	1.19	12.27	5.88	13.66	-13.01	1	54.71
2N	76.25	-8.74	-12.28	**6.17**	10.87	14.85	19.41	-18.40	1	**40.46**
2Nbis	85.14	-4.10	-3.47	5.91	13.29	14.06	**20.23**	-19.32	1	44.81
3N	75.06	-9.02	-12.22	4.64	12.03	13.80	18.88	-18.28	1	42.67
3Nbis	85.51	-4.41	-3.42	5.21	11.06	13.24	18.02	-17.15	1	49.93

According to the tones on greyscale, the methylene blue is decolorized on all the materials, including the untreated ones (Tables 10 and 11). If we consider the lightness values (dL*), the sample 2N shows the most intensive discoloration followed by 2Nbis, 3Nbis and 3N samples. The da* and db* values are positive, meaning that color for all the samples is shifted to longer wavelength (red-yellow). If we consider the color difference values (dE*) the highest discoloration is shown by sample 2Nbis due to higher values of da* and db*, knowing that the total color difference is calculated using the following formula:

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

The contradictories values, especially if we take into account the % Strength SUM, are determinate by the non-uniformities of the materials which don't allowed a uniform dyeing of the fabrics and the dependence of the color measurement by a multitude of parameters (surface texture, uniformity, instrumental geometry, dyes shades, etc.)

Table 12: *Chromatic coordinates of the cotton knit after 5 washing cycles and exposed 9 hours to natural solar light*

Material	L*	a*	b*	dL*	da*	db*	dE*	dC	tone	% Strength SUM
Blank	87.72	-2.02	-1.49	3.18	2.19	3.71	5.36	-4.19	2.50	68.80
2N	72.94	-7.01	-9.91	1.41	5.46	9.57	11.11	-10.99	1.50	85.98
2Nbis	87.82	-1.88	0.81	5.51	6.28	9.77	12.86	-10.07	1.00	65.14
3N	73.00	-7.10	-10.39	8.07	7.16	15.95	19.25	-17.37	1.00	50.01
3Nbis	88.33	-2.09	0.85	**8.89**	7.76	13.20	17.71	-13.54	1.00	44.09

The values of brightness and % Strength SUM (Table 12) demonstrate that the most intensive discoloration is shown by 3Nbis followed by 3N and 2N bis. The color difference is almost double or triple comparing with blank sample.

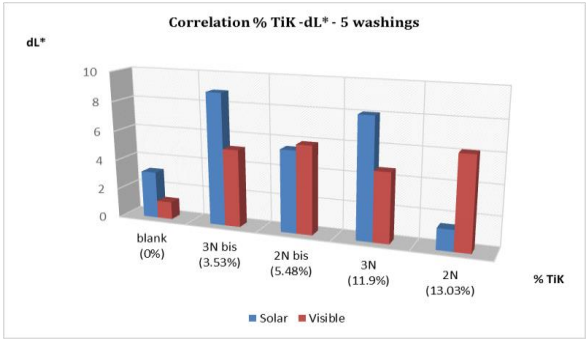


***Fig. 3**: Correlation % TiK -dL* - 5 washings*

Based on dL* values, it can be concluded that, except the sample 2N, the efficiency of N-TiO_2 is higher under the solar light than under visible light (Fig. 3).

2. CONCLUSIONS

The obtained results showed that after 5 washings, the particles adherence to the substrate is high and the photocatalytic effects are not significantly impaired. The cotton knit treated with N-TiO_2 nanoparticles show an improved photocatalytic effects under visible light.

Acknowledgements

The authors acknowledge the financial support from the UEFISCDI in the frame of programme PN II through the research project No. 87/2014 (CLEANTEX) and EUREKA-EUROSTARS programme through the project 334E /19.12.2013.
We thank Professor KIM SUNG JIN, Kumoh National Institute of Technology, South Korea for N-TiO_2 samples.

REFERENCES

[13] A. Selvaraj, R. Parimiladevi, K.B. Rajesh, "*Synthesis of Nitrogen Doped Titanium Dioxide (TiO2) and its Photocatalytic Performance for the Degradation of Indigo Carmine Dye"*, J. Environ. Nanotechnol. vol. 2, No. 1, pp. 35-41, 2013.

[14] X. Cheng, X. Yu, Z. Xing, J. Wan, *"Enhanced Photocatalytic Activity of Nitrogen Doped TiO2 Anatase Nano-Particle under Simulated Sunlight Irradiation"*, Energy Procedia, 16, 598–605, 2012.

[15] H. Yu, X. Zheng, Z. Yin, F. Tao, B. Fang, K. Hou, *"Preparation of nitrogen-doped TiO2 nanoparticle catalyst and its catalytic activity under visible light"*, Chin. J. Chem. Eng. 15 (6), 802–807, 2007.

[16] I. Dumitrescu, O. G. Iordache, A. Popescu, E. Varzaru, S. Kim, B. Basim, G. Ükelge, *"The photocatalytic effects of textiles treated with TiO_2 and Fe/TiO_2"*, Industria Textila, 241, vol. 66, nr. 5, pp. 297 – 305, 2015.

[17] Lin, L. Method of Making Fabric with Photo-Catalyst. U.S. 2005/0227557 A1, 13 October 2005

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A VIEW ON THE ROMANIAN TEXTILE INDUSTRY IN THE EUROPEAN CONTEXT

GHERGHEL Maria-Ariana[1], GHERGHEL Sabina[2]

[1] West University of Timişoara, Doctoral School of the Faculty of Law, Eroilor 9A, 300575, Timişoara, Romania, maria.gherghel90@e-uvt.ro

[2] University of Oradea, Faculty of Energy Engineering and Industrial Management, Department of Textiles, Leather and Industrial Management, B.St. Delavrancea 4, Oradea, Romania, sgherghel@uoradea.ro

Corresponding author: Gherghel, Maria-Ariana, E-mail: maria.gherghel90@e-uvt.ro

Abstract: *The textile market of the European Union is a highly competitive one, being recognised at an international level as one of the most important players in this domain. An important factor that has led to this achievement was the creation of the EU Single Market, which provided the fundamental principle of free movement of goods. Also, the European legislative acts had a crucial role by aligning national laws regarding textiles. The Romanian textile industry is traditionally well-known for its quality, but in these new circumstances, has to face other forces and to struggle to maintain a certain position. There have been observed decreases in the production of textile products, even thuogh the manpower in Romania is one of the chepest in the European Union. The intense use of the "lohn" system, first considered as a ramp rescue for the textile industry, has contributed to the loss of identity of the Romanian companies. However, there can be identified several means of refreshing this industry, first of all by the awareness of the current situation, and then by having the courage to move forward, to start creating our own brands, to not lose sight of the quality factor and mainly by innovating.*

Key words: *EU single market, regulation, production, lohn, innovation.*

1. INTRODUCTION

The sector of textile and clothing is one of the most important areas in the European manufacturing industry. At the level of the European Union, there are approximately 1.7 million people working in this specific field, a fact which has the ability to generate a turnover of EUR 166 billion [1].

The first European acts regarding the textiles were [2]:

- Directive 96/74/EC of the European Parliament and the Council of 16 December 1996 - on textile names;
- Commission Directive 97/37/EC of 19 June 1007 – adapting to technical progress Annexes I and II to Directive 96/74/EC of the European Parliament and of the Council on textile names;
- Directive 96/73/EC of the European Parliament and of the Council of 16 December 1996 - on certain methods for the quantitative analysis of binary textile fibre mixture;

- Directive 2008/121/EC of the European Parliament and of the Council of 14 January 2009 on textile names (recast);
- Council Directive of 26 February 1973 on the approximation of the laws of the Member States relating to the quantitative analysis of ternary fibre mixture.

1. THE INTERNAL TEXTILE MARKET OF THE EUROPEAN UNION

The Regulation (EU) No 1007/2011 of the European Parliament and of the Council of 27 September 2011 on textile fibre names and related labelling and marking of the fibre composition of textile products and repealing Council Directive 73/44/EEC and Directives 96/73/EC and 2008/121/EC of the European Parliament and of the Council had the role to align laws in all the member countries, in order to enable the correct and safe functioning of their internal markets and also to ensure that every citizen takes act of his rights and obligations, which are, by this mean, both guaranteed and protected.

It is possible that the question "why it was so important for the European Union to adopt an act which had the ability to align the names of the textiles?" arises. The answer is very simple and it implies the knowledge of an essential principle that is fundamental for a proper textile-market between the borders of the Union: free movement of goods within the European single market. To be more specific, different textile fibre names would have caused a tremendous prejudice in trading and at the same time it would have affected the rights of the consumer. The free movement of goods, the first of the four fundamental freedoms of the internal market is guaranteed by the abolition of custom duties and quantitative restrictions and also by the prohibition of measures having equivalent effect. The principle of mutual recognition, eliminating physical and technical barriers, by promoting standardization, was added for the completion of the internal market [3].

As it was pointed out before, the first acts regarding textiles were Directives and the newest one is a Regulation. It is important to mention that there are many differences between these two types of European acts, even though they are both part of the secondary legislation of the European Union (because the Treaties form the primary one). The regulation is a legislative act which has to be applied across all member states, being compulsory in all its elements as it is adopted. On the other hand, the directive is an act that sets a goal which has to be achieved by the European countries, using means and methods that are chosen by each member state; the receiving state is obliged to transpose the Directive within a certain period and until that moment the act does not create rights and obligations for the citizens. So, it is far more useful for the textile industry that the provisions related to it are gathered in a Regulation.

The proper functioning of the internal market for the textile sector involves some of the following highlights:

- Harmonize requirements for the name, composition and labeling textile products;
- Protecting the consumer's interests by providing correct information;
- Instructions on the use of dangerous chemicals in the treatment of textiles;
- Harmonization of rules that protect the designs;
- Environmental protection;
- State aid for the synthetic fibres industry.

2. THE TEXTILE MARKET IN ROMANIA

In Romania, the textile and clothing field is also very spread, but lately the industry is facing a problem regarding issues related to significant decreases in production. For example, during the period January – November 2015, in comparison with the same period of time in 2014, the sector of

manufacture of textiles has decreased by 9,3%; also, if we take into consideration the industrial branches in which an accentuated downward slope of the labor productivity has been observed, in the exact period of time as above, the percentage of the manufacture of textiles is -16,3% [4].

The industrial output indices of the manufacture of textiles (unadjusted series) for the period 2014/2015, in our country, are shown below [4]:

Table 1: *The industrial output indices - unadjusted*

Year/ Month	Jan.	Feb.	March	April	May	June	July	August	Sep.	Oct.	Nov.	Dec.
2014	140,5	143,8	139,4	120,8	139,6	125,0	119,8	90,0	131,3	134,8	133,1	109,7
2015	122,3	126,3	130,3	111,4	99,5	104,4	114,5	78,0	127,0	136,5	129,5	-

The industrial output indices of the manufacture of textiles (adjusted series for number of working days) for the period 2014/2015, in our country, are [4]:

Table 2*: Industrial output indices - adjusted*

Year/ Month	Jan.	Feb.	March	April	May	June	July	August	Sep.	Oct.	Nov.	Dec.
2014	144,8	148,3	147,5	119,0	143,9	126,4	117,1	95,3	129,3	131,8	138,2	116,1
2015	129,4	130,3	134,3	112,7	105,5	105,7	111,7	80,6	125,0	137,1	134,9	-

Beside this, the exports of textile products generated an outcome of 796,5 mil. EURO in January – September 2015, which represents 104,3% against the same period of 2014 [4].

3. CONCLUSIONS

Romania, as a member state of the European Union, should exploit better the advantages of its status, and apply all the favorable conditions that the membership created for the country.

However, there are some issues that have to be highlighted and which seriously affect the textile industry in our country:

- The instability of the economic policies and the unpredictability in this domain;
- The bureaucracy, right from the beginning of taking the decision to create a company;
- The great amount of taxes and fees that the state requires;
- The lack of information (like training-classes, for example) regarding accessing European funds in this area;
- A pour infrastructure, the lack of highways that would facilitate the transport of goods;
- The inflation.

If we take into consideration the manpower, which is the most used in the textile industry, it is well known that the workforce in Romania is one of the cheapest in the European Union. Despite this, there has to be specified the fact that the employees in our country are highly trained

Along with trade liberalization and then the fact that Romania joined the European Union, the textile industry in our country was forced to compete with stronger forces in this area, such as China, India, Turkey, countries that possess significant resources of raw materials and in which the State strongly supports manufactures [5]. The Romanian textile industry had to cross a difficult period of adaptation to a continuously in change market. This situation generated the use of the "lohn" system. The "lohn" can be defined as a specific type of international contract, widely practiced in countries with cheap labor force, whereby a producer undertakes to execute a product at the order of a beneficiary, gaining remuneration [6].

At a first glance, it may look like the use of the "lohn" system might develop considerably the textile industry in our country. In fact, this practice has led to the loss of the identity of the manufacturing companies in Romania. These companies use the patterns of the foreign ones and so, even if the products made in Romania reach the whole European Union, the client does not know this.

As a final conclusion, for Romania to be an international player in this industry, in and out the borders of the European Union, it is important that the Romanian companies trade products with their own brand, and keeping them at a high quality from the perspective of the European legislation. Of course, it would be of great help if the Government would support the textile industry. On the other hand, to be competitive on a very "wild" market it is essential to innovate, to always come with new projects, new ideas and to be able to create links with other areas such as medicine.

REFERENCES

[1] *"Textiles and clothing industries"*, [Online] Available: http://ec.europa.eu/index_en.htm.

[2] Legislative acts, [Online]. Available: http://eur-lex.europa.eu/homepage.html?locale=en.

[3] "*Free movement of goods"*, [Online]. Available: www.europarl.europa.eu.

[4] National Institute of Statistics, *"Industry statistical bulletin, nr. 11/2015",* [Online]. Available: http://www.insse.ro/cms/.

[5] O. Folcut, D-M. Pociovălişteanu, R. Despa, R. Mustea, I. Ivanescu, M. M. Ivanescu, *"Romanian textiles and clothing industry – present and perspectives"*, Analele Universităţii "Constantin Brâncuşi" din Târgu Jiu, Secţiunea Economie, Nr. 3/2009, [Online], pp. 244-247, Available: http://www.utgjiu.ro/.

[6] *"Industria textilă şi de confecţii – sector industrial de tradiţie în Regiunea Centru"*, [Online]. Available: http://www.adrcentru.ro/.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

COMPARATIVE STUDY OF TWO DYEING METHODS USING REACTIVE DYE

HINOJOSA Belén, MONTAVA Ignacio, BOU-BELDA Eva, DÍAZ Pablo

[1] *Universitat Politècnica de Valencia, Alcoy (Alicante), SPAIN*

Corresponding author: Bou, Eva Email: evbobel@upv.es

Abstract: *Environment preservation is a common worry not only for people but for companies as well. Industry is more and more concern about the necessity of developing new and more respectful processes. Dye is one of the most important processes in the textile industry but it is also considered as no too safe regarding environment issues. This process uses large amounts of water and generates big volumes of wastewater. Following this issue, new regulations and laws emerge to control the waste generated. This leads to the companies and increased costs in terms of wastewater treatments and high water consumption. In this research we compare two systems on garment finishing application, the conventional bath process and the new Ecofinish system that is able to save water and product. To compare these processes, we carried out a reactive dyeing using both systems in order to determine the quality differences in the final product. For this purpose, the samples have been tested to washing and rubbing fastness, according to UNE EN ISO 105 C10 and UNE- EN ISO 105 X12 standards, respectively. This study confirms that this system achieves water savings and reduces the wastewater produced, getting a good dyeing. This process can be considered as an alternative to the conventional one.*

Key words: *reactive dye, Ecofinish, dyeing, washing fastness, rubbing fasteness, exhaustion.*

1. INTRODUCTION

In recent decades, society has become increasingly concerned with protection of the environment. The textile dyeing industry faces the need to address its responsibility towards a wide range of health, safety and environmental issues, some of which are generic to the industry and some specific to the processe operating in particulas cases [1]. This industry is challenging day to day by the requirement to satify the demands of increasingly stringent legislation and controls introduced by goverments and regulatory agencies to ensure compliance with enviroment issues. For this reason, many authors are studying new methods [2], [3], products [4] and developing new systems [5], focused on achieving more environmentally friendly dyeing process.

The company Care Applications S.L.U. has developed an accessory that complements conventional exhaust dyebath machines to treat clothes, called Ecofinish. This accessory can get a water and product saving by vaporizing the solution.

In this study we compare both finishing processes to treat clothes, the conventional exhaustion process and the new system Ecofinish. We dyed cotton fabric using reactive dyes. The reactive dyeing process is carried out by the exhaustion system. This type of dye is water soluble and depending of the reactive group, will have a higher or lower affinity by the cellulosic fibers.

The aim of this study is to determine the washing and rubbing fastness of fabrics dyed using both processes. Moreover, we compare the amount of water, salt, CO_3Na_2 and complexing agent used en each dyeing method and we could see that dyed samples by Ecofinish system achieve the same properties which are obtained by the bathing process despite the water and product saving.

2. EXPERIMENTAL

2.1 Materials

To carry out this study, cotton fabric with the next features was used:

Table 1: *Characteristics of the fabric used.*

Sample	Composition	Structure	Density		Weight
			Warp	Weft	
Sample	96% Co 4% EA	Sarga 2E1 B 2,1	61,1 yarn/cm Title: 1/50 Nm	29,4 yarn/cm Title: 1/50 Nm	185g/m^2

We used reactive turquoise dye CI Reactive Blue 21 (Novacron Turquoise H-GN). Sodium carbonate, soap complexing agent and salt were used as auxiliary products.

2.2 Exhaustion dyeing

Table 2 shows the process followed by reactive dyeing in exhaustion machine for clothes treatment.

Table 2: *Steps for reactive dyeing.*

Steps	%	mL/L	Product	g	Water (L)	L:B 1:X	Temp. (ºC)	Time (min)	pH	Velocity r.p.m.
Preparation	0,5		Soap	5	20	20	50	10		27
		2	Sodium carbonate	40	20	20	35	20	10	27
Washing off					20	20		2		27
Dyeing		60	Salt	1200	20	20				27
		1	Complexing agent	20						
			Indirect heating				40			
	4		Dye	40	5			10		
			Indirect heating				70	10		
		20	Sodium carbonate	400				30	11	
			Maintenance	4				30		
Washing off					20	20	50	3		27
Neutralized		1	Acetic acid	20	20	20		5		27
Washing off		1	Soap	20	20	20	90	10		27
Washing off					20	20	70	3		27
Washing off					20	20	50	3		27
Washing off					20	20		3		27

2.3 Ecofinish dyeing

The following table lists the steps to perform the reactive dye through the Ecofinish system:

Table 3: *Steps for reactive dyeing.*

Steps	%	mL/L	Product	g	Water (L)	L:B 1:X	Temp. (ºC)	Time (min)	pH	Velocity r.p.m.
Preparation	0,5		Soap	5	20	20	50	10		27
		2	Sodium carbonate	40	20	20	35	20	10	27
Wash off					20	20		2		27
Spin-dry	50									
Dyeing	4		Dye	40	1	1		20		27
		20	Sodium carbonate *	20					11	
Drying							150	20		
Wash off					20	20	50	3		27
Neutralized		1	Acetic acid	20	20	20		5		27
Soaping		1	Soap	20	20	20	90	10		27
Wash off					20	20	70	3		27
Wash off					20	20	50	3		27
Wash off					20	20		3		27

* Add the alkali just at the time that the product is nebulized to prevent the dye hydrolyzes.

The Ecofinish system is an accessory that is installed in conventional exhauting machines for applying treatments on garment. The main difference between the conventional process is that the Ecofinish sprays the dissolution on the fabric and this allows the water and product savings.

3. RESULTS AND DISSCUS

In Table 4 we can see the consumption that takes place in both processes for 1 kg of textiles material:

Table 4: *Water and product consumption for 1kg garment.*

Consuption	Water (L)	CO_3Na_2 (g)	Salt (g)	Complexing agent (mL)	Dye (g)
Exhaustion	20	400	1200	20	40
Ecofinish	1	20	0	0	40
Savings with Ecofinish (%)	**95%**	**95%**	**100%**	**100%**	**0%**

These results show the water and product consumption made by two systems and we check the water, CO_3Na_2, salt and complexing agent saving achieved by the use of Ecofinish system.

The major environmental problem associated with the use of the reactive dyes is their loss in the dyeing process. The fixation efficiency is in the range 60–90%. Consequently, substantial amounts of unfixed dyes are released in wastewater. We used a 95% less of water by ecofinish system, for this reason, we achieve to reduce the amount of wastewater and the treatment cost.

Reactive dyes applied by exhaust methods require large amounts of salt to get high intensity of color, however if ecofinish system is used, the salt is not necessary to carry out the dye. Reduction of salt in the effluent reduces pollution of rivers and streams where the biological equilibrium depends to a large extent on the salt content of the water. The complexing agent is not used in the system which is studied in this work, but it is necessary the use of complexing agent in

exhaust system to get high level fixation of the reactive dye on the cotton fibers, being this type of product a pollutant substance.

In the next table are the results of the washing fastness, this shows the discharge and degradation rates of the samples dyed by the conventional process and by the Ecofinish system.

In the next table are the results of the washing fastness, this shows the discharge and degradation rates of the samples dyed by the conventional process and by the Ecofinish system.

Table 5: *Washing fastness results*

Sample	Degradation rate	Discharge rate	
		Wo	Co
Exhausted Sample	3	2	3-4
Ecofinish Sample	4	5	4-5

In the washing fastness test, the Ecofinish system improves his properties regarding the colourin discharge and degradation rates.

Table 6 shows the results of the rubbing fastness, indicating the dry and wet degradation and discharge rates.

Table 6: *Rubbing fastness results*

Sample	Degradation index		Discharge index	
	Dry	Wet	Dry	Wet
Exhausted Sample	4-5	4	4-5	3-4
Ecofinish Sample	4-5	4	4-5	3

In this table we could appreciate that the results in both systems are the same or very similar in the case of wet discharge result.

5. CONCLUSIONS

In this study we can see that the washing fatness is better when sample is dyed using Ecofinish system and rubbing fastness results are similar in both processes studied. Therefore, we can conclude that Ecofinish system can improve the results fastness obtained by the conventional exhaustion process, also take place a high water and product saving. This is the most important value of the new system, because the final product properties have been not affected despite these savings.

REFERENCES

[1] R. M. Christie, *"Environmental aspects of textile dyeing",* 2007, Elsevier.

[2] Y. Cai, M. T. Pailthorpe, S. K. David, *"A new method for improving the dyeability of cotton with reactive dyes",* Textile research journal, 1999, 69(6), pp. 440-446.

[3] M. Marti, A. De La Maza, J. L Parra, L. Coderch, S. Serra, *"Dyeing wool at low temperatures: new method using liposomes",* Textile Research Journal, 2001, 71(8), pp. 678-682.

[4] R. Mussak, & T. Bechtold, *"Natural colorants in textile dyeing. In Handbook of natural colorants",* John Wiley & Sons, Ltd. Chichester, 2009, pp.315-337.

[5] A. Roessler, X. Jin *"State of the art technologies and new electrochemical methods for the reduction of vat dyes"*, Dyes and pigments, 2003, 59(3), 223-235.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE INFLUENCE OF THE NUMBER OF RIPPLE OF POLYACRYLONITRILIC FIBERS COTTON TYPE ON YARN PROPERTIES

HRISTIAN Liliana[1], BORDEIANU Demetra Lacramioara[1], BŐHM-RÉVÉSZ Gabriella[2]

[1]"Gheorghe Asachi" Technical University of Iasi, Faculty of Textile, Leather & Industrial Management, Department of Engineering and Design of Textile Products, Blvd. Mangeron, No.28, Iasi, Romania

[2]University of Oradea, Department of textiles-Leather and Industrial Management, B.St.Selavrancea Str. No. 4, 410058, Oradea, Romania,

Corresponding author: Hristian Liliana, e-mail: hristian@tex.tuiasi.ro

Abstract: *In this study we aimed the influence of the number of undulations of polyacrylonitrile fibers, cotton type, on the properties of yarns with Nm50/1 fineness, made on BD 200 the rotor spinning machine. Rotor spinning of the synthetic fibers is largely influenced by some characteristics of the fibers as being: the quality and quantity of the avivage, frequency of undulations and the number of defects fiber.*
Tensile properties and structural characteristics aspect of the yarns carried on BD 200 rotor spinning machine are determined, at the fiber content, the structural model and the technological parameters of processing, by the result of the transfer of fibers proprieties, into the meaning fiber-yarn. The yarns structural compactness, determined by the degree of twisting and tensional properties are defining for the quality of yarns and warrants the corresponding to their destination.
Structural characteristics of the yarns which are characterized by complexity and diversity of their actions were studied by determining the linear irregularity (U%) , standard deviatin (CV%) and the imperfections in the form of thinnin (S), thickening (G), neppines (N), relative to 1000 m yarn.

Key words: *fibers undulations fibers, linear irregularity, breaking length, rotor spinning machine, yarns resistance.*

1. INTRODUCTION

The rotor yarns are characterised by significant quality parameters, such as unevenness of linear density, the number of faults, and hairiness, which are better than those of ring yarns, and can be accepted as yarns of high quality [1]. The quality of the spun yarn can be significantly improved, while using equally raw material, by a suitable selection of the spinning system and the type of the spinning machine used [2].

Open-end (OE) rotor spun yarns have certain characteristics which differentiate them from conventional ring-spun yarns. This is because of differences which can be noted between their production method and structure [3]. In contrast to ring spinning, twisting during rotor spinning takes place from the inside onwards. Yarn elongation at break generally decreases as the rotor speed increases. This variation may be attributed to the increase in yarn tension at higher speeds and with

bigger rotor diameters [4-7]. Rotor-spun yarns have therefore always been successful where they could be manufactured more cheaply than ring-spun yarns and proved suitable for the range of application in question [6-9].

Based on Uster Statistics it is apparent that the elongation at break of rotor-spun yarns is higher than that of comparable ring-spun yarns, albeit only marginally in some cases [10-13]. This is especially positively noticeable in the working capacity of rotor-spun yarn, in that the differences relative to ring-spun yarn are smaller than for countrelated yarn tenacity [12-14].

Rotor is the cheapest technique and produced yarn evenness is also better than ring yarn. It is also a fast process. But limitation of rotor yarn is less strength of the produced yarn. If it is possible to increase rotor yarn strength then the yarn will be the best one. So researchers should give emphasize on rotor spinning process.

2. EXPERIMENTAL PART

2.1. Materials and methods

The main features of polyacrylonitrile fibers, cotton type, studied by us are presented in Table 1.

Table 1: *The medium characteristics of fibers*

Characteristics		Options				
The number of undulations (ond./cm)		3.6	3.9	4.5	4.8	5.1
The length density	Tdtex	1.5	1.6	1.7	1.7	1.6
	CV_{Tt}	4.5	3.2	2.3	5.5	4.4
Breakout force	Pr (cN)	4.2	4.3	4.3	4.1	4.5
	CV_{Fr}	22.7	16.5	19.3	22.3	25.6
Elongation at break ε (%)		39.4	27.7	45.5	54.4	20.1
Tenacity	τ (cN/tex)	2.23	2.69	2.54	2.06	3.01
	CV	10.5	20.8	34.1	60.8	64.5
The degree of wrinkling (%)		12.0	11.0	16.2	15.1	11.5
Undulations stability(%)		93.4	94.5	91.4	54.0	54.8

All of the fibers were processed on BD 200 rotor spinning machine, achieving yarns with Nm 50/1 fineness, based on the same spinning plan and in preparation of spinning were used three mill passages. At the rotor spinning machine, for rotor, it was adopted a commonly speed, used in industrial practice, by 36 000 rev/min and for the carried cylinder, a speed of 6500 rev/min.

Linear density of yarns made by us was checked through the gravimetric method, according to SR EN ISO 2060. The tensional properties of the yarns were determined on electronic dynamometer Mezdan TensoLab 10 yielding the stress-strain diagrams, on which we have calculated the indices for assessing these proprieties.

-yarns tenacity ,determined by the formula:

$$\tau_F = \frac{P_r}{Tt} \quad \text{(cN/tex)} \qquad \textbf{(1)}$$

where: P_r is the breaking load force (cN);

- length breaking, determined using the equation:

$$Lr = \frac{P_r \cdot Nm}{1000} \quad \text{(km)} \qquad \textbf{(2)}$$

Structural characteristics and the appearance of yarns were determined using USTER electronocapacitive installation. Capacitive electronic control methodology together with the gravimetric control methodology form an evaluation system of the irregularity, so it has an indisputable technological utility. The complexity and diversity of expressions of the structural features and layout of the yarns were studied by determining the linear irregularity ($U_{\%}$), standard deviations ($CV_{\%}$) and imperfections in the form of Thin (S), Thick (G), Neps (N), relative to 1000 m yarn.

Control of regularity of linear density, on short parts of yarns and the control of frequent defects are performed according to standardized procedure for testing yarns [15]:

-capacitive transducer or the slot in the block called evenness tester of the electronocapacitive USTER is chosen depending on the values of yarns numbering, in this study carried out for Ttex 20 (Nm50/1) is the 7th slit of the capacitive measuring device;

-measuring domain 100%; Normal test mode; test speed of 25 m/min; analysis time 5 min/sample;

-yarn tested-length: 1000m (8 formats yarn x 1 sample/format);

-control indicator imperfections limits: -50% thinning (step 3); Thickening +50% (step 3); Neps +200% (step 3).

The recorded values will be compared with nomograms,from USTER statistics yet for assessing the quality of the Nm 50/1 yarn, by polyacrylonitrile cotton type fibers, made on the BD200 spinning rotor machine.

The properties of blended rotor spun yarn depend upon various factors such as fibre characteristics, machine variables and processing variables. Twist factor is one of the main processing variables in the rotor spinning system.

2.2. Results and discussions

For the Nm 50/1 yarns, made on BD200, rotor spinning machine, using all the cotton type polyacrylonitrile variants, we have determined the average values of the physical and mechanical properties and the structural and layout characteristics, shown the Table 2.

As seen in the graphic representation of Fig. 1, the length breaking of the yarns decreases with increasing of undulations frequency, except yarns spun from fibers which have an average number of undulations of 5.1 ond/cm, but the fibers tenacity is 26%, 10%, 15%, 33% higher than the tenacity of fibers from the other variants.

From the graph shown in Fig. 2, it is observed that the value of the coefficient of breaking strength variation increases with the increasing of frequency undulations. In textile manufacturing processes the most important factor that acts against the fibers is tensile fibers.

Under the action of traction forces, the undulations, specially at chemical fibers, support irreversible changes, which will reflect the default in appearance and properties of finished products. U_{ef} linear and CV_{ef} quadratic irregularity, presented in Fig. 3 and Fig. 4 register minimum values for the fineness of Nm 50/1 yarns, which are obtained from fibers with the lowest frequency of undulations.

If a fiber is required to a tensile strength less than a density decreases force, the undulations do not disappear, but they change all the features so that the changes can be appreciated simply through the degree of reduction of the frequency undulations.

Irregularity assessment of the linear irregularity or standard deviaton are done by specific indices of testing methods, of which the function is different from producer to consumer:

- the producer is more interested in measuring efficiency through the consistent pace and interpretations;
- it studies the compatibility consumer studies the compatibility between the yarns indices and indices used in the design and the impact of irregular shapes on the appearance of finished products.

Table 2: *Physico-mechanical properties and structural characteristics of the yarns Nm 50*

Characteristics			Options				
Undulations (ond./cm)			3.6	3.9	4.5	4.8	5.1
The density length		Ttex	20.6	20.1	20.4	19.9	20.0
		Nm	48.7	49.8	49.1	50.22	49.9
		CV_{Nm} (%)	4.5	3.2	2.3	5.5	4.4
Breakout force		Pr (cN)	224.4	211.2	200.9	171.4	222.2
		CV_{Pr} (%)	10.6	10.4	10.6	11.4	12.7
Elongation at break ε (%)			21.7	18.0	22.9	21.2	18.2
The breaking length Lr (km)			10.9	10.5	9.9	8.6	10.5
Torsion		T (ras/m)	942	952.9	938.7	990.6	953.6
		CV_T (%)	4.2	3.5	5.0	3.8	3.8
USTER values	Linear irregularity	U_{ef} (%)	14.5	14.9	16.3	15.1	15.8
	Quadratic irregularity	CV_{ef} (%)	16.7	16.9	17.9	17.2	17.4
	1000 m imperfections yarn	Thin, S	14	15	49	-	20
		Thick, G	58	14	90	-	65
		Neps, N	50	8	54	-	59

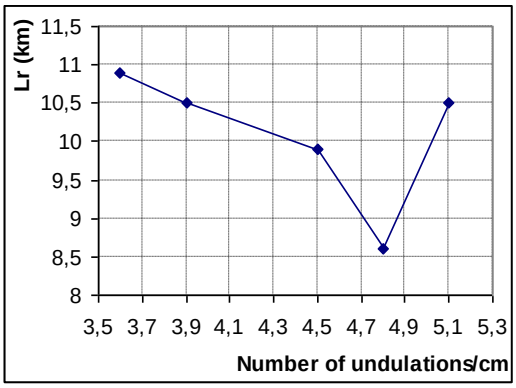


Fig. 1: *Frequency undulations influence on the length breakage of the Nm50/1 yarn*

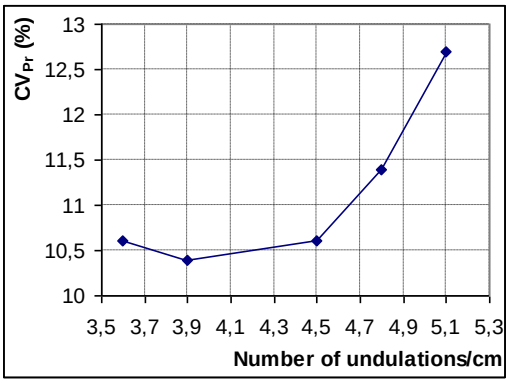


Fig. 2: *Frequency undulations influence on the coefficient of variation of the force breaking of the Nm50/1 yarn*

Yarn imperfections variation, obtained from Nm 50/1 fiber fineness, made by BD 200 rotor spinning machine, is shown in Fig. 5, 6 and 7, in which, it is found that in case of the variant where the number of undulations is 4.8 ond /cm, there were no thinning, thickening and neps on 1000 m yarn, tested on USTER electronocapacitive installation. As seen in Fig. 8 the coefficient of variation of the twist yarn is influenced by the frequency of undulations because it represents a measure of orientation of fibers in the simple yarn structure technologically.

The linear density irregularity on short piecewise is higher than that prescribed in regulations (CV=13%). By framing CV_{ef} values for these five variants studied, through USTER statistics, the obtained values fall on the global fabrication step of 75%, reflecting the realization of an inferior quality yarn, so the price-quality ratio is inappropriate.

Values obtained in the case of imperfections in the form of thinning and thickening are included on the global stage (50%), corresponding to an average level of quality and reflecting the appropriate processing phases that carry out the rolling operations, in the technological flow. Values

obtained when the neps fits into the global stage (75%) corresponding to an inferior quality level caused by quality of raw materials or processing machine phases on the trenching/card from the technological flow.

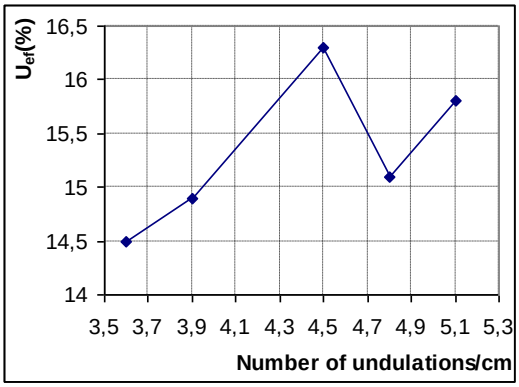


Fig. 3: *Influence of undulations frequency on linear irregularity of Nm50/1 yarn*

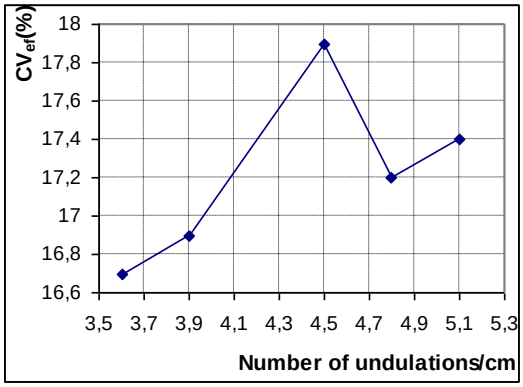


Fig. 4: *Influence of undulations frequency on quadratic irregularity of the Nm50/1 yarn*

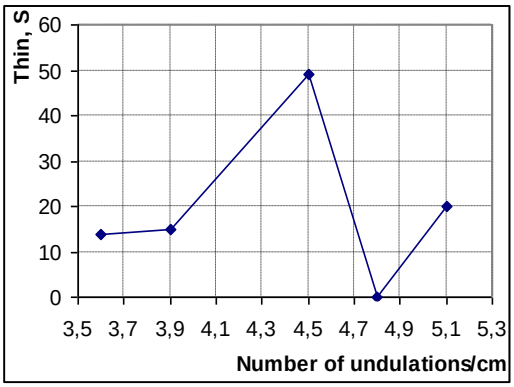


Fig.5: *Influence of undulations frequency on thinning of the Nm50/1 yarn*

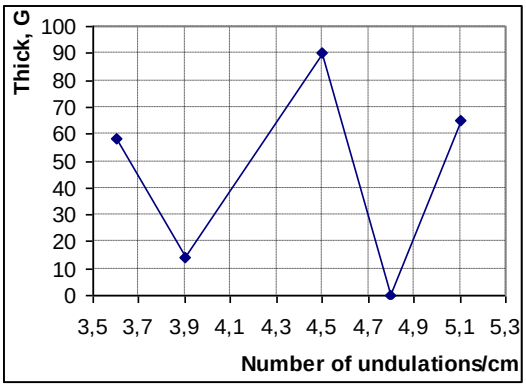


Fig. 6: *Influence of undulations frequency on thickening of the Nm50/1 yarn*

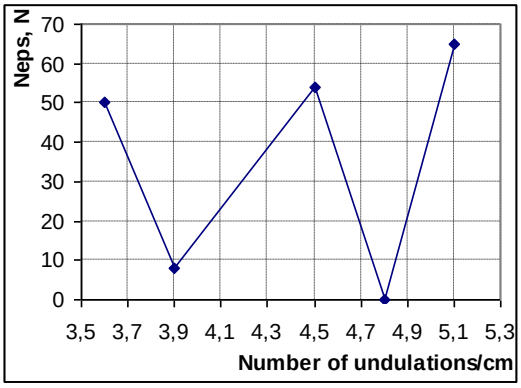


Fig. 7: *Influence of undulations frequency on neps of the Nm50/1 yarn*

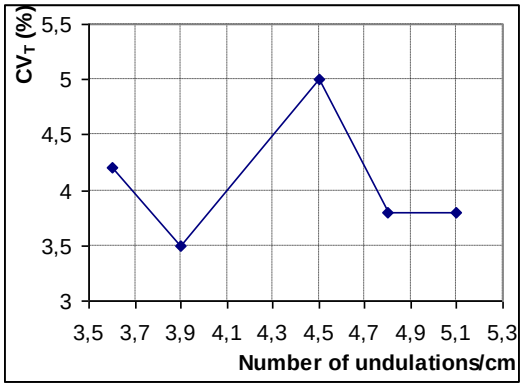


Fig. 8: *Influence of undulations frequency on the non-uniformity of twist for the Nm50/1 yarn*

2. CONCLUSIONS

Polyacrylonitrile fibers, cotton type, behave well in OE rotor spinning process.

The undulations frequency influences the tensile properties and structural and appearance characteristics of the yarns.

From these experiments it follows that the best results can be obtained when using fibers with low frequency undulations.

From the experimental obtained results can be estimated the optimal undulations frequency, to 3.6 ond /cm. From these fibers were made yarns, in three steps of twisting.

The increased twist coefficient has not ensured an increased resistance of the yarns, but influenced considerably the number of breaks.

REFERENCES

[1] G. Basal, W. Oxenham, "*Comparison of Properties and Structures and Compact and Conventional Spun Yarns*", Textile Research Journal, vol. 76, No. 7, pp. 567, 2006.

[2] M. Ben Hassen, M. Renner M., "*Experimental Study of High Drafting System in Cotton Spinning",* Textile Research Journal, vol. 73, No. 1, pp. 55, 2003.

[3] L. R. Manea,, R. Scarlet, A. L. Leon and I. Sandu, "*The Control of Process of Nanofibers Production Through Electrospinning",* Revista de Chimie, 52, nr. 5, pp. 640-644, 2015.

[4] E. Y. Mogahzy, "*Yarn Engineering*", Indian Journal of Fibre & Textile Research. vol. 31, pp. 150-159, 2006.

[5] H. J. Hyrenbach, "*The benefits of rotor yarn structure in terms of processing characteristics and application*", Melliand Textilberichte, No.4, pp. 42, 2002.

[6] K. Yong, I.Kim, "*Quantitative Grading of Spun Yarns for Appearance*" Journal of Textile Engineering. Vol. 52, No. 1, 2006

[7] L. Hristian, D.L. Bordeianu, P. Iurea, I. Sandu, K. Earar, *„Study of the Tensile Properties of Materials Destined to Manufacture Protective Clothing for Firemen",*Revista de Materiale Plastice, Vol. 51, no. 4, pp. 405-409, 2014.

[8] T. Jackowski, B. Chylewska, D. Cyniak, *„Cotton Yarns from Rotor Spinning Machines of 2nd and 3rd Generation"*", Fibres & Textiles, Vol. 8, No. 3, pp. 12-15, 2000.

[9] W. Polini, L. Sorrentino *Influence of winding speed and winding trajectory on tension in robotized filament winding of full section parts,* Composites Science and Technology, Vol. 65, Issue 10, pp. 1574-1581, 2005.

[10] D.L. Bordeianu, *"Tehnologii si utilaje in filaturi"* vol. 1, Ed. Ancarom, Iasi, 1997.

[11] L. R. Manea, E. Nechita , M. C. Danu and M. Agop "*On the Complex Systems Deformation Thermodynamics at Nanoscale",* J. Comput. Theor. Nanosci. 12, pp. 4693-4699, 2015.

[12] M.S. Neculăiasa, L. Hristian *Metrologie Textilă* Vol. I, pg. 326, Ed. Performantica, Iaşi, 2004, ISBN 973-7994-36-1

[13] K. Earar, M.N. Matei, A.V. Sandu, L. Hristian, C. Bejinariu, I.G. Sandu, "*The Role of Functional Polymers in the Optimisation of Acrylic Biomaterials used in Amovable Prosthetic Restoration I. The experimental protocol using the Iosipescu test"* Revista de Materiale Plastice, Nr. 1, 52, 2015, pp. 98-103

[14] D.L. Bordeianu, L. Hristian "*Aspects concerning the cleaning of simple and twist cotton-type yarns"* Buletinul Institutului Politehnic Iaşi, Tomul LIX (LXIII), Fasc 1-2, Secţiunea Textile Pielărie, pp. 9-16, 2013.

[15] http://www.uster.com/de/service/uster-statistics/

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ADOBE ILLUSTRATOR AND GIMP - AN APPROACH TO GARMENT DESIGN

INDRIE Liliana[1], BUZLE Marius[2]

[1] University of Oradea, Faculty of Energy engineering, Department Textiles, Leather and Industrial Management, 410058, Oradea, Romania, E-Mail: lindrie@uoradea.ro

[2] ROMANOEXPORT Industry SA, Alexandru Vlahuta Str., no. 70, Oradea, 410086, Romania, E-Mail: marius.technologist@gmail.com

Corresponding author: Indrie, Liliana, E-mail: liliindrie@uoradea.ro

Abstract: *Designing clothes has become easier with the use of clothing design softwares. One of the most popular and basic software made for garments design is Addobe Illustrator. It enables designers and small to medium businesses to create clothing designs with easy access to all assets, including images, colors, brushes, and type styles. While Illustrator has all the necessary elements and features that are ideal for creating designer clothing, GIMP provides basic set of tools for image editing. When used in combination with one another, these two programs provide just about all the tools an apparel designer needs to draw fashion design sketches, technical flat sketches, CAD presentations, graphic artworks, design embroideries etc. In this paper we show how to use the instruments of those two softwares in order to draw a woman jacket's garments components and to fill with texture the jacket created. By utilising Illustrator's Symbol we created libraries of jacket components (puller zipper, label), then the brushes to design the zipper detail. Finnaly, by a drag and drop we added the zipper, the zipper puller and the label. GIMP gave us access to precise fabric textures which make our output so realistic that you can almost touch the fabric.*

Key words: *drawing, garment components, jacket flat sketch, Illustrator's Symbol, Illustrator's Brushes, Patterns in GIMP*

1. INTRODUCTION

Adobe Illustrator and GIMP (GNU Image Manipulation Program) are two of the most powerful image-editing and illustration programs available. Due to their versatility and affordability, both of them are very popular in the fashion industry-graphic designers, illustrators, artists often use both the products to create professional-quality graphics.

Illustrator is a vector-based softwere ideal to create artwork which can be scaled and printed at any size and resolution while maintaining full detail and clarity. With proper tuition, it is possible to produce fashion flat sketches, CAD sketch presentations, fashion illustrations and other images that are commonly resized and rearranged in order to produce creative, accurate product designs.

GIMP is an image manipulation program which can be used to do design logos, crop and resize all kinds of photos, alter a photo's colors, combine and manipulate images, and even convert images between formats. GIMP comes with patterns to help to stitch together the interesting looking textures that are often seen in documents and on the Web.

When used in combination with one another, these two programs provide just about all the

tools an apparel designer needs to draw fashion design sketches, technical flat sketches, CAD presentations (rendered flat sketches), create and modify textile designs, repeats and colorways, design embroidery, graphic artwork etc.

2. DESIGNING THE JACKET MODEL

The present paper is a continuation of an idea which the authors presented extensively in an article previously published [1] and it shows how to use the instruments and working techniques for vector graphics from Adobe Illustrator program [2], [3] [4] in order to draw components of a woman's jacket and GIMP program [5], to fill with texture the jacket created in Illustrator in order to visualize how the coat will look in the completed garment.

The model designed is a jacket for women, for the cold season, the material used is 100% wool. The product is smart casual, arched on the waist, without a bend, it could be worn both as an office outfit as well as a casual one.

The closing system for this jacket is an offset one – the closure is not done in the center of the front part, but it's being shifted left. Both front parts of the product have leather inserts, the stich between these inserts and the front mark are unquilted. The zipper used is a metallic one of nickel finish type.

The jacket is collarless – it has no collar, the neck neckline is a little high just giving the impression of a very narrow collar.

The pockets are placed in the front stitch, each one with uncovered metal zipper, with the same finish as the one used for closing the front parts.

The sleeves are simple, the elbow stitch is unquilted and at its ending there is a zipper just like the one from the pockets.

The back of the product consists of four (4) parts – back (2) and gusset (2), the stitch between the back and the gusset mark being quilted.

The inside is lined without a pocket inside.

2.1. Creating the model in Adobe Illustrator

We started by making the model of the jacket using the instruments of Adobe Illustrator programme.

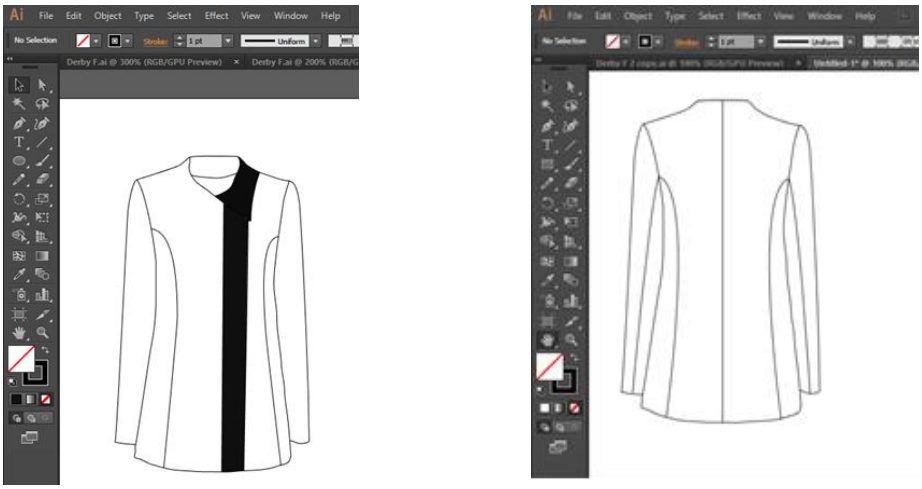


Fig.1: *The jacket model created in Adobe Illustrator*

Illustrator's Symbol offers the possibility to create libraries of garment components, (buttons, rivets, pockets etc.). We created the puller zipper and the label that can be called upon and added to any sketch using a drag and drop so these basic elements never have to be redrawn.[6]

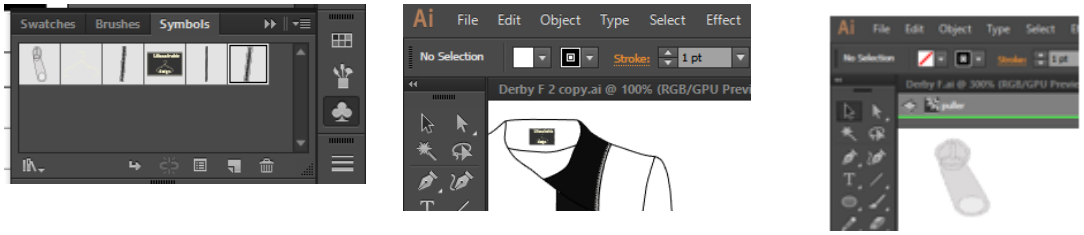


Fig. 2: *Library of zipper puller and label in Illustrator's Symbol*

Also, using brushes we created zipper detail.

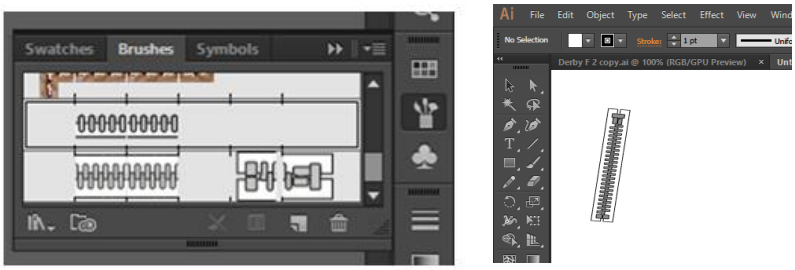


Fig. 3: *Use of Brushes to create clothing zipper*

Then we added the zipper, the zipper puller and the label on the drawn model by a drag and drop.

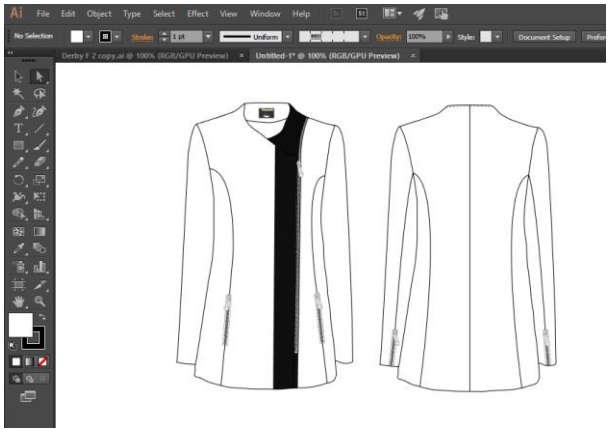


Fig. 4: *Jacket flat sketch*

2.2. Importing the model in Ghimp to fill it with Herringbone texture

In order to visualize how the coat will look in a completed garment, we have exported the model from Illustrator as a .jpg file to be colored in GIMP. To add a new pattern to Gimp's collection, we downloaded from the Internet a picture of the material out of which the jacket-fabric will be made Herringbone [6].We saved it in a format that GIMP can use (.png) and we used it to fill with texture the jacket created in Illustrator.

a) ***b)***

Fig. 5: *The Woman jacket image*
a) Done in Ghimp; b) Manufactured

3. CONCLUSIONS

We wish to conclude by affirming that the use of llustrator and GIMP softwares makes the job a lot faster. The Illustrator is great for creating reusable components application; it allows the use of symbols and brush stroke libraries to create and store different silhouettes, basic garment shapes, useful accessories, stitches and trims. On the other hand, there are countless ways of creating interesting patterns in GIMP, using the wide variety of fabrics available on the Internet or by taking a picture of the material to be used for aking the garment.

REFERENCES

[1]. L. Indrie, L., M. Buzle, M. Suteu, M., Prichici, "*Optimization of garment design using specialised software, Economics Management Information Technology (EMIT)",* Vol IV, nr. 2, 2015, ISSN 2217-9011, e-ISSN 2334-653, Serbia, pp. 2-10

[2]. J. Hughes. (2013, August 19). Illustrator – Best Fit CAD for the Design Community. [Online]. Available: http://www.apparelthing.com/adobe-illustrator-best-fit-cad-for-the-design-community/

[3]. Adobe Creative Team, "Adobe Illustrator CS2", Editura All, Bucuresti, 2008

[4]. C. Radulian, "Adobe Illustrator 9", Editura Teora, Bucuresti, 2002

[5]. G.C. Manea, "Image Editing - GIMP 2.8", Colectia: ECDL - Permisul European de Conducere a Computerului, Editura Euroaptitudini, Bucuresti, 2013

[6].v*** Herringbone fabric, [Online]. Available: https://www.google.ro/search?q=herringbone+fabric+swatches&biw=1366&bih=667&tbm=isch&tbo=u&source=univ&sa=X&ved=0ahUKEwibmJCQt5XMAhVpYJoKHf8xCdUQsAQIHA , Accessed 10.04.2016

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FIBONACCI TILINGS IN FASHION DESIGN

KAZLACHEVA Zlatina[1]

[1]Trakia University of Stara Zagora, Faculty of Technics and Technologies of Yambol
Graf Ignatiev 38, 8600, Yambol, Bulgaria, E-Mail: zlatinka.kazlacheva@trakia-uni.bg

Abstract: *The Fibonacci sequence is a symbol of beauty and harmony and by this reason geometrical objects in its proportions are used in the design. There are some versions of Fibonacci series tiling, which are constructed with equilateral geometrical figures – squares or triangles, as the sides' lengths are equal to the numbers of the Fibonacci series, or the lengths of the sides of the squares or equilateral triangles are each to other in proportions, which are equal to Fibonacci sequence. The paper presents design of ladies' dresses with the both ways of constructing of Fibonacci tilings with squares, the variants in a spiral pattern and the variant with squares which are put side by side, and the version of Fibonacci tiling with triangles in form of double spiral named Fibonacci rose. Nine models of ladies' dresses are shown. As a result of the use of Fibonacci tilings for designing of aesthetic, beautiful and harmonic clothing, it can be concluded that in fashion design Fibonacci squares and Fibonacci rose can be used in different ways of color combinations, proportions toward the clothing sizes, and as a frame of creations of design elements. The different position, proportions and color combinations of use of Fibonacci squares and Fibonacci rose in fashion design according to the body type and size can cover some bodily defects and enhance the beautiful forms.*

Key words: *Fibonacci squares, Fibonacci rose, fashion design, lady's dress*.

1. INTRODUCTION

The Fibonacci sequence is a symbol of beauty and harmony and by this reason geometrical objects in its proportions are used in the design. [1]

The Fibonacci numbers are the sequence of numbers $\{F_n\}_{n=1}^{\infty}$ defined by the linear recurrence equation

$$Fn = Fn\text{-}1 + Fn\text{-}2 \quad \textbf{(1)}$$

with F1 = F2 = 1. As a result of the definition (1), it is conventional to define F0 = 0. The Fibonacci numbers for n = 1, 2, ... are 1, 1, 2, 3, 5, 8, 13, 21, ... [2]

There are some versions of Fibonacci series tiling, which are constructed with equilateral geometrical figures – squares or triangles, as the sides' lengths are equal to the numbers of the Fibonacci series, or the lengths of the sides of the squares or equilateral triangles are each to other in proportions, which are equal to Fibonacci sequence.

With the Fibonacci Series, there are two ways of constructing the series with interlocking squares. In the version, presented in Figure 1, we constantly circle the block to find the next addition site, and end up with a spiral pattern. In the version, which is shown in Figure 2, we put two squares side by side, add another square to the longest side, and repeat, darting from left to right as we decide where to put the next square. [3]

The version which uses equilateral triangles to form a double-spiral is shown in Figure 3. This tiling version is named Fibonacci rose. [3]

The paper presents fashion design of ladies' dresses with the both ways of constructing of Fibonacci series tilings with squares and the version of Fibonacci tiling with triangles named Fibonacci rose.

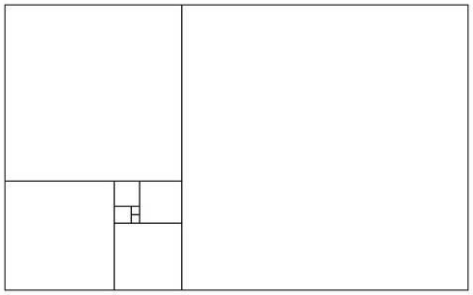


***Fig. 1**: Fibonacci series tiling with squares forming a spiral pattern*

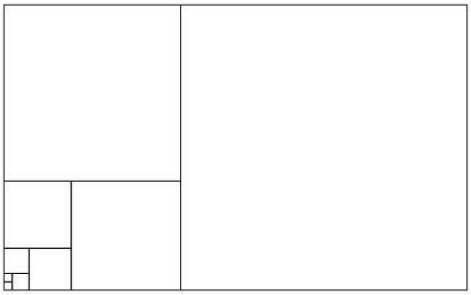


***Fig. 2**: Fibonacci series tiling with squares which are put side by side*

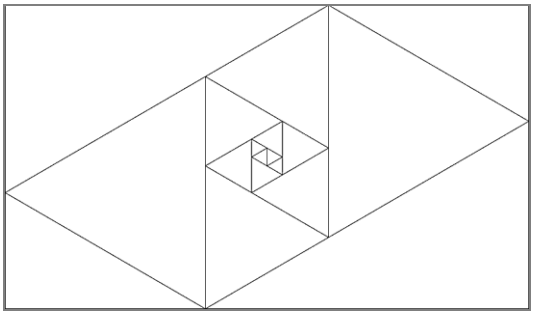


***Fig. 3**: Fibonacci tiling with equilateral triangles Fibonacci rose*

2. FASHIN DESIGN WITH FIBONACCI SQUARES AND ROSE

Figure 4 presents a lady's dress with Fibonacci series tiling with squares in a spiral pattern, which is shown in figure 1. The first square of the tiling is situated in center of the waist area. Analysis of the color decisions shows that the best color combination is that with four colors in fourth directions. [4] Every fourth square is in one and the same color. The 1st, 5th, 9th, … squares are in the first color, the 2nd, 6th, 10th, … squares are in the second color, the 3rd, 7th, 11th, … squares are in the third color, and the 4th, 8th, 12th, … squares are in in the fourth color. In this way the squares, which form a set in one and the same direction, are colored in one and the same color.

Figure 5 shows a lady's dress with Fibonacci series tilling with squares which are put side by side, presented in figure 2. In the dresses the tiling is situated in the upper part as the first and the second squares are in vertical direction by the shoulder. In the model, Fibonacci series tiling is in bi-colored combinations in which two squares, colored in one and the same color are covered by two squares, which are in another color [4] as the 1st, 4th, 5th, 8th, 9th, … squares are colored in one and the same color, and 2nd, 3rd, 6th, 7th, 10th, 11th, … squares are colored in another color. [4]

Figure 6 presents a lady's dress with "quad-spiral" version of Fibonacci tiled squares, which are put side by side. [3] The center of the quad-spiral is situated in the center of the waist. In the fourth Fibonacci tilings of the spiral are used another bi-color combination in which the odd numbers squares are in one color and the even numbers squares are in another color. [4]

The Fibonacci tilings with squares can be used as frames of entered geometric elements and the models of ladies' dresses in Figures 7, 8, and 9 are examples of the use of the entered element in the spiral Fibonacci square tiling in design.

The Fibonacci tiling in Figure 1, in which the squares form a spiral pattern, is the base of the creation of Fibonacci spiral. [5] Figure 7 presents a lady's dress with Fibonacci spiral in which many spirals design shapes similar to butterflies.

Figure 8 shows a lady's dress with some spiral pattern Fibonacci squares tilings with entered diagonals in every square, which form spiral shapes too.

The designs of both models in Figures 7 and 8 use both the spiral Fibonacci squares tiling and the entered elements – Fibonacci spiral in Figure 7 and spiral shape, formed by entered diagonals in Figure 8. In the both models the entered elements ant the frames of Fibonacci tilings are arranged in vertical directions in the whole lengths of the dresses. The entered elements divided Fibonacci square tiling in two areas which are colored in different colors.

The entered geometric elements can be used in the fashion design without the frame of the tiling and Figure 9 presents a model of a lady's dress with a spiral from circles which are a result of entering in a spiral Fibonacci square tiling. The spiral starts in the center of the waist area and the model of the dress use bi-colored model – one color for the circles and another for the background.

Figure 10 presents a model of a lady's dress with Fibonacci rose. The start of Fibonacci rose is situated in the center of the waist. The model is in bi-colored model as the triangles in the both directions are colored in different colors. [6] Another way of coloring is when the both spirals shapes, formed by Fibonacci rose triangles are colored in different colors. [3]

Like Fibonacci square tiling Fibonacci rose can be used as frame of entered geometric elements and the models of ladies' dresses in Figures 11 and 12 are examples of the use of the entered element it the triangles. [6]

A double spiral formed with curved lines can be created around the double spiral shaped by triangles in Fibonacci rose. Figure 11 shows a model of lady's dress with double curved spiral in the frame of Fibonacci rose. The center of the rose is located in the center of the waist and the both areas between the both curved spirals are colored in two different colors. [6]

Circles can be entered in the triangles of Fibonacci rose and in result the circles form a double spiral. Figure 12 presents the use of double spiral of circles without the frame of Fibonacci rose in the design of a lady's dress. The start of the spiral is situated in the center of the waist area. The both circles' spirals are colored in two different colors and the background in third one.

3. CONCLUSIONS

As a result of the use of Fibonacci tilings for designing of aesthetic, beautiful and harmonic clothing, it can be concluded that in fashion design Fibonacci squares and Fibonacci rose can be used in different ways of color combinations, proportions toward the clothing sizes, and as a frame of creations of design elements.

Fibonacci tilings can be used in fashion design as application, fabrics' design, pieces of the main clothing parts, etc.

The different position, proportions and color combinations of use of Fibonacci squares and Fibonacci rose in fashion design according to the body type and size can cover some bodily defects and enhance the beautiful forms.

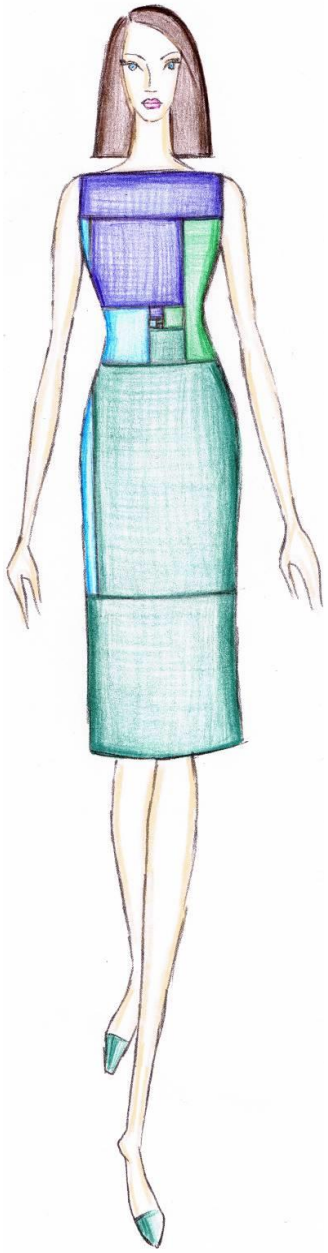


***Fig. 4**: Design of a lady's dress with Fibonacci series tiling with squares forming a spiral pattern*

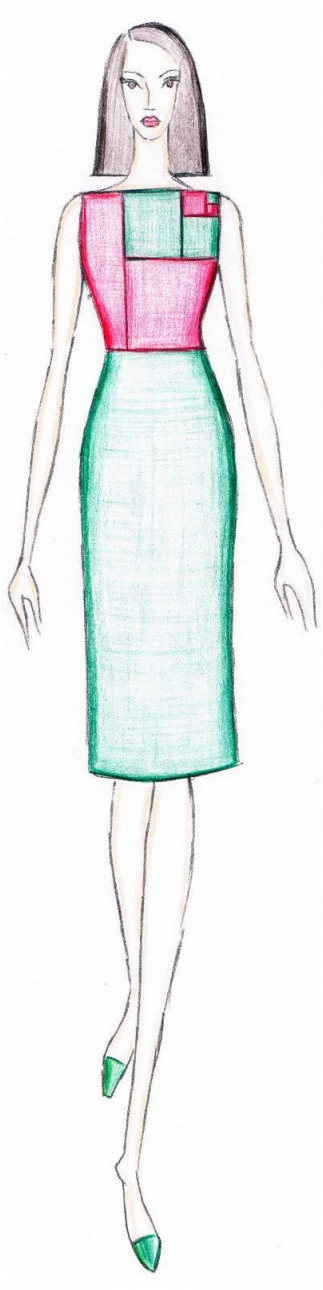


***Fig. 5**: Design of a lady's dress with Fibonacci series tiling with squares which are put side by side*

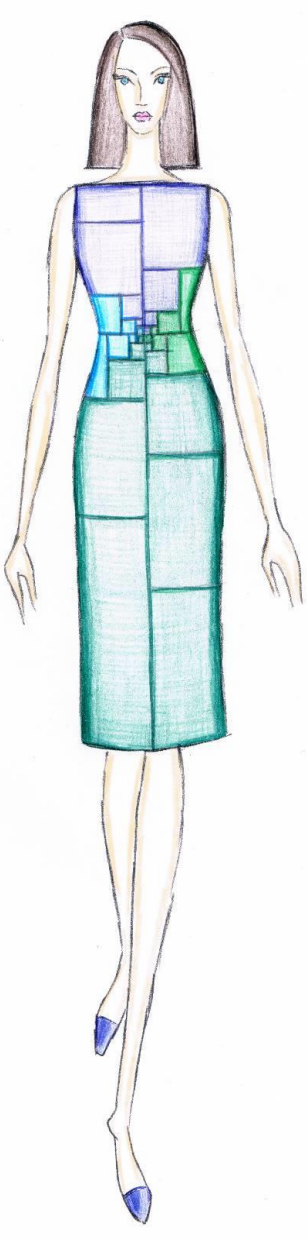


***Fig. 6**: Design of lady's dress with a quad-spiral version of Fibonacci tiled squares which are put side by side*

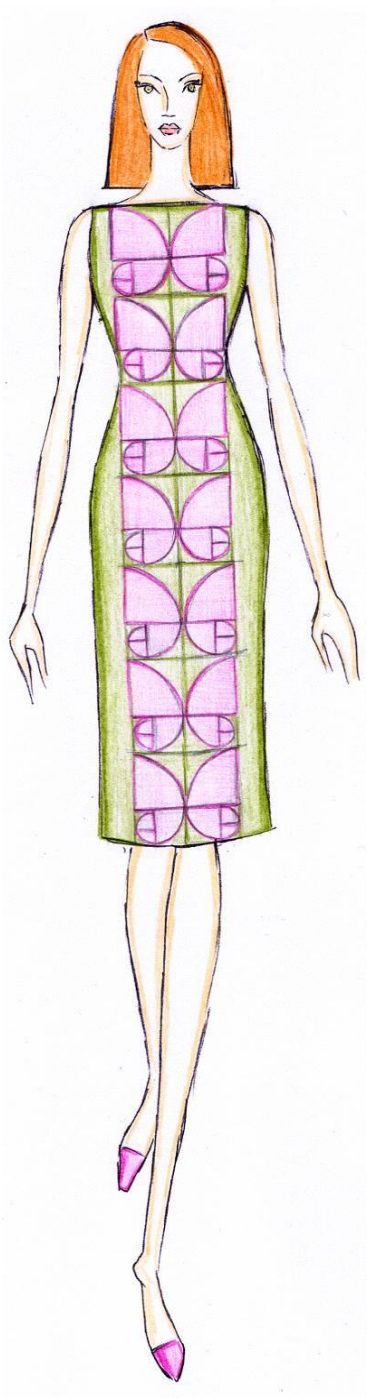


***Fig. 7**: Design of a lady's dress with Fibonacci spiral in the frame of Fibonacci series tiling with squares forming a spiral pattern*

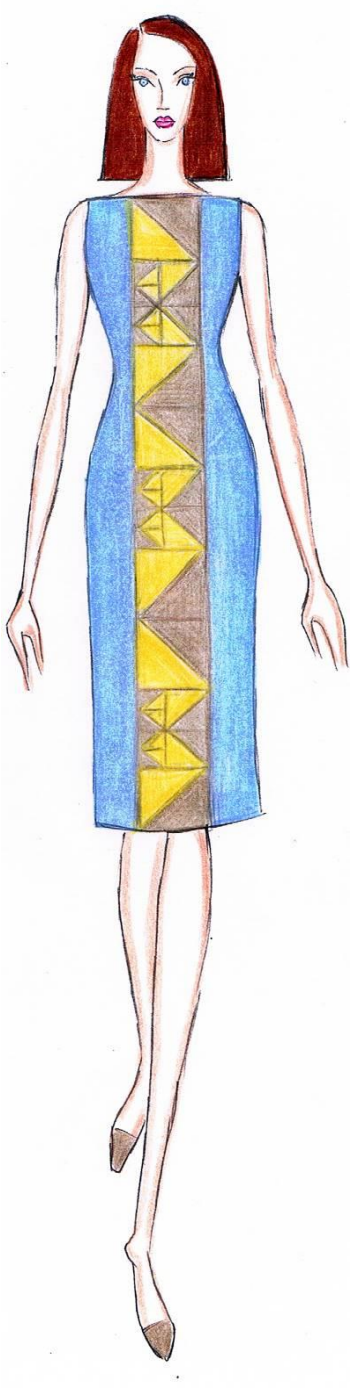


***Fig. 8**: Design of a lady's dress with a spiral shape from diagonals entered in the frame of Fibonacci series tiling with squares forming a spiral pattern*

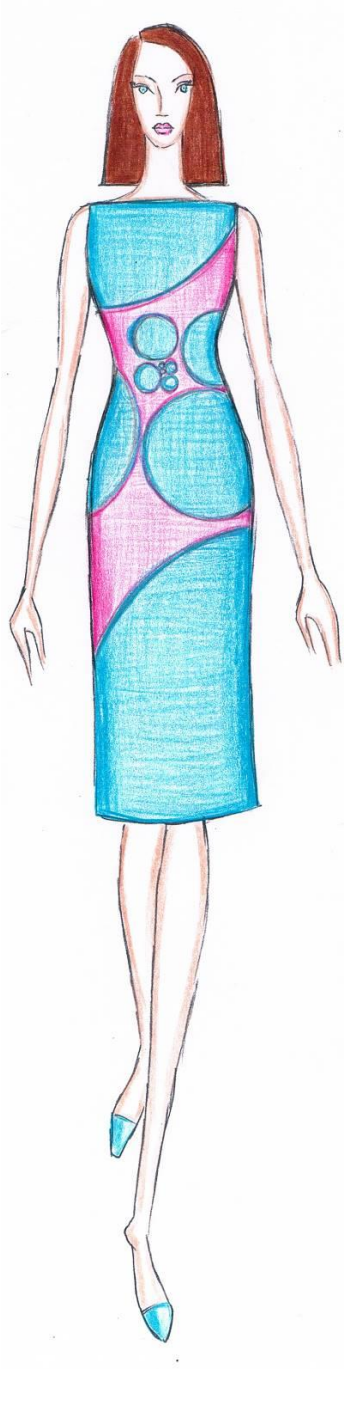


***Fig. 9**: Design of a lady's dress with a spiral of circle, result of entering in the frame of Fibonacci series tiling with squares forming a spiral pattern*

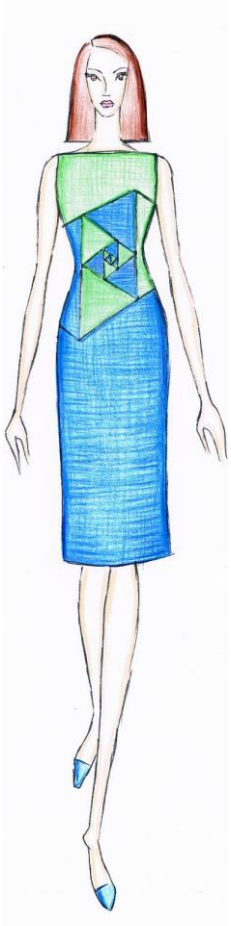


***Fig. 10**: Design of a lady's dress with Fibonacci rose*

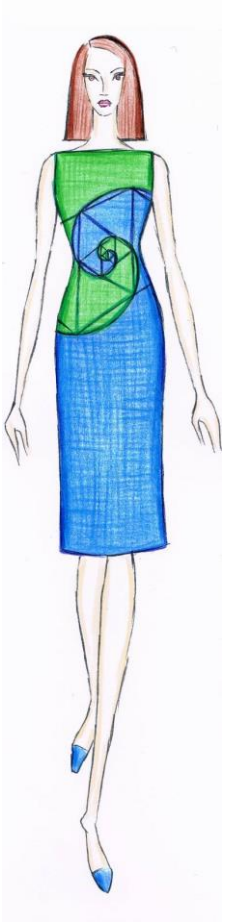


***Fig. 11**: Design of a lady's dress with Fibonacci rose and a double curved spiral around triangles of Fibonacci rose*

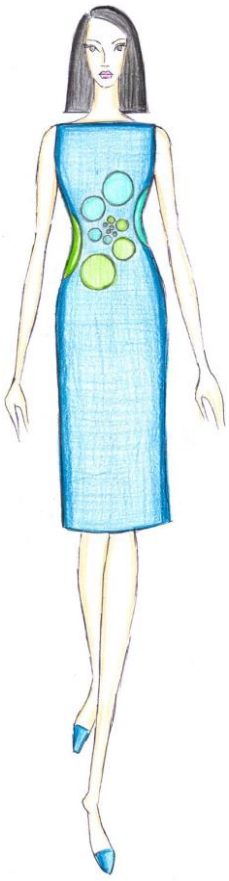


***Fig. 12**: Design of a lady's dress with double circles' spiral, result of entering in the frame of Fibonacci rose*

REFERENCES

[1] Z. Kazlacheva. "*Fibonacci Geometry is Fashionable*". Journal of Textile Engineering and Science, vol. 4, no. 4, doi: 10.4172/2165-8064.1000e122, 2014.

[2] E. W. Weisstein, P. Chandra. "*Fibonacci Number*". MathWorld – A Wolfram Web Resource. [Online]. Available: http://mathworld.wolfram.com/FibonacciNumber.html

[3] E. Baird. (2009). "*Fibonacci Series Tiling with Triangles*". ErkDemon. [Online]. Available: http://erkdemon.blogspot.com/2009/06/fibonacci-series-tiling-with-triangles.html

[4] Z. Kazlacheva. "*Fibonacci Squares in Fashion Design*", ARTTE Applied Researches in Technics, Technologies and Technologies, vol. 2, no. 2, pp. 91-98, 2014.

[5] D. Reich. "*The Fibonacci Sequence, Spirals and the Golden Mean*". Mathematics, Temple University. [Online]. Available: https://math.temple.edu/~reich/Fib/fibo.html

[6] Z. Kazlacheva. "*Fibonacci Rose in Fashion Design*", ARTTE Applied Researches in Technics, Technologies and Technologies, vol. 2, no. 3, pp. 224-230, 2014.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ASSESSMENT CRITERIA OF FUNCTIONALITY GEOTEXTILES USED IN ROAD CONSTRUCTION

LUCA Cristinel[1], CIOARĂ Ioan[2]

[1] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Textiles & Leather Engineering and Industrial Management, Technology and Textile Design Department, Dimitrie Mangeron Blvd., No. 28, 700305, Iaşi, Romania,
E-Mail: luca_cristinel@yahoo.com

[2] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Textiles & Leather Engineering and Industrial Management, Technology and Textile Design Department, Dimitrie Mangeron Blvd., No. 28, 700050, Iaşi, Romania,
E-Mail: icioara2012@yahoo.com

Corresponding author: Luca, Cristinel, E-mail: luca_cristinel@yahoo.com

Abstract: *This work was performed in order to assess the functionality of geotextiles used in road construction. To increase the quality of road works requires the use of geotextiles in their structure. Depending on the role and the benefits they offer, geotextiles have a number of physical properties, hydraulic, endurance and optimal characteristics regarding their degradation. Geotextile properties were identified and divided according to their characteristics area. Thus, there were obtained textile properties oriented towards geotextiles and properties geared to the application field respectively reinforcement, drainage, and filtration. Value engineering works at the level of constructive product conception and production. The instrumentation is done by functional analysis, value functions and design or redesign of geotextile based on the necessary functions. Systematic research method allowed geotextiles dimensioning functions in order to obtain products in terms of quality, reliability and maximum operational performance. Functions obtained from the analysis are appropriate for a single property. After obtaining the set of decisions was possible functions geotextiles hierarchy after the significance of their use. Establishing the importance of the coefficients or characteristics hierarchy after their weight requires the comparison of the features between them and grading them in proportion to their degree of importance. The ranking of these functions is beneficial when designing or redesigning geotextiles.*

Key words: *geotextile, value, hierarchy, functions, road cosnstruction*

1. INTRODUCTION

Geotextiles are technical textiles used in road construction with the aim of reinforcement and stabilize the embankment road, groundwater drainage, separation and control erosion, [1]. Many factors such as road widening, climatic factors, foundation conditions, traffic activity, relocation of utilities led to the search for solutions, one of which is the use of geotextiles.

The use of geotextiles brings a substantial contribution to the mechanical characteristics or increases the stability of the road. Geotextiles, through their characteristics and structure, put into the ground, associated with the earth or with another type of material, constitutes filter elements, draining, separation, reinforcement in works for protection or improvement of foundation soil characteristics.

2. GENERAL INFORMATION

Geotextiles identification derives from the need to know the type of geotextile to be used depending on the physical characteristics, hydraulic, endurance, characteristics relating to the degradation of geotextiles and as the role geotextile fulfils in the constructive assembly, [2]. Also for the optimal choice of geotextile you have to know what function or accumulation of functions, is requested of that material:

- Reinforcement - use of tensile strength of geotextiles to improve the mechanical characteristics of earth or of other construction materials;
- Filtering - retention of land and other particles subjected to hydrodynamic forces that occur as a result of fluid flow;
- Drainage - collection and transport of precipitation groundwater in the plan of geotextiles;
- Separation - prevents interference between adjacent lands and filling materials;
- Protection - prevents the local damage or the damage of a geotechnical system with the help of a geotextile, [3].

There were identified a number of important properties that could be used for objective assessment of geotextile. These properties are arranged according to area traits analyzed in two categories: properties oriented to the type of geotextile (which are important for the quality of material used in road construction) and properties geared to the application of geotextile (which highlights the ability of a geotextile to meet some requirements imposed). The main properties of geotextiles grouped into two categories can be found in Table 1.

Choosing the type of geotextile should be carried out after a criteria of functionality to ensure primarily the properties required in use.

Table 1: *Specific properties of geotextiles*

No.	Properties oriented geotextiles	Properties oriented field of application
1.	Tensile strength	Reinforcement
2.	Breaking elongation	Reinforcement
3.	Mass per unit area	Filtering and separation
4.	Material thickness	Reinforcement, filtering and separation
5.	Stamping resistance	Reinforcement, filtering and separation
6.	Tear resistance	Reinforcement, filtering and separation
7.	Permeability	Filtering
8.	Transmissivity	Drainage
9.	Creep resistance	Reinforcement
10.	Biological damage resistance	Reinforcement, filtering, separation and drainage
11.	Environmental factors resistance	Reinforcement, filtering, separation and drainage
12.	Endurance resistance	Reinforcement
13.	Abrasion resistance	Reinforcement
14.	Porosity	Filtering

Value engineering is a systematic method of research-design according to which the functions of the geotextile material, needs to be dimensioned and made using minimal costs in terms of quality, reliability and maximum performance. Value analysis is based on the examination of the functional parameters of the product realized or his value in use (usefulness) setting each function which leads to the desired parameters using minimal costs. Value analysis acts to maximize operational parameters and minimize costs, both in the design phase of product design and that of production. The way of investigating the techniques of value engineering involves the following steps:

- Functional Analysis - it is a powerful technique of value analysis which shows the specific relationships between all the functions of the material, tests the validity of the studied functions, helps to identify the mission of the functions, widens the knowledge of all project team members of value analysis. Functional analysis is completed with drawing up the list of functions of the analyzed product;
- Functions Value - answer the questions: "How important is the function and how well meets user requirements?" and "What performance does the product meets ". Good performance requires the product to have a predetermined level of quality and reliability.
- Product design and redesign based on the required functions.

The functions of a product are elementary use values, components of global value in use of the product, homogeneous content and having measurable qualities from technical point of view [4], [5]. Drawing up the classification functions of geotextile is based on its definition of the conditions in which they work. Nomenclature of functions represents the totality of the studied functions of the object to meet the requirements.

As noted in Table 2 are found the functions identified as necessary for the geotextile, technical elements of assessment of the functions and their typology according to the standardized classification criteria.

Table2: *Geotextile functions*

Symbol	Function name	Technical dimension	Tipfunction type
F1	Be resistant to breaking	Tensile strength, [6]	Primary, objective, necessary, general
F2	To have breaking elongation	Breaking elongation, [6]	Primary, objective, necessary, general
F3	To have a constant mass	Mass per unit area, [7]	Primary, objective, necessary, general
F4	To have an uniform thickness	Material thickness, [8]	Primary, objective, necessary, general
F5	Be resistant at impact with rigid materials	Stamping resistance (SR EN ISO12236:2007)	Primary, objective, necessary, general
F6	Be resistant to multi-axial stretch	Tear resistance, [9]	Primary, objective, necessary, general
F7	To be permeable to water vapor	Permeability (SR EN ISO 11058:2010)	Primary, objective, necessary, general
F8	To be able to transport and drain liquids	Transmissivity (SR EN ISO12958:2010)	Primary, objective, necessary, general
F9	Be resistant to continue stress	Creep resistance, [10]	Primary, objective, necessary, general
F10	Show resistance to attack of bacteria and fungus	Biological damage resistance, [11]	Secondary, objective, necessary, specific to geotextile
F11	Show resistance to UV and environmental factors	Environmental factors resistance, [12]	Secondary, objective, necessary, specific to geotextile
F12	Be resistant to bending-stress durability without failure	Endurance resistance	Secondary, objective, necessary, specific to geotextile
F13	No mass loss during contact with abrasive element	Abrasion resistance, [13]	Secondary, objective, necessary, specific to geotextile
F14	To separate the phases of a heterogeneous mixture	Porosity (SR EN ISO 12956:2010)	Secondary, objective, necessary, specific to geotextile

Use values of the functions are unequal, so each of them takes part differently in the completion of the value in use of geotextile, fact which enables us to rank them in accordance with

the importance of the need met. For hierarchy the functions is used the technique of imposed decisions. This involves comparing the functions two by two and application of scores by the form (1-0), (0.5-0.5) or (0-1). The score 0 represents a low importance level, 0.5 – medium level of importance and 1 - the maximum level of importance [4], [5].

The total number of decisions resulted from comparing the n functions of the geotextiles is calculated with the equation:

$$D = C_n^2 = \frac{n(n-1)}{2} \quad \textbf{(1)}$$

Establishing the importance of the coefficients or characteristics hierarchy after their weight requires the comparison of the characteristics between them and grading them in proportion to their degree of importance. The coefficient of importance for each function is calculated with the equation (2), in which N represents the sum of the score awarded and D represents the total number of decisions:

$$I = \frac{N}{D} \quad \textbf{(2)}$$

3. MATERIALS AND METHODS

The 14 functions of the geotextiles represented in table 2 are divided in 9 primary functions and 5 secondary functions. According to the equation (1) we get the following:

- Decisions for primary functions

$$D_p = C_9^2 = \frac{9 \cdot (9-1)}{2} = 36 decisions \quad \textbf{(3)}$$

- Decisions for secondary functions:

$$D_s = C_5^2 = \frac{5 \cdot (5-1)}{2} = 10 decisions \quad \textbf{(4)}$$

In tables 3 and 4 are presented the comparative analysis of primary and secondary functions. The values of the coefficients of importance are given by the ranking of the primary and secondary functions. When designing or redesigning the geotextiles, will be taken into account this hierarchy of functions.

Table 3: *Comparative analysis of primary functions*

Function	Decisions																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
F1	1.0	0.5	1.0	1.0	0.5	1.0	1.0	0.5													
F2	0.0								1.0	0.5	1.0	0.5	1.0	1.0	0.5						
F3		0.5							0.0							1.0	1.0	0.5	1.0	1.0	0.5
F4			0.0							0.5						0.0					
F5				0.0							0.0						0.0				
F6					0.5							0.5						0.5			
F7						0.0							0.0						0.0		
F8							0.0							0.0						0.0	
F9								0.5							0.5						0.5

Table 3 (continuation): *Comparative analysis of primary functions*

Functions	Decisions															Sum of the score awarded	Functions coefficient of importance
	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	N	I
F1																6.5	0.81
F2																5.5	0.69
F3																5.5	0.69
F4	1.0	0.5	1.0	1.0	1.0											5.0	0.63
F5	0.0					1.0	0.5	0.0	0.0							1.5	0.19
F6		0.5				0.0				1.0	1.0	0.5				4.5	0.56
F7			0.0				0.5			0.0			1.0	1.0		2.5	0.31
F8				0.0				1.0			0.0		0.0		1.0	2.0	0.25
F9					0.0				1.0			0.5		0.0	0.0	3.0	0.38

Table 4*. Comparative analysis of secondary functions*

Function	Decisions										Sum of the score awarded	Functions coefficient of importance
	1	2	3	4	5	6	7	8	9	10	N	I
F10	1.0	0.5	0.5	0.5							2.5	0.63
F11	0.0				1.0	1.0	1.0				3.0	0.75
F12		0.5			0.0			1.0	1.0		2.5	0.63
F13			0.5			0.0		0.0		1.0	1.5	0.38
F14				0.5			0.0		0.0	0.0	0.5	0.13

Following this analysis we see that the primary functions that must meet the geotextile which will be installed in road geometry are F1 (0.81), F2 (0.69) and F3 (0.69), meaning it must have a very good tensile strength and breaking elongation and have no mass loss during use. As a medium level of importance were obtained functions F4 (0.63) and F6 (0.56). These two functions indicate that a geotextile must maintain its thickness during use and be resistant to tearing. The functions F5 (0.19), F7 (0.31), F8 (0.25) and F9 (0.38), meaning resistance to stamping, permeability, transmissivity and creep resistance does not affect the structure of the road, having a low level of importance.

With regard to secondary functions, the highest level of importance holds F11 function (0.75) and assumes that the geotextile has a very good environmental factors resistance. F10 (0.63) and F12 (0.63) functions are of medium importance level. Functions F13 (0.38) and F14 (0.13) indicates that the porosity and abrasion resistance of the geotextile does not constitute a major importance in the structure of the road.

4. CONCLUSIONS

The use of geotextiles in road construction is a viable solution to increase of their quality.

The properties of geotextiles must relate to the field of application of geotextile in road construction. Designing and redesigning geotextile requires in-depth knowledge of the conditions in which it is used so as to effectively define functions that the geotextile must meet the operational phase of the product.

Assessment of geotextiles functionality requires the application of specific value engineering techniques that allow initially objective hierarchy of its properties and then redesigning by properties priority.

REFERENCES

[1] M. Zamfir, *"Textile neţesute"*, Ed. Performantica, Iaşi, 2008.

[2] R. S. Kumar., "*Textiles for industrial applications"*, Ed. CRC Press, Great Britain, 2014 pp. 217-242

[3] L. Kellner, A. Gazdaru, V. Feodorov,*"Geosinteticele in construcţii"*, Vol 1, Ed. Inedit, Bucureşti, 1994, pp. 51-87

[4] Gh.Condurache, R.M. Ciobanu, M. Niculae, *"Analiza si ingineria valorii*", Ed. Performantica, Iaşi 2004.

[5] I. Cioară, L. Cioară, *"Criterii de apreciere a functionalitatii mediilor filtrante obtinute prin tesere",*Industria textilă nr.1,Bucureşti, 2009

[6] EN ISO 10319: 2015, *"Geosynthetics – Wide – width tensile test"*

[7] SR EN ISO 29073-1:1998, "*Materiale textile. Metode de încercare pentru neţesute. Partea 1: Determinarea masei pe unitatea de suprafaţă*"

[8] SR EN ISO 9073-2: 2000, "*Materiale textile. Metode de încercare pentru neţesute. Partea 3: Determinarea grosimii*"

[9] SR EN ISO 9073-4: 2004, "*Materiale textile. Metode de încercare pentru neţesute. Partea 4: Determinarea rezistenţei la sfâşiere*"

[10] SR EN ISO 13431: 2004, "*Geotextile şi produse înrudite. Determinarea comportării la fluaj din tracţiune şi rupere din fluaj*"

[11] SR EN ISO 12225: 2001, "*Geotextile şi produse înrudite. Determinarea rezistenţei microbiologice prin incercarea de ingropare in sol*"

[12] SR EN ISO 12224: 2001, "*Geotextile şi produse înrudite. Determinarea rezistenţei la intemperii* "

[13] SR EN ISO 13427: 2004, "*Geotextile şi produse înrudite. Simularea deteriorarii prin abraziune (încercare cu bloc glisant)*"

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY OF THE INFLUENCE OF SYNTHETIC COMPONENT IN MIXTURES WITH WOOL ON THE PHYSICAL-MECHANICAL PROPRIETIES

OANA Dorina[1], OANA Ioan–Pavel[1]

[1,]University of Oradea, Department of Engineering and Industrial Management in Textiles and Leatherworks, Faculty of Energy engineering and Industrial Management, B.St.Delavrancea str. No. 4, 410058, Oradea, Bihor, Romania, E-mail:textile@uoradea.ro

Corresponding author: Oana. Ioan-Pavel, E-mail: oanaioanpavel@yahoo.com

Abstract: *The main physical-mechanical properties of the yarns are: linear density (Tex), tensile strength, tenacity, elongation at break, twisting and mechanical work of fracture, there is a strong correlation between them. The tensile properties are the basic characteristics of yarns, influencing how they behave in the technological processes of mechanical processing (preparation for weaving or knitting, proper weaving or knitting) determining the technological parameters of equipment adjusting during the technological processes and also their productivity. The tensile properties of yarns constitute qualitative characteristics, because their value depends on the quality of the yarn and also on the finite product obtained from processing yarns.*
In this paper was done a comparative study of the tensile properties of two batches of mixed woolen yarns (wool with polyester and wool with polyamide), the mixture being in the same proportions, but the yarns have different fineness and have very close twist values, both batches of yarns were designed for knitted products. Batch I consists of 70% wool yarns and 30% polyester, linear density Ttex = 55.56 tex and twist of 350 twists/meter. Batch II consists of 70% wool yarns and 30% polyamide, a linear density of Ttex = 71.34 tex and twist of 330 twists/meter (so a thicker yarn than the one from batch I).
Following the analysis between the two batches is clear that the woolen yarns in batch II have much higher tensile properties.

Key words: *Fibers, fineness, tensile proprieties, tensile strength, quality, uniformity, wool*

1. INTRODUCTION

In this paper was done a comparative study of the tensile properties of two batches of mixed woolen yarns (wool with polyester and wool with polyamide), the mixture being in the same proportions, but the yarns have different fineness and have very close twist values, both batches of yarns were designed for knitted products. Batch I consists of 70% wool yarns and 30% polyester, linear density Ttex = 55.56 tex and twist of 350 twists/meter. Batch II consists of 70% wool yarns and 30% polyamide, a linear density of Ttex = 71.34 tex and twist of 330 twists/meter (so a thicker yarn than the one from batch I).

Textiles (knitted fabrics, unconventional textile, knitting, etc.) are formed of yarns that are arranged in a certain order, called structure [1], [2]. The yarn is the element underlying the formation of a textile product, and the product structure is the way in which the yarn or yarns are combined. In order to diversify the variety of textile structures, a diversification of the yarns types is realized and

several variants of blended yarns are produced. The mixed yarns are called heterogeneous yarns, which are yarns made of fibers or filaments of different nature [3] [4].

2. THE EXPERIMENTAL PART

In order to study the tensile proprieties of the yarns the following physical-mechanical characteristics are analyzed: yarns tensile strength, elongation at stretch, effort-elongation diagram and irregularity of such caracteristics [5]. The tensile strength tests were performed for ten samples of each batch of yarns for the comparative study of the tensile properties. To determine the experimental samples was used USTER® TENSOJET 4 device presented in Figure 1.

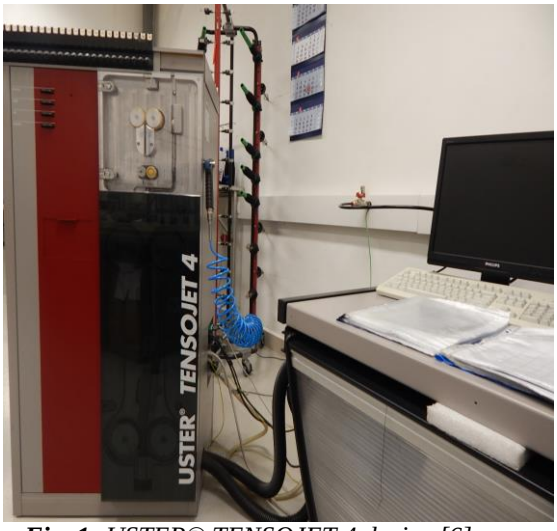


Fig. 1: *USTER® TENSOJET 4 device [6].*

After conducting these tensile strength tests the values of tensile characteristics were obtained: tensile strength, elongation at break, tenacity and the mechanical work at break and also the mathematical statistical processing of the these values by calculating the coefficient of a square variation (cv%) for these values. / We also conducted effort-elongation diagrams and charts variation of the unevenness variation of these two parameters.

For batch I of 70% woolen yarns and 30% polyester we obtained the average value tensile force at break of 696.3 cN and elongation at break averaging 16.09%. Having a linear density of Ttex = 55.56 tex it results an average tenacity of 12.53 cN/tex, and the average work of fracture (Work) is 3937 cN.cm.

As a result of the yarn tests in the two batches we obtained the following.

In Figure 2 is represented the dispersion diagram of tear resistance of the yarns in batch I, rendering the irregularity of tear resistance for the ten samples of yarns from batch I.

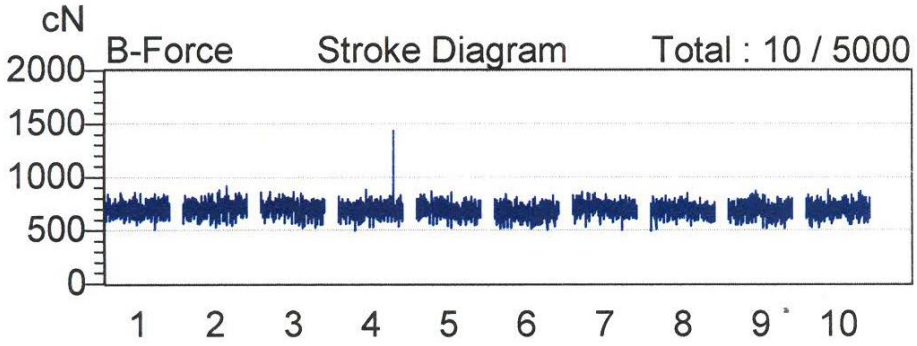


***Fig. 2**: Dispersion diagram of tear resistance for the yarns in batch I*

In Figure 3 is represented the diagram of elongation at break of yarns in batch I, rendering the irregularity of elongation at break for the ten samples of yarns from batch I

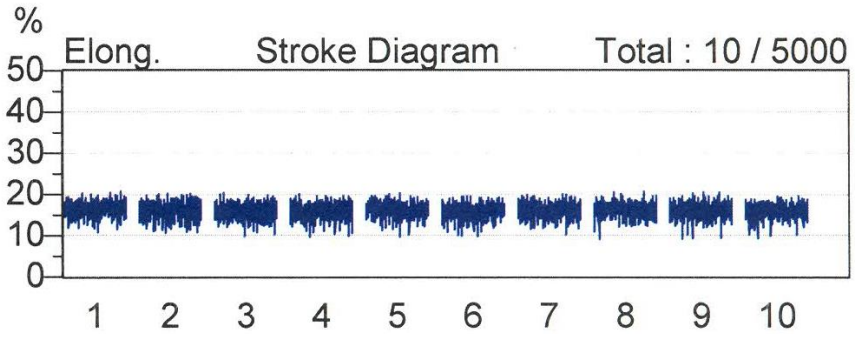


***Fig. 3**: Dispersion diagram of elongation at break for yarns from batch I*

In Figure 4 is represented the effort-elongation diagram that shows the variation of tensile force and elongation at break for the ten yarns in batch I.

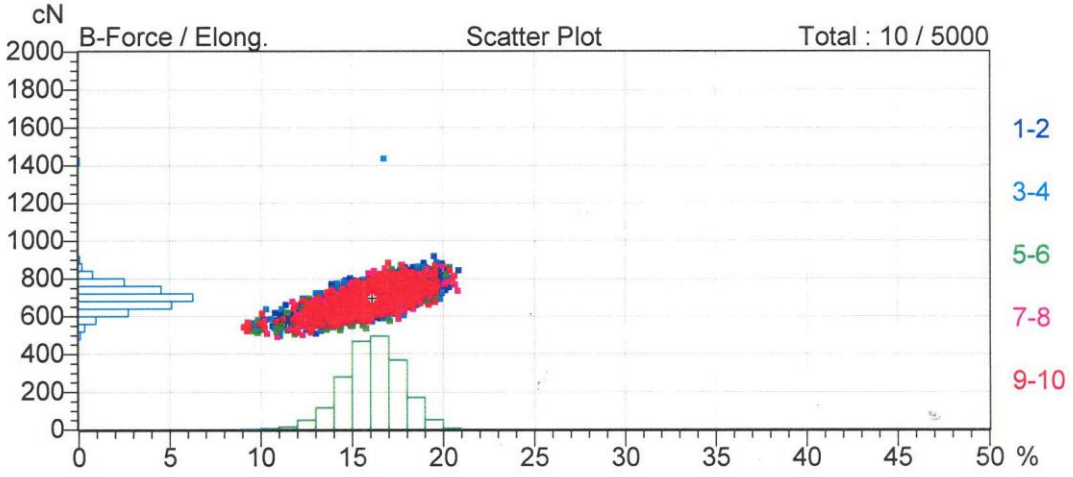


***Fig. 4:** Effort-elongation diagram of yarns from batch I*

In Table 1 are found the individual values for the tensile forces of the ten samples of yarns and the elongation at break corresponding to these forces. Based on these data is achieved the statistical and mathematical processing of this individual data thus obtaining: tenacity, arithmetic mean, coefficient of variation for the yarns in - Batch I

***Table 1**: Statistical and mathematical processing of individual data of yarns – Batch I*
Total10/5000 Sigle test (4)

Nr.	B-force cN	Elong %	Tenacity cN/Tex	B-Work cN cm
1/500	704.5	196.46	12.68	4072
2/500	711.4	16.10	12.8	4008
3/500	704.0	15.93	12.67	3920
4/500	695.1	15.94	12.51	3916
5/500	696.2	16.18	12.53	3961
6/500	674.6	15.96	12.14	3789
7/500	709.2	16.21	12.77	4053
8/500	684.5	16.19	12.32	3901
9/500	685.8	16.07	12.34	3871
10/500	697.7	15.86	12.56	3876
Mean	696.3	16.09	12.53	3937
Cv	8.66	10.24	8.66	16,68
s	60.29	1.65	1.09	656,6
Q95	1672	0.05	0.06	18,20
Min	491.4	9.07	8.84	1633
Max	1435	20.83	25.83	8070
Po.o1(0)				
P0.05(2)	501.2	9.23	9.02	1727
P0.1 (5)	509	9.36	9.16	1777
P0.5(25)	532.1	10.79	9.58	2074

For batch II of yarns with 70% wool and 30% polyamid we obtained an average tensile force value at break of 938.5 cN and average elongation at break of 28.4%. With a linear density Ttex = 71.34 tex results an average tenacity 13.15cN/tex and average mechanical work of fracture (Work) is 9237 cN.cm.

In Figure 5 is represented the dispersion diagram of tear resistance for yarns in batch 1, rendering the irregularity of tear resistance for the ten samples of yarns from batch II.

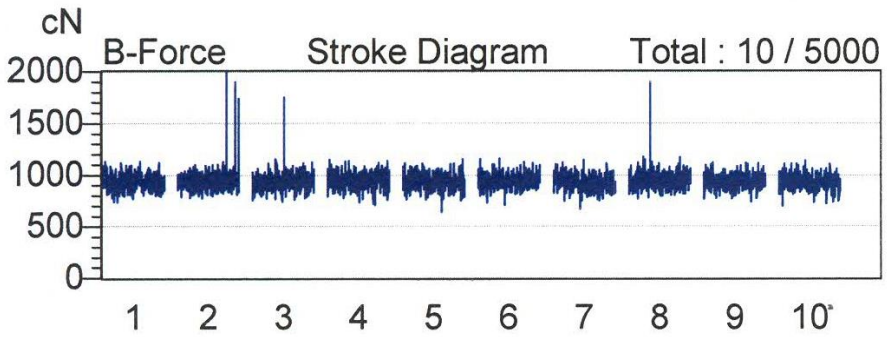


***Fig. 5**:* Dispersion diagram of tear resistance for the yarns in batch II

In Figure 6 is represented the dispersion diagram of elongation at break of the yarns from batch II, rendering the irregularity of elongation at break for the ten samples of yarns from II

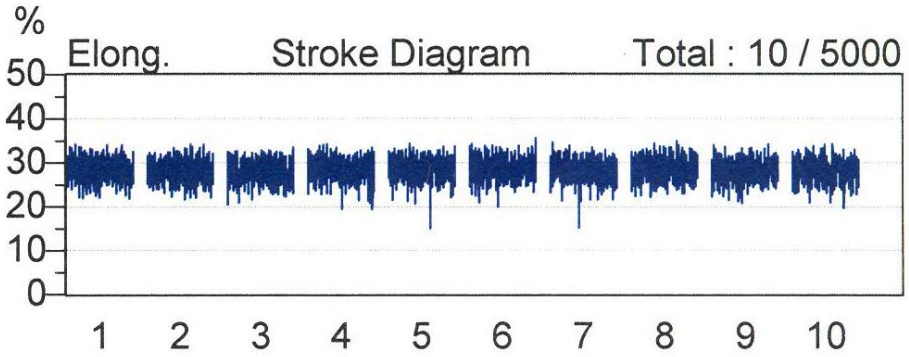


***Fig. 6**: Dispersion diagram of elongation at break for yarns in batch II*

In Figure 7 is represented the effort-elongation diagram that shows the variation of the tensile force and elongation at break for the ten yarns in batch II.

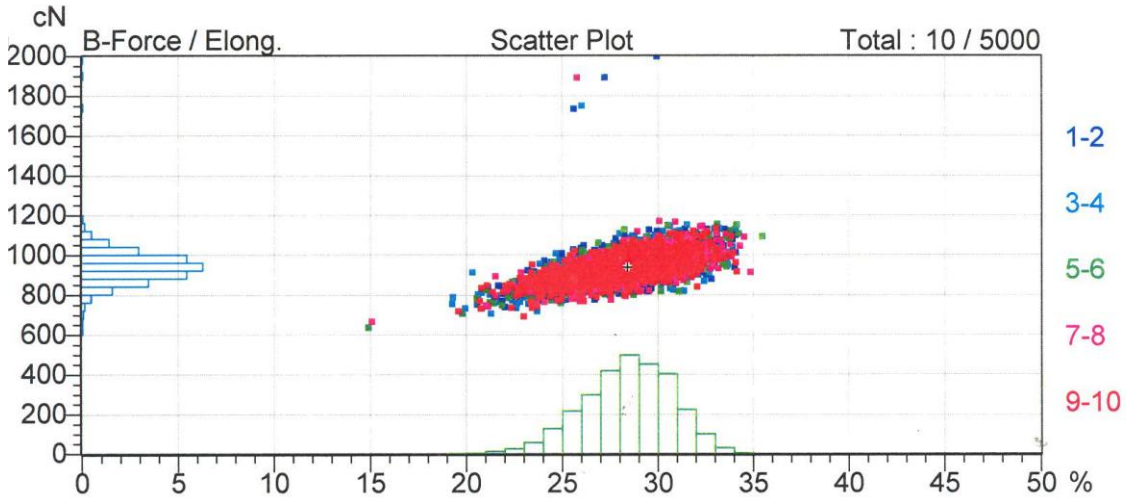


***Fig. 7:** Effort-elongation diagram of the yarns from batch II*

In Table 2 are found the individual values of the tensile forces of the ten samples of yarns and the elongation at break corresponding to these forces. Based on these data is achieved the statistical and mathematical processing of these individual data thus obtaining: tenacity, arithmetic mean, coefficient of variation for the yarns in – Batch II

***Table 2:** Statistical and mathematical processing of individual data of yarns – Batch II*
Total10/5000 Sigle test (4)

Nr.	B-force cN	Elong %	Tenacity cN/Tex	B-Work cN cm
1/500	937.8	28.44	13.13	9242
2/500	946.8	28.16	13.25	9253
3/500	936.3	27.9	13.11	9105
4/500	945	28.43	13.23	9325

5/500	934.2	28.51	13.08	9213
6/500	942	27.71	13.19	9357
7/500	927.2	28.38	12.98	9118
8/500	951.7	28.85	13.32	9472
9/500	930.8	28.30	13.03	9134
10/500	932.9	28.25	13.06	9151
Mean	938.5	28.40	13.14	9237
Cv	7.94	8.36	7.94	13.88
s	74.5	2.37	1.04	1282
Q95	2066	0.07	0.03	35.53
Min	634.6	14.89	8.88	3331
Max	1996	35.47	27.94	20190
Po.o1(0)				
P0.05(2)	689.7	19.22	9.66	4927
P0.1 (5)	704.8	19.55	9.87	5159
P0.5(25)	755.9	21.34	10.58	5927

Comparing the tensile properties values that were determined we obtained for Batch 1: average tensile strength of 336.6cN and average mechanical work of fracture cN.cm 2198 and for batch 2: average tensile strength of 337.3 cN and average mechanical work of fracture 2255 cN.cm. We notice that the second batch of yarns has slightly higher values for these tensile properties.

3. CONCLUSIONS

As a result of these comparative analyses of yarns tensile properties of the two batches and in particular the values of tenacity represents the fact that the woollen yarns from batch II - 70% wool and 30% polyamid have much higher tensile properties - better than batch I consisting of 70% wool and 30% polyester. Decisive is the synthetic component of polyamide which confirms once again its superior qualities in terms of tensile properties.

REFERENCES

[1] Bordeianu D., Gribincea, V.,"*Fibre textile- Proprietăți generale* ", Editura Performantica Iași, 2002

[2] Bordeianu D., "*Fibre textile*", Editura Universităţii din Oradea, 2005

[3] Avram, D., Avram M., Buhu, L., *"Structura firelor*", Editura Gh. Asachi Iaşi, 2002

[4] Constantin Preda, Cristian Preda, „*Metode şi aparate pentru controlul calităţii materialelor textile destinate confecţionării produselor de îmbrăcăminte*" Editura BIT, Iaşi,1996

[5] Oana, D., Oana, I.P., Indrie, L., *"Structuri textile – Colecție de aplicații practice*",Editura Universității din Oradea,2005

[6] D. Oana[1], M. Șuteu[2], I. Oana[3] *Studiul neregularității alungirii firelor de lână în amestec cu mătase naturală cu ajutorul aparatului Uster® Tensojet 4* Analele Universitații din Oradea,2015-

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE STUDY OF ACTIVITY REGARDING THE PROCESSES QUALITY ACCORDING TO ISO STANDARD 9004-2.1

OANA Ioan – Pavel [1], OANA Dorina[1]

[1] University of Oradea, Department of Textiles –Leather and Industrial Management, Faculty of Energy Engineering and Industrial Management, B.St.Delavrancea str. No. 4, 410058, Oradea, Bihor, Romania,
E-mail:textile@uoradea.ro

Corresponding author: Oana. Ioan-Pavel, E-mail: oanaioanpavel@yahoo.com

***Abstract**: Among the activities regarding processes quality according to ISO 9004-2.1 there is one refering to planning to keep under control the processes, achieved by: documentation of current activities, development of documented work instructions, establishing checkpoints and quality inspection techniques, assess the potential effectiveness of technological processes.*
A first step in this direction represents the presentation of the general elements that contribute to insuring the quality of each stage of manufacturing processes, the data being possible to suit for individual cases. It shall be noted that in industrial practice these quality assurance measures are designed interdependent. Preventive control during the technological processes has an important role in improving the technological processes in textiles and also increasing the quality performance of products in order to improve production and creating a recognizable brand in the world market.
Quality of products manufactured in textiles has a decisive role in the present, when facing with an excess of production in this domain and a special competition between firms in the world market. A company that wants to continue to exist and develop must regularly check the quality/satisfaction degree obtained for the products manufactured. The application of quality control system implies a reference system compared to what can be measured by which we obtain "the quality level required and expected." The referential system can be formed in a set of performance indicators so we can say that a company continues to be competitive as far as it established and achieved a series of performance indicators and in addition it controls these indicators every day.

***Key words:** control, cloth spread, cutting, transferring onto screens, humid-thermal treatments, stitching operations,*

1. INTRODUCTION

Quality of products manufactured in textiles has a decisive role in the present, when facing with an excess of production in this domain and a special competition between firms in the world market. A company that wants to continue to exist and develop must regularly check the quality/satisfaction degree obtained for the products manufactured. The application of quality control system implies a reference system compared to what can be measured by which we obtain "the quality level required and expected." The referential system can be formed in a set of performance indicators so we can say that a company continues to be competitive as far as it established and achieved a series of performance indicators and in addition it controls these indicators every day.

2. ENSURING THE QUALITY OF MANUFACTURING PROCESSES

2.1. Ensuring the transferring onto screens quality

Transfering onto screen is the operation of framing patterns/templates on the material and consists in finding the optimal arrangements in order to reduce the specific consumption. It is obvious that transferring onto screens does not actually appear as an act of manufacturing process unless it concerns changing the pre-established markers. Transferring onto screens must contain a number of technical information regarding [1], [2]:

- Elements for identifying the pattern
- Positioning the patterns on the fabric, the deviations permitted from the nominal direction of the parts are determined mainly by the way of attaching their deformations. Thus if the deformation elements are only fixed by humid-thermal treatment, the permitted deviations are of maximum 10^0, and for the elements that are fixed by additional seams or hardening materials, the deviation angle is allowed to be 15^0
- Items that ensure positioning accuracy of product elements, arranged both on the outer contour of the parts and also on the inside. They can be V-shaped or semicircular and because they are made with pneumatic device they have a tolerance layout contour ranging from ± 1 mm and ± 2 mm and a depth of 4-5 mm.

The general principles of optimum achievement of this process stage vary, receiving the technological indications and restrictions regarding the method of optimum classification and grouping of sizes and waists, considering the restrictive conditions imposed by the characteristics and peculiarities of materials required by model and the cutting tool. Thus, for the arrangement of parts which requires a high precision of cutting, the distance between parts is of 3 mm. The signs for positioning and control are marked inside the parts to be visible during cutting. The transferring onto screens quality depends on the number of products enframed, the height of the pattern and the type of framing. According to the complexity of the model and the height of the material, the parts can be done across the width or half its width. The framing method depends a lot on the material width, frequent underdimensions below the tolerance limit requiring changes in the initial framing, with direct implications on specific consumption. Oftentimes, practical consumption is different from that obtained at the technical service, because the framing at a small scale is done usually on the maximum width of the fabric, plus 2 cm compared to the nominal width.

Other factors are dependent on the material are colour palette, colour ratio and drawing sense, surface features, graining direction or orientation of elements. Thus for the materials with checked, striped drawing, which need symmetries of pair parts, the symmetrical parts will be assigned with a technological backup, following the warp yarn direction. In these cases the transferring onto screens will be done on the doubled material. For the strenghtening materials often is done with a rolls cut with a disc knife, thereby eliminating transferring onto screens.

2.2. Ensuring the quality of cloth spread

Cloth spread aims to assure the simultaneous severing of parts for cutting and placing the layers of cloth spread, taking into account the restrictive conditions imposed by the nature of the raw material and the technological process used [3].

Cloth spread quality must be assessed according to the following factors:

- the characteristics of raw materials,
- factors dependent on the achievement of technological act
- peculiarities of the product.

The characteristics of the textile surface will influence maintaining the position of cloth spread layers, while the thickness will have direct influence on the height of the cloth spread. For materials with high coefficient of slipping the cloth spread height will be limited and will be additionally secured with clamps or by scoring. Where friction coefficients have different values on the two sides of the material, the cloth spreading will be done with the front part of the material facing in the same direction. Stiffness and elasticity of the materials influence the way the layers are arranged and the easiness of the edges overlapping on a longitudinal side of the cloth spread. According to the variation of the materials' width, the cloth spread can have both longitudinal sides perpendicular to the surface of the worktop or only one side. The tolerances for vertical wall are ± 3 mm, and for the cloth spread ends are of ± 5 mm. In case of synthetic materials, there often occur undesirable phenomena due to static electricity generated by the material in the process of cloth spreading. They can sometimes affect the cut parts, the difficulties appeared either when separating the layers adjacent to parts, or in the process of sewing to join the two parts.

Cloth spreading must be done without tension and without being too loose. In the case of manual cloth spreading, for the ones stretched loosely, especially items with lower stiffness can occur creases on the cloth surface, which affects negatively the quality of the severing and the cutting, causing additional repositioning maneuvers. Tensed cloth spreadings will be done on the longitude after the spreading is realized. In the case of an immediate cutting, by subsequent contractions there occur underdimensioning of parts that are directly proportional to strain of the cloth spread. For mechanized or automated cloth spreading these defects are removed. Depending on the fabric quality the binding of the cloth spreading is achieved. Binding involves overlaying of two ends in a spread and aims primarily at removing from tha cloth spread of fault. Errors regarding the direction or sense when repositioning the materials create irreparable defects in the future product. The height of the cloth spread will be dependent on the technical characteristics of the cutting machines, the equipment features and the number of products in the order.

2.3 Ensuring quality of severing and cutting

Analysis of manufacturing the clothing products reveals the fact that the cutting operations are taking place both in the cutting and also preparation sections, in the process of manufacturing cutting is used for correcting the parts, for making some matching signs, and also for some phases performed by semiautomatic machines: straight or round head buttonhole machines and cutting the opening of the pockets with the machine for pockets with re-threads and for cutting the thread.

For classic cutting, the cutting-off operation is preceded by severing the cloth spread, which facilitates the handling of sections when travelling towards the fixed cutting machine with belt.

The quality of the cutting is dependent on a number of factors, including:

- the number of component parts of the product and the complexity of their contour;
- the characteristics of the tool and the cutting instrument (the character of cutting tool movement);
- textile material and cloth spread characteristics (rigidity, thickness and fibrous composition of the material).

One of the decisive criteria regarding the quality of the cutting is the type of cutting tool. The most widely used cutting tools are belt-knives operated in various ways:

- reciprocating motion on the vertical, for mobile cutting off machines and those with double articulated arm used in cutting the contour parts;
- continuous translational motion, for stationary machines with 3-4 wheels of starting the cutting belt, machines used for cutting on the contour parts;

- special motion, by combining the movements of lifting-lowering, rotating on its own axis and parallel plan motions, for the automated cutting systems.

For the reciprocating motion, the cutting edge triggers a lifting-lowering movement and the cloth spread material, the cutting quality is not optimal. For automatic machines this drawback is removed by fixing the cloth spread layers with vacuum. For the translational movement, due to the cutting belt in the same direction, the edges are less damaged, the system being possible to be applied on any type of material. There is an inconvenient: the manual moving of the cloth spread, which determines an increase of the contact time between the cloth spread and the cutting tool, with negative repercussions on the look of the the cloth spread edges. For thermoplastic materials it should be avoided welding or melting of the edges, by correlating the velocity of the belt with the speed the cloth spread.

Knife sharpening angle influences both the quality of cutting and wear resistance of the knife. Since the angle value is directly proportional to the resistance to wear and inversely proportional to the cutting quality, it is required to set a best interval, taking into account the relative position of knife-material and also the material's characteristics.

If the knife is perpendicular to the material, it is recommended:

- 15°–20°, for regular materials;
- 30°–35°, for tough materials.

Cutting is done exactly on the contour of the parts parts, by marking the control signs with signs of 4-5 mm, cut perpendicularly on the contour line [4]. As a result of cutting there are shape deviations and the size of the pattern reference, tolerance is between 1-11 mm, being dependent on the length and complexity of the contour line. For one colour materials the permitted deviations are higher, while for stripes and checked materials the deviations are minimal or zero. Whatever type of fabric, the deviations from the direction of the warp yarn maximum permissible is 0.20 mm.

In the case of materials with high coefficient of unravelling, sizing and correct marking are done with difficulty although the depth of signs gets up to 4-5 mm. For materials with high slipping coefficint the precision of markings should be maximum considering that normally the tolerance is small. The parts positioning in the product will determine the precision required by the cutting. Thus, for the basic materials the precision will be higher than for linings, for the parts of the basic material the precision of the cutting is of ± 1 mm and for linings is ± 2 mm, however, in both cases, for sewing with automatic machine, the deviations are zero.

2.4. Ensuring the quality of humid-thermal treatment

The main purpose of humid-themral processes for garments is to ensure some stable deformations, by the action of external forces (tensile, compression, etc.), changing the accumulated tensions of the fabric during mechanical force and fixing the technological effect, traced in certain temperature conditions, humidity and pressure, in a determined interval.

2.5 Ensuring the quality of stitching operations

The processes of products manufacturing consist of separate elements and subassemblies and their subsequent assembly [5], [6]. They exhibit many differences dictated by the technological constructive features of the product, equipment and material properties, as described in Figure 1.

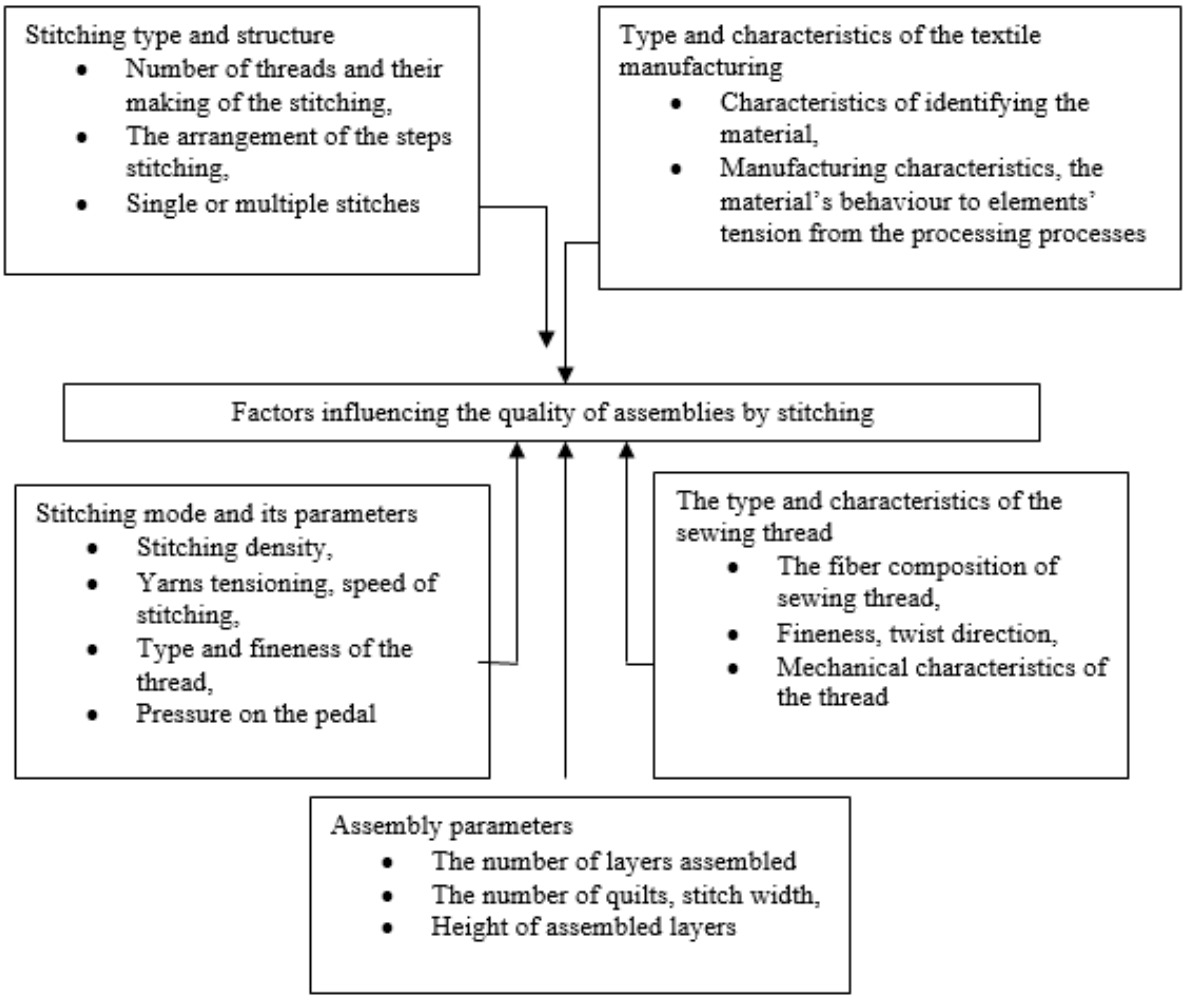


Fig.1: *Factors influencing the quality of assemblies by stitching*

3.CONCLUSIONS

Preventive control during the technological processes is increasingly important for improving the technological processes in textiles and also increasing the quality performance of products in order to improve production and creating a recognisable brand in the world market. The products quality manufactured in textiles has a decisive role at the moment, when faced with an excess of production in this area and a special competition between firms in the world market.

This is one reason for making special efforts which could improve the quality of technological processes in confections.

REFERENCES

[1] I. P., Oana"*Controlul şi auditul calităţii*" EdituraUniversităţii din Oradea, 2008
[2] A.Florea „*Controlul şi auditul calităţii*" Editura Gh. Asachi, Iaşi, 2001
[3] C. Preda, „*Controlul calităţii produselor*" EdituraRotoptint Iaşi, 1983
[4] C. Preda, C. Preda, „*Metode şi aparate pentru controlul calităţii materialelor textile destinate confecţionării produselor de îmbrăcăminte*" Editura BIT, Iaşi,1996
[5] S. Mitu "*Bazele tehnologiei confecţiilor textile,* " Editura Performantica Iaşi,2005
[6] I. Potoran., "*Procese şi maşini în confecţii,* " Editura tehnica Iaşi,1985

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

FUNCTIONALISATION OF TEXTILE FABRICS WITH STABILIZED TiO_2 DISPERSIONS

POPESCU Alina[1], CHIRILA Laura[1]

[1] The National Research & Development Institute for Textile and Leather, Textile Chemistry and Environment Protection Research Department, 030508, Bucharest, Romania, E-Mail: certex@ns.certex.ro

Corresponding author: POPESCU, Alina, E-mail: alina.popescu@certex.ro

Abstract: *This study approached the experimentation of deposition by padding of some TiO_2 P25 dispersed photocatalytic systems on RIPSTOP fabric, made of 100% cotton yarns Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. As stabilizers for photocatalytic dispersions the following products have been used: dodecyltrimethylamonnium bromide (DTAB), 2-[2-(2-methoxyethoxy)ethoxy] acetic acid (TODA) and poly(ethylene)glycol (PEG). Prior to functionalisation treatment, preliminary preparation in three successive steps were applied on textile materials (enzymatic desizing, hot alkaline treatment and bleaching), being followed by cationisation with a polyethylene polyamine resin or a pre-treatment with different crosslinking agents based on acrylic copolymer, polycarbonate urethane polymer or urethane resin. The photocatalytic activity of the textile materials treated with synthesized dispersions was investigated using methylene blue as pollutant. The evaluation was made before and after one washing cycle, in order to determine the durability to washing of applied treatments. Electron microscopy was used for viewing the distribution of TiO_2 particles on the surface of textile materials treated with the photocatalytic dispersions. Ti content existing on the surface of the textile materials was performed by energy dispersive X-ray spectroscopy. The sample treated with photocatalytic dispersion stabilized with TODA showed the higher photocatalytic activity, for which the greatest degree of discoloration was achieved after six hours UV irradiation. Pre-treatment with crosslinking type urethane resin offers good durability to washing of photocatalytic dispersions stabilized with TODA and PEG, confirmed by obtaining a discoloration after washing comparable to that obtained for the unwashed sample.*

Key words: *TiO_2, photocatalytic activity, washing durability, SEM, EDX*

1. INTRODUCTION

Chemical contamination can be manifested through the use of chemical warfare agents in military actions, in case of accidents and also in terrorist attacks [1]. Nowadays, it it obvious that there are increasing risks of chemical contamination by pesticides, widely used toxic chemicals, simoultaneously with an increasing need for the development of more effective protective materials for these purposes, which will not only represent a barrier against toxic chemicals, but will also perform a decontamination (decomposition) of toxic chemicals. One way to achieve self-decontaminating properties of textiles is to employ nanotechnologies. Nanotechnology has been used to obtain of new advanced functionalities for textile materials. TiO_2 nanoparticles are non-toxic and chemically stable under exposure to high temperatures, with photocatalytic activity, self-cleaning, UV protection and antibacterial properties [2-5]. To obtain textiles with decontaminating

properties of chemical warfare agents, this study approached the experimentation of deposition by padding of some TiO_2 P25 dispersed photocatalytic systems.

2. EXPERIMENTAL PART

2.1 Materials

Nano titanium dioxide TiO_2 P25 was used as photocatalyst with the anatase crystalline structure and average particle size of 21nm from Degussa Evonik (Germany). As stabilizers for photocatalytic dispersions, the following reagents have been used: dodecyltrimethylamonnium bromide – DTAB (synthesis grade, Aldrich), 2-[2-(2-methoxyethoxy)ethoxy] acetic acid – TODA (98,4%, Aldrich) and poly(ethylene) glycol–PEG (PEG 400, 99%, Scharlau Chemie) [6]. Deposition of dispersed photocatalytic systems was performed on RIPSTOP fabric, with fibre composition of 83% cotton/17% filament polyester, made of 100% cotton yarns, Nm 70/1 and a network of polyester filament yarns 330 dtex, both in warp and weft directions. Prior to functionalisation treatment, textile fabric has been treated with different cationisation or crosslinking agents, supplied from LJ Specialities (UK): Itofix EZF (polyethylene polyamine resin), Itobinder AG (acrylic copolymer), Itobinder U30 NEW (polycarbonate urethane polymer) and Itocoat LJ25 (urethane resin). The photocatalytic activity of the textile fabrics treated with dispersions was investigated using methylene blue as pollutant.

2.2. Synthesis of photocatalytic dispersions

Synthesis, characterization and evaluation of photocatalytic activity of dispersions is presented elsewhere [6]. The synthesized dispersions have been coded as following: TiO_2_DTAB, TiO_2_TODA and respectively TiO_2_PEG.

2.3. Preliminary preparation of textile materials

To ensure proper hydrophilicity of the textile fabrics, respectively for a smooth running of functionalization stage, three successive steps for preliminary preparation were applied: enzymatic desizing, hot alkaline treatment and bleaching.

2.4. Pretreatments of textile materials

Pretreatment of textile materials with cationization agent

Cationization of textile material was performed in order to modify the surface electric charge of cellulose fibers, namely to introduce positively charged sites (cationic groups), able to attract the anionic groups through ionic attraction forces. This operation was conducted by impregnating the textile material on the laboratory padder with Itofix EZF. Impregnated textile material was subsequently subjected to drying operation.

Pretreatment of textile materials with various crosslinking agents

Pretreatment of textile material was performed by padding on the laboratory padder with three types of crosslinking agents, followed by drying of the impregnated material at a temperature of 120^0C for 2 minutes. Codification of all experimental variants as well as the componence of pretreatment baths are shown in Table 1.

2.5. Treatment of textile materials with photocatalytic dispersions

To deposit photocatalytic dispersions and to fix TiO_2 nanoparticles on the textile materials the following technological operations were successively carried out: impregnation→ drying → curing. Impregnation of pretreated textile materials with photocatalytic dispersions was performed by padding, on the laboratory padder, under the following conditions: 2 passes, 2 bar squeezing

pressure. Drying of the impregnated textile materials was carried out at a temperature of 120^0C for 2 minutes. Curing was performed differently, depending on the type of crosslinking agent used, as follows: Variant A – 0 minutes ; Variant B -170^0C, 1 minute ; Variant C - 150^0C, 4 minutes, Variant D - 150^0C, 4 minutes; Variant E - 160^0C, 2 minutes. Codification of the experimental variants in order to deposit and fix TiO_2 nanoparticles on the textile fabrics is shown in Table 1.

Table 1: *Codification of experimental variants in order to deposit and fix TiO_2 nanoparticles*

Content of pretreatment bath	Photocatalytic dispersion	Code of material treated with photocatalytic dispersion
-	TiO_2_DTAB	A_TiO_2_DTAB
10 g/L Itofix EZF		B_TiO_2_DTAB
20 g/L Itobinder AG		C_TiO_2_DTAB
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_DTAB
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_DTAB
-	TiO_2_TODA	A_TiO_2_TODA
10 g/L Itofix EZF		B_TiO_2_TODA
20 g/L Itobinder AG		C_TiO_2_TODA
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_TODA
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_TODA
-	TiO_2_PEG	A_TiO_2_PEG
10 g/L Itofix EZF		B_TiO_2_PEG
20g/L Itobinder AG		C_TiO_2_PEG
30 g/L Itobinder U30, 1g/L Itocatalyst SCS		D_TiO_2_PEG
20 g/L Itocoat LJ 25, 1g/L Itocatalyst A		E_TiO_2_PEG

2.6. Methods

2.6.1. Evaluation of photocatalytic activity of functionalizaed textile materials

Photocatalytic activity of textile fabrics treated with synthesized dispersions was evaluated by determining the photodegradation efficiency of methylene blue dye (MB) used as aqueous solution of 0.008 g/L. Textile materials treated with each type of photocatalytic dispersion were immersed for 5 minutes in MB solution. Subsequently, the samples were stored in the dark for 1 h - for the adsorption-desorption equilibrium to be reached and subjected to UV irradiation for 6 hours using the "dark room" type CN 15 LC (Vilber Lourmat, France). Incorporated lamps (2 x 15 W) were the sources of ultraviolet radiations and emitted radiation of λ_{max} (emission) = 365 nm. Evaluation of the photocatalytic activity was performed by measuring the color difference of the irradiated samples compared with non-irradiated samples (reference). Color measurements were performed according to ISO 105 J03:2001, using the Spectroflash 650 spectrophotometer (Datacolor, Switzerland) and the light source was the illuminant D65/10. Values obtained for chromatic parameters and color difference are the average of 5 individual measurements. For each textile material subject to a certain type of pre-treatment (series A, B, C, D, E), but not including treatment with photocatalytic dispersion, the degree of MB discolouration has been determined. These samples were immersed in the same conditions in MB solution, stored in the dark and exposed to UV irradiation for 6 hours.

2.6.2. Durability to washing

To test the durability to washing of applied treatments, the samples treated with photocatalytic dispersions have undergone a washing cycle using Scourotester equipment (Metrimpex, Hungary) under the following conditions: 2g/L detergent containing no phosphate and

bleaching agent, at a temperature of 40^0C for 30 minutes. Samples were subsequently rinsed and freely dried horizontally. The washed and unwashed samples were immersed for 5 minutes in a solution of methylene blue (0.008 g/L), stored in the dark for 60 minutes and then exposed for 6 hours to UV irradiation (λ_{max}=365 nm). Evaluation of treatment durability to washing was conducted qualitatively by determining the photocatalytic activity remaining on the textile fabrics after washing, by spectrophotometric measurement of color difference between the washed-irradiated sample and the washed-non-irradiated sample. The results obtained, in terms of photocatalytic activity, were evaluated as compared to standard unwashed samples.

2.6.3. Electron microscopy

Vizualization of distribution of TiO_2 particles on the surface of textile materials was conducted using Quanta 200 (FEI, Netherlands) electron microscope with X-EDS module integrated.

2.6.4. Energy-dispersive X-ray spectroscopy

Highlighting the Ti content existing on the surface of the textile materials treated with the photocatalytic dispersions was performed by energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSIONS

3.1. Evaluation of photocatalytic activity of the functionalized textile materials

Color difference parameters were determined considering as reference the non-irradiated samples treated with photocatalytic dispersions, their values being given in Table 2.

Table 2: *Color difference parameter values obtained for functionaslized samples*

Variant code	Colour difference parameters				Variant code	Colour difference parameters			
	DL*	DC*	DH*	DE*		DL*	DC*	DH*	DE*
A_ TiO_2_DTAB	3.08	-8.77	-2.75	9.71	**A_TiO_2_TODA**	4.98	-11.52	-2.98	12.90
B_ TiO_2_DTAB	3.83	-11.35	-5.87	13.34	**B_TiO_2_TODA**	2.59	-8.61	-4.20	9.92
C_ TiO_2_DTAB	6.88	-15.28	-4.12	17.26	**C_TiO_2_TODA**	5.05	-12.15	-2.10	13.32
D_ TiO_2_DTAB	4.46	-10.70	-2.49	11.86	**D_TiO_2_TODA**	5.85	-13.39	-2.55	14.84
E_ TiO_2_DTAB	3.34	-9.55	-1.32	10.20	**E_TiO_2_TODA**	4.84	-10,97	-2.11	12.18
A_ TiO_2_PEG	3.08	-9.22	-2.54	10.05	**A_MB**	-0.85	-0.39	0.01	0.94
B_ TiO_2_PEG	3.67	-9.84	-5.20	11.72	**B_MB**	-0.60	-0.75	-0.52	1.09
C_ TiO_2_PEG	0.70	-5.64	-2.83	6.35	**C_MB**	-0.87	-0.35	0.50	1.06
D_ TiO_2_PEG	1.91	-7.96	-4.04	9.13	**D_MB**	0.72	-2.51	0.11	2.61
E_ TiO_2_PEG	4.23	-10.18	-3.94	11.70	**E_MB**	0.01	-1.81	0.55	1.89

Analyzing the values of color differences it can be found that discolouration of MB dye, without the contribution of TiO_2 nanoparticles is low, the difference in lightness between the non-irradiated control samples and the irradiated ones having negative subunitary values (darker than the non-irradiated reference) in samples A, B and C, or positive in samples D and E. Textile materials treated with photocatalytic dispersions without the addition of chemicals for fixing (code A) shows the photocatalytic efficiency, the difference in lightness obtained between the irradiated and non-irradiated samples having positive values, 3-4 absolute units higher as compared to non-irradiated reference. The biggest difference in lightness (DL*=4,98) has been obtained for dispersion stabilized with TODA, followed by DTAB and PEG with equal values obtained for DL* (DL*=3,08). Preliminary treatments performed with different crosslinking agents (series B, C, D and E) for fixing the TiO_2 P 25 Degusa on the textile materials do not decrease the photocatalytic effect.

3.2. Durability to washing

The washing durability of the samples treated with synthesized dispersions was determined by assessing the photocatalytic effect after 1 washing cycle by color measurement, the results being shown in Table 3. By analyzing the values of color measurement performed it can be seen that the difference in lightness of the samples pre-treated with resins (series B, D, C and E) decreases after the washing process, generally indicating a degree of semi-permanent fixation of performed treatments. Among the performed pretreatments series, it can be noted ITOCOAT LJ25 treatment, for which the value of difference in lightness after washing has been comparable to that obtained for the unwashed sample (samples E_TiO_2_TODA and E_TiO_2_PEG). The product ITOBINDER AG also provides a good fixation degree for the photocatalytic dispersion D_TiO_2_DTAB.

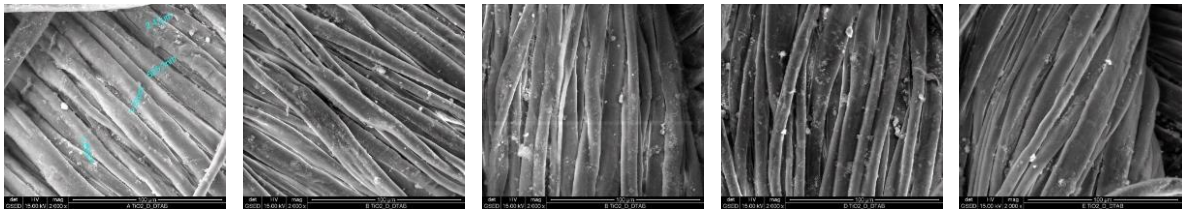
Table 3: *Color difference parameter values obtained for treated samples with photocatalytic dispersions before and after washing*

Sample code	DL*		Sample code	DL*		Sample code	DL*	
	U	W		U	W		U	W
A_TiO_2_DTAB	4.39	1.70	**A_TiO_2_TODA**	7.23	4.37	**A_TiO_2_PEG**	7.91	5.46
B_TiO_2_DTAB	2.96	1.10	**B_TiO_2_TODA**	3.85	2.03	**B_TiO_2_PEG**	5.06	3.94
C_TiO_2_DTAB	5.05	3.79	**C_TiO_2_TODA**	4.57	2.54	**C_TiO_2_PEG**	6.27	3.81
D_TiO_2_DTAB	7.20	5.45	**D_TiO_2_TODA**	4.27	3.51	**D_TiO_2_PEG**	3.93	2.86
E_TiO_2_DTAB	5.97	1.42	**E_TiO_2_TODA**	5.86	5.93	**E_TiO_2_PEG**	3.74	4.87

Legend: U = unwashed samples, W = washed samples

3.3. Electron microscopy

Electronic images obtained at a magnification of x 2000 for textile materials treated with photocatalytic dispersions are shown in Figure 1.



a. b. c. d. e.

Fig. 1: Electronic images recorded at a magnification X 2000 obtained for: a. - A_ TiO_2_DTAB, b. - B_TiO_2_DTAB, c. - C_TiO_2_DTAB, d. - D_TiO_2_DTAB, e. - E_TiO_2_DTAB

Electronic images recorded for textile materials treated with TiO_2 based dispersions reveal that they are covered with a relatively uniform layer of particles, which are less agglomerated, of different shapes and sizes. By analyzing the electronic images recorded for textile materials treated with photocatalytic dispersions, it can not be made a clear delimitation between the applied pre-treatment variants (A, B, C, D, E) and which is the most efficient solution in terms of TiO_2 particles immobilization on the surface of the textile material.

3.4. Energy-dispersive X-ray spectroscopy - EDX

Cuantification of the Ti content existing on the surface of textile materials treated with synthesized photocatalytic dispersions is shown in Table 4. The highest quantity of Ti was obtained for samples treated with PEG-stabilized dispersions (code A and E, respectively). However, there can not be made a correlation between the degree of discoloration (photocatalytic effect) and the quantity of Ti found on the surface of each treated textile material.

Table 4: *Ti content existing on the surface of textile materials treated with photocatalytic dispersions*

Variant code	Ti content		Variant code	Ti content		Variant code	Ti content	
	Wt (%)	At (%)		Wt (%)	At (%)		Wt (%)	At (%)
A_TiO_2_DTAB	5.74	1.76	**A_TiO_2_TODA**	3.22	0.96	**A_TiO_2_PEG**	5.95	1.81
B_TiO_2_DTAB	2.58	0.77	**B_TiO_2_TODA**	4.21	1.27	**B_TiO_2_PEG**	2.75	0.82
C_TiO_2_DTAB	3.75	1.12	**C_TiO_2_TODA**	3.37	1.00	**C_TiO_2_PEG**	3.11	0.92
D_TiO_2_DTAB	4.72	1.42	**D_TiO_2_TODA**	2.47	0.73	**D_TiO_2_PEG**	4.37	1.32
E_TiO_2_DTAB	3.06	0.91	**E_TiO_2_TODA**	4.17	1.26	**E_TiO_2_PEG**	5.85	1.78

5. CONCLUSIONS

Textile materials treated with TiO_2 P25 dispersions showed photocatalytic efficiency, the colour intensity of irradiated samples being much lighter than that of non-irradiated samples. The sample treated with photocatalytic dispersion stabilized with TODA showed the best photocatalytic efficiency. Preliminary treatments performed with different crosslinking agents do not decrease the photocatalytic effect. Pre-treatment with Itocoat LJ25 offers good durability to washing of photocatalytic dispersions stabilized with TODA and PEG, confirmed by obtaining a discolouration grade after washing comparable to that obtained for the unwashed sample. Electron microscopy revealed the presence of microparticles deposited on the surface of the textile material in a relatively uniform layer of particles with different shapes and sizes. Functionalized textile material show a Ti content ranging between 2.47 - 5.95 %, the highest quantity of Ti being obtained for samples treated with PEG-stabilized dispersions. However, there can not be made a correlation between the degree of discoloration and the quantity of Ti found on the surface of each treated textile material.

ACKNOWLEDGEMENT

This work was performed through Partnerships in priority domains Programme – PN II, implemented with the support of MENCS – UEFISCDI, project no. 282/2014, project title *"Sustainable innovative system for photocatalytic auto-decontamination of protection equipment's CBRN "*, acronym CB-PhotoDeg.

REFERENCES

[1] Ž. Senić, S. Bauk, M. Vitorović-Todorović, N. Pajić, A. Samolov and D. Rajić, *"Application of TiO_2 nanoparticles for obtaining self-decontaminating smart textiles"*, Scientific Technical Review, vol.61, pp. 63-72, 2011.

[2] S. Ortelli, M. Blosi, S. Albonetti, A. Vaccari, M. Dondi and A. L. Costa, *"TiO_2 based nano-photocatalysis immobilized on cellulose substrates"*, J. Photochem. Photobiol., vol. 276, pp. 58-64, 2014.

[3] K. Qi, X. Wang and J. H. Xin, "*Photocatalytic self-cleaning textiles based on nanocrystalline titanium dioxide"*, Textile Research Journal, vol. 81, pp. 101–110, 2011.

[4] M. Radetić, *"Functionalization of textile materials with TiO_2 nanoparticles"*, Journal of Photochemistry and Photobiology, vol. 16, pp. 62-76, 2013.

[5] Y. Zhang, F. Huang, F. Wang, W. Duan, J. Li, Y. Shen and A. Xie, *"Functionalization of cotton fabrics with rutile TiO_2 nanoparticles: Applications for superhydrophobic, UV-shielding and self-cleaning properties"*, Russian Journal of Physical Chemistry A, vol. 86, pp. 413-417, 2012.

[6] C. Bogatu, D. Perniu and A. Duta, *"Challenges in developing photocatalytic inks"*, Powder Technology, 2015, doi: 10.1016/j.powtec. 2015.09.018.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

AN ANALYSIS OF THE INFLUENCE OF THE TEXTILE MATERIAL DOUBLING PROCESS BY THERMOFUSING ON VAPOR PERMEABILITY

Viorica PORAV[1], Cristina SECAN[2]

[1, 2] University of Oradea, Faculty of Energy Engeneering and Industrial Management, Department of Textiles – Leather and Industrial Management, B. Şt. Delavrancea no. 4, 410058, Oradea, România.

Corresponding author: Viorica PORAV[1] E-Mail: viorica.porav@gmail.com
Cristina SECAN[2] E-Mail: cris_secan@yahoo.com

Abstract: *To confer shape and volume parameters, to ensure dimensional stability of surfaces and contours, some parts of clothing are doubled using the process of thermofusion with certain woven or nonwoven chemicalized materials. A priority in the work of producers of fabrics and textiles is to ensure comfort parameters and functions of apparel products are met and respected. Clothing products should ensure optimum insulation, air permeability, moisture absorption and transfer in order to give the wearer wellbeing and safety. In this paper we propose to analyze the influence of the technological process of doubling on the vapour permeability of the doubled assembly, compared with the permeability of the non-doubled material. As materials made of natural fibers are increasingly required, we focused on two natural fiber fabrics – 100% linen and 100% cotton - and a mixed natural fiber material – 64% linen, 34% viscose and 2% elastane. They were each doubled using thermofusion with woven or nonwoven chemicalized materials composed of wool mixed with polyamide. Laboratory measurements allow us to conclude to what extent the vapor permeability of the thermofused assemblies is influenced.*

Key words: *vapour permebility, hygroscopicity, clothing comfort parameters, chemicalized woven materials, chemicalized nonwoven materials, thermofusing.*

1. INTRODUCTION

Analysis of the influence of thermofusing processes on the parameters of comfort lead to the choice of suitable doubling materials that keep these parameters in optimal limits. Manufacturers of textiles and clothing are permanently preoccupied with creating clothing assemblies, especially multilayered assemblies, that do not severly adversely affect the characteristics of the base materials [1, 2, 3].

2. GENERAL INFORMATION

Vapour permeability is a material's property to let water vapour pass from an environment with high relative humidity, to an environment low relative humidity. Due to this property humidity from the body surface can be removed through materials or clothing [4, 5, 6].

3. MATERIALS AND METHODS

The water vapour permeability of a fabric can be measured in laboratory conditions, by noting the difference in mass due to the amount of vapour absorbed by a hygroscopic substance or

layer from the conditioning atmosphere, in direct contact or through the textile material to be analyzed [4].

3.1. Materials

We used circular samples of:

- 100% linen (**1**), 100% linen doubled using thermofusion with woven chemicalized materials composed of wool mixed with polyamide (**1'**), 100% linen doubled using thermofusion with nonwoven chemicalized materials composed of wool mixed with polyamide (**1"**);
- 100% cotton(**2**), 100% cotton doubled using thermofusion with woven chemicalized materials composed of wool mixed with polyamide (**2'**), 100% cotton doubled using thermofusion with nonwoven chemicalized materials composed of wool mixed with polyamide (**2"**);
- mixed natural fiber material – 64% linen, 34% viscose and 2% elastane (**3**), mixed natural fiber material – 64% linen, 34% viscose and 2% elastane, doubled using thermofusion with woven chemicalized materials composed of wool mixed with polyamide (**3'**), mixed natural fiber material – 64% linen, 34% viscose and 2% elastane, doubled using thermofusion with nonwoven chemicalized materials composed of wool mixed with polyamide (**3"**).

3.2. Methods

Of each type of doubled material or assembly, four circular samples were taken, which cover the Herfeld glasses. The results obtained represent the arithmetic mean of the determinations for each type of sample. Materials doubled or not, are fixed to the mouth of each Herfeld glass, which contains 50 cm^3 of distilled water. The glass is introduced into the exicator environment, i.e. with 0% relative humidity, created using calcium chloride. The initial weight of the glass, water and material (M_1) assembly is measured and then at different time points after exposure to the low humidity environment (M_v). The difference in mass allows the calculation of the vaporisation index or of the vapor passage resistance of a material or a doubled textile assembly[4].

Vapor permeability is calculated using the formula [4]:

$$P_v = M_1 - M_v \ [g] \quad \textbf{(1)}$$

Vaporization coefficient (μ) is calculated using the formula [4]:

$$\mu = P_v / S \times T \ [g/m^2 h] \quad \textbf{(2)}$$

Where: S – vaporization surface [m^2]
T – vaporization time [hours]

4. RESULTS

Table 1: *Vapour permeability and vaporization coefficient for the three matherials in there three variounts.*

No.	Material type	Initial mass M_0(g)	Mass variation in different time intervals $\Delta M = M_0 - M_i$ (g)								μ (g/m^2 h)	PV (g)
			1h	2h	3h	4h	5h	24h	48h	72h		
			M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8		
0.	*1.*	*2.*	*3.*	*4.*	*5.*	*6.*	*7.*	*8.*	*9.*	*10.*	*11.*	*12.*
1.	**1**	109,54	109,47	109,42	109,36	109,30	109,25	108,75	107,95	107,58	10,26	0,58
2.	**1'**	102,03	101,89	101,84	101,78	101,74	101,70	101,33	100,80	100,34	7,220	0,49
3.	**1"**	121,66	121,48	121,42	121,32	121,30	121,25	120,87	120,32	119,87	7,370	0,50
4.	**2**	100,69	100,61	100,56	100,49	100,41	100,35	99,78	98,78	98,27	11,13	0,75
5.	**2'**	111,41	111,27	111,24	111,20	111,16	111,10	110,90	110,42	110,02	7,850	0,37
6.	**2"**	112,48	112,38	112,37	112,32	112,28	112,23	111,95	111,56	111,21	8,600	0,49
7.	**3**	101,62	101,56	101,49	101,43	101,37	101,32	100,53	99,56	98,69	19,53	0,92
8.	**3'**	112,96	112,93	112,89	112,81	112,75	112,69	112,15	111,44	110,72	12,47	0,71
9.	**3"**	111,14	111,09	111,05	110,97	110,91	110,85	110,24	109,47	108,78	13,12	0,73

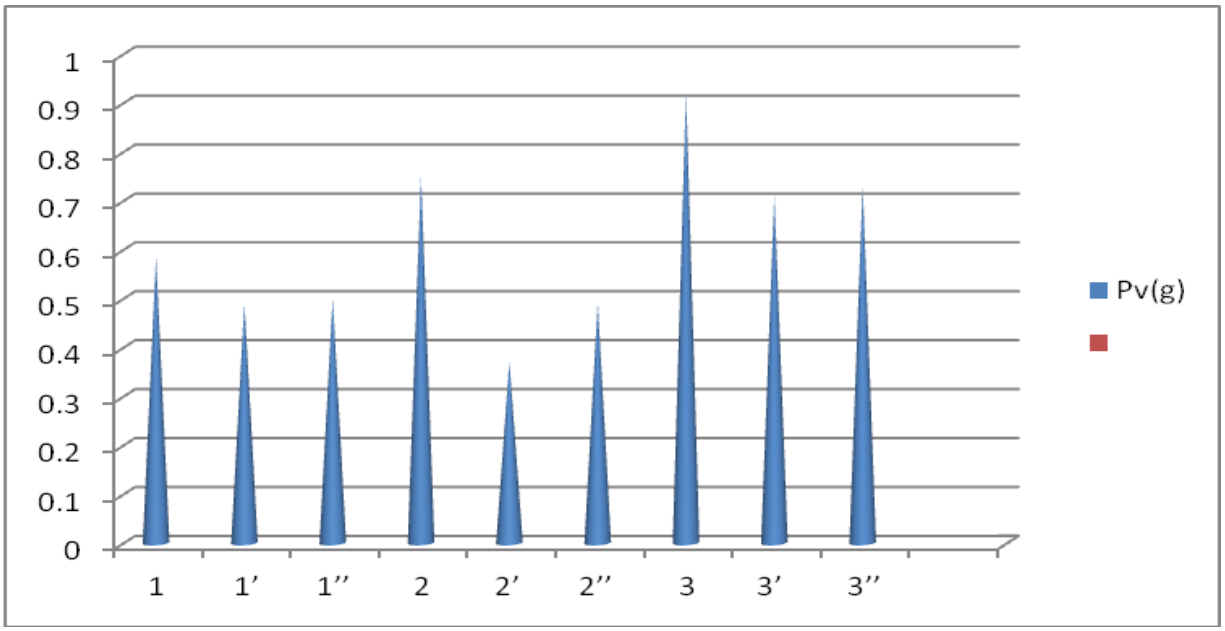


Fig. 1: *Vapour permeability for the three matherials in there three variounts.*

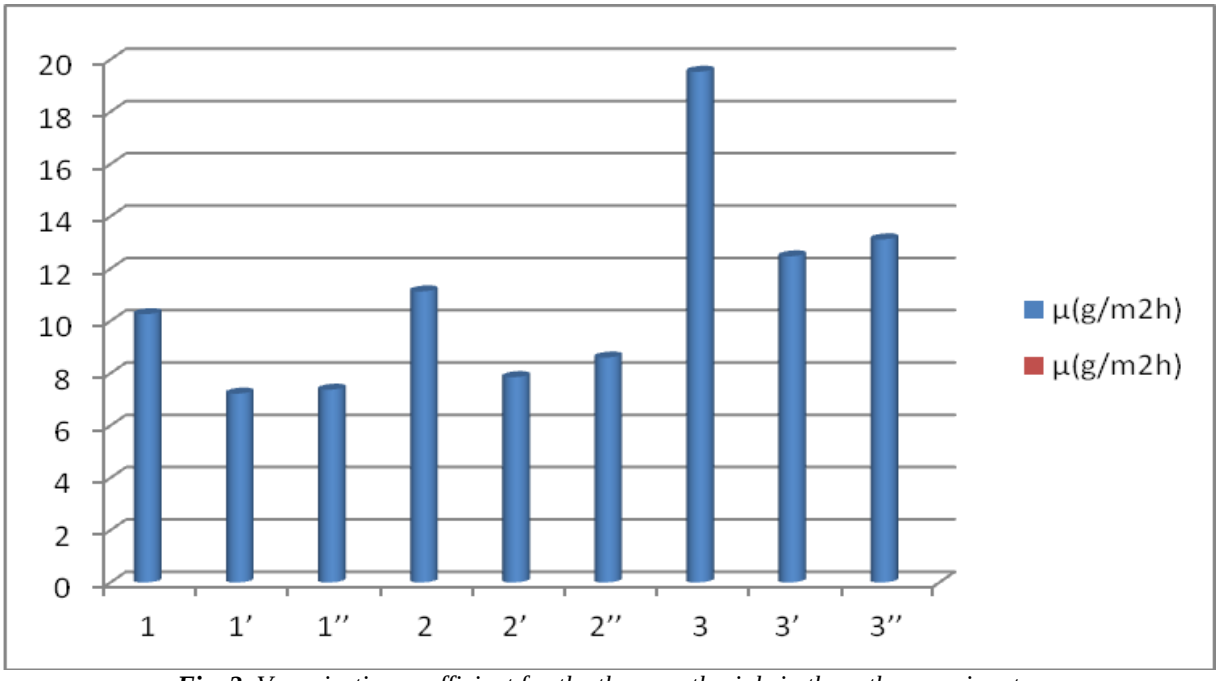


Fig. 2*: Vaporization coefficient for the three matherials in there three variounts.*

It is noted that the vapor permeabilities (Pv) in all three materials, unfused or fused with chemicalized woven or non-woven materials, have decreased values, starting with unfused materials, then thermofused with chimicalized unwoven materials and finally thermofused with chimicalized woven materials. The thickness of the material and the structure of the assembly of layers influences the vapor permeability. Also the resulting of vaporization coefficient (μ) demonstrates a significant influence of doubling process by thermofusing, on vapour permeabiliality for the three types of materials, unfused or fused with woven or nonwoven chemicalized materials.

Also is demonstrate the viscose influence on vapor permeabilities (Pv) and vaporization coefficient (μ) of material 3, 3'şi 3'',because the high level of them higroscopicity.

5. CONCLUSIONS

Producers of textile clothing should note that for products intended for the cold season it is optimal that parts of clothing are thermofused with chemicalized woven materials, which have a lower coefficient of vaporization. We specify that for the cold season, it is indicated that parts of the products are backed with chemicalize woven materials, thanks to a low coefficient of vaporization, knowing that for this season, the important parameter is insulation, while air permeability and absorption of moisture parameters are less important. For intermediate seasons, such as spring and autumn, it is advisable to use a nonwoven chemicalized material which provides average permeability values with respect to those indicated for the winter, and summer respectively.

REFERENCES

[1] S. Mitu, M. Mitu, "Bazele tehnologiei confecţiilor", Vol. I., Ed. Performantica, pag. 38-40, 2005.

[2] A. Brumariu, " Proiectarea îmbrăcămintei", Ed. Gh. Asachi Iaşi, pag. 341-348, 1989.

[3] ***AGIR, "Manualul inginerului textilist", Ed. AGIR, pag. 833-834, 2003.

[4] S. Mitu, "Confortul şi funcţiile produselor vestimentare", Ed. Gh. Asachi Iaşi, pag. 193-202, 1999

[5] Z. Hoblea, "Structuri textile", Ed. Gh. Asachi Iaşi, pag.56-61, 1999.

[6] ***AGIR, "Manualul inginerului textilist", Ed. AGIR, pag.806-828, 2003.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PART I. STUDY REGARDING THE OPTIMIZATION OF THE BIOSCOURING TREATMENT IN ULTRASOUND ON 60 % COTTON + 40 % COTTONISED FLAX MATERIALS

PUSTIANU Monica[1,2], SÎRGHIE Cecilia[2], BÖHM-RÉVÉSZ Gabriella[3], DOCHIA Mihaela[2]

[1] "Aurel Vlaicu" University of Arad, Romania, Faculty of Engineering
Postal address, 310330 Arad, Romania, E-Mail: pustianumonica@yahoo.com

[2] "Aurel Vlaicu" University of Arad, Romania, Research Development Innovation in Technical and Natural Science Institute
Postal address, 310330 Arad, Romania, E-Mail: pustianumonica@yahoo.com, dochiamihaela@yahoo.com, cecilias1369@yahoo.com

[3] The University of Oradea, Faculty of Energy Engineering and Industrial Management
Postal address, 410087 Oradea, Romania, revesz_gaby@yahoo.com,

Corresponding author: Dochia Mihaela, E-mail: dochiamihaela@yahoo.com

Abstract: *In the past years the commercial products for the bioscouring treatment were usually dedicated only for 100 % cotton or only for 100% lignocelluloses fabrics. The development of hemp/cotton or flax/cotton mixtures fabrics leds to the necessity of finding of the most apropiate products that could be used for different enzymatic treatments on these types of fabrics.The usage of the commercial product SERA ZYME C-PE for bioscouring treatment in ultrasound conditions on 60 % cotton + 40 % cottonised flax was studied in this work. The optimization of the Bioscouring treatment in ultrasound on 60 % cotton + 40 % hemp materials using the same commercial product was previous published. In order to assess more accurately the influence of some process parameters of the bioscouring treatment in a mathematical modeling of the process was made and a central compound rotatable program with two independent variable: x_1 - the concentration of enzyme (%) and x_2 - treatment time (minutes) was used. The independent variable considered was y_1 – the weight loss. The aim of this study was to investigate the behaviour of cottonised flax/cotton mixtures for the same conditions of bioscouring treatment used as for hemp/cotton mixtures.*

Key words: *cotton, cottonised flax, enzymes, bioscouring treatment with ultrasound, weight loss*.

1. INTRODUCTION

The aim of the removal of the impurities present in the cellulosic materials is to obtain a good absorbency or wettability of the materials necessary for further dyeing and finishing processes. This treatment is referred to as scouring when conventional alkaline processes are followed. And the treatment is referred to as bioscouring when environmentally friendly enzymes are used. The conventional treatment is carried out at higher temperatures with alkalis, which has the disadvantages such as high energy consumption and polluted wastewaters [1]. The bioscouring treatment unlike the classical alkaline treatment is more environmentally friendly by less energy consumption and preserves the fiber's structure and strength by using specific enzymes to remove

non-cellulosic impurities [2, 3]. For the enzymatic treatment the commercial product SERA ZYME C-PE [4], based on 5-15 % Pectate Lyase (E.C.4.2.2.2) in phosphate buffer solution of 0.1 Molar monosodium/disodium phosphate (pH = 7.5) was used. All the experiments were carried out in ultrasound. The producer instructions for usage of SERA ZYME C-PE for 100 % cotton fabrics is to carried out the process less then 20 minutes at 1g/L enzyme concentration [4]. Considering that the lignocellulosic materials shows higher non-cellulosic impurities content we appreciated that the treatment conditions (time and enzyme concentration) for such blended fabrics should be slightly higher than for 100 % cotton fabrics. In this respect the bioscouring treatment for 60 % cotton/40 % cottonised flax blended fabrics was performed in ultrasound with a variable concentration of enzyme (1-3 %) and a larger range for the treatment time (20-60 min.). By measuring the weight loss, the optimum working parameters for the Bioscouring treatment in ultrasound were determined.

2. EXPERIMANTAL PART

Plain woven of 60 % cotton + 40 % cottonised flax composition was used. The woven material has the width 120 ± 3 cm, weight 220 ± 10 g/m^2, warp sett 200 ± 10 fibers/10cm, weft sett 170 ± 10 fibers/10 cm. The treatment was performed in ultrasound in a multi-frequency ultrasonic cleaning unit; model TI-H-10 from Elma Schmidbauer GmbH, Germany. The energy of sonication applied was 200 W (ultrasonic power effective) and 800 W (ultrasonic peak performance max). For the bioscouring treatment a variable concentration between 1-3 % of comercial enzyme was used, 2 mL/L HEPTOL NWS which is a sequestrant agent with binding role for the metal ions in water with high hardness, regardless of temperature; 2 mL/L SULFOLEN 148 a wetting and scouring agent; 10 % of the fleet of treatment was pH = 7.5 buffer solution of 0.1 Molar (sodium phosphate/disodium phosphate,); liquid to fabric ratio - H 10:1, at temperature T = 55 ^{0}C and time - t = (20-60) minutes [5]. After a series of preliminary determinations, to achieve a minimum number of experiments, these were conducted using a central, rotatable second order compound program with two independent variables [6, 7]. The variation limits and experimental plan are presented in Tables 1 and 2.

Table 1: *The variation limits of independent variables*

Value. code / Real value	-1,414	-1	0	1	+1,414
x - enzyme concentration	1	1,7	2	2,7	3
y - time (minutes)	20	34	40	54	60

Table 2: *The experimental plan with two independent variables*

Exp. No.	x	y
1.	-1	-1
2.	1	-1
3.	-1	1
4.	1	1
5.	-1.414	0
6.	1,414	0
7.	0	-1,414
8.	0	1,414
9.	0	0
10.	0	0
11.	0	0
12.	0	0
13.	0	0

3. RESULTS AND DISCUSSIONS

Experimental matrix and the measured values of the response function are shown in Table 3:

Table 3: *Experimental matrix and the measured values of the response function*

No.	Independent variables				Answers
	x		y		x
	x (cod.)	X - Enzyme concentratio [%]	y (cod.)	y Time [min.]	(Y) Weight loss [%]
1.	-1	1.70	-1	34.00	3.04
2.	1	2.70	-1	34.00	1.59
3.	-1	1.70	1	54.00	2.85
4.	1	2.70	1	54.00	1.25
5.	-1.414	1.00	0	40.00	3.55
6.	1.414	3.00	0	40.00	1.11
7.	0	2.00	-1.414	20.00	2.06
8.	0	2.00	1.414	60.00	2.18
9.	0	2.00	0	40.00	4.03
10.	0	2.00	0	40.00	2.57
11.	0	2.00	0	40.00	1.40
12.	0	2.00	0	40.00	1.39
13.	0	2.00	0	40.00	1.89

3.1. Mathematical model interpretation obtained

In order to assess more accurately the influence of some process parameters of the Bioscouring treatment in US of 40 % flax + 60 % cotton blended fabric - the concentration of enzyme (%) and treatment time (minutes) – on the weight loss, a mathematical modeling of the process was made, using a central compound rotatable program with two independent variables**.** The two chosen independent variables are: x - the concentration of enzyme [%] and y - time (minutes). As goal-function the weight loss (%) (denoted by Y) was chosen. Enzyme concentration varies between 1-3 % and the treatment time between 20 - 60 minutes. The second order central compound rotatable program has the following mathematical expression:

$$Y = b_0 + b_1x + b_2y + b_{12}xy + b_{11}x^2 + b_{22}y^2 \quad \textbf{(1)}$$

For the experimental data a program in Mathcad Professional and Excel was used, and a regression equation was obtained [6, 7, 8, 9]. Coefficients of the regression equation are presented in Table 4.

Table 4: *Regression equation coefficients, dispersion and the verification of the significance of the dispersion equation coefficients using the Student test*

Regression equation coefficients		Calculated dispersion "S"	The coefficients significance using Student test $t_T=t_{\alpha,\nu} = t_{0,05;6} = 2,132$; (If tc> t_T-term is significant)		
b0	2.256538	S=0.021251	tc0	9.281732	significant
b1	-0.81252		tc1	-5.34737	significant
b2	-0.04504		tc2	-0.29642	nesignificant
b11	0.027727		tc11	0.158621	nesignificant
b22	-0.07733		tc22	-0.44236	nesignificant
b12	-0.0375		tc12	-0.1234	nesignificant

The regression equation obtained after eliminating insignificant coefficients is:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(2)}$$

3.1.1. Verification of the coefficients significance

Verifying the significance of coefficients is important because it can confirm or invalidate the created model. The Student test compares the average of a random variable with mean standard deviation. For the central part of the program, in which all independent variables have zero code value the dispersion "S" is calculated. The dispersion value was shown in Table 4. The significance of the regression equation coefficients was tested using Student test with critical table value for the test $t_{\alpha,\nu} = t_{0,05;6} = 2,132$. The test values and the significance of the coefficients were presented in Table 4.

3.1.2 Verification of the model adequacy

The appropriate model was verified using Fisher test and percentage deviation.The deviations values are shown in Table 5. To verify the model adequacy and its ability to express the studied phenomenon mathematical, the Y_{calc} values were calculated and the deviation "A" between the measured and calculated values was established according to Table 5. It can be observed that some of the individual deviations do not fit within the limits imposed by ± 10 %, which indicates a poor adequacy of the model.

Table 5: *Adequacy calculation model*

No.	Y meas	Ycalc.	(Ymas. – Ycalc.)^2	Deviation "A"	Average square of residuals "PMrez"	Dispersion of reproducibility "S_0^{2}"	Ratio Fc = PMrez / S_0^2	Statistics Fc<F'c $F'_c = F_{v1, v2, \alpha} = F_{5;5;0,01} = 6,59$	Fisher test Fc>Ft $Ft=F_{v1, v2, \alpha} = F_{12;12;0,05} = 2,69$
1.	3.04	3.02	0.0001	0.427					
2.	1.59	1.47	0.0127	7.109				Fc=	Fc=
3.	2.85	3.01	0.0262	-5.681				0.017482	2.082723
4.	1.25	1.31	0.0038	-4.950					
5.	3.55	3.46	0.0079	2.510					
6.	1.11	1.16	0.0028	-4.781					
7.	2.06	2.16	0.0111	-5.127	4.9473	1.21558	0.01748	0.017482 <6,59	2.082723 <2,69
8.	2.18	2.03	0.0200	6.502					
9.	4.03	2.25	3.1451	44.006				Appropriate model	In-appropriate model
10.	2.57	2.25	0.0982	12.196					
11.	1.40	2.25	0.7336	-61.181					
12.	1.39	2.25	0.7508	-62.340					
13.	1.89	2.25	0.1343	19.393					

The degree of concordance of the mathematical model was verified using F'_c statistics. Initially the average square of residuals PM_{rez} and the reproducibility of dispersion S_0^2 were calculated, obtaining the values shown in Table 5. The ratio $Fc = PMrez/S_0^2$ was compared with the critical value $F'_c = F_{v1, v2, \alpha} = F_{5;5;0,01} = 6,59$. To verify deviation of the survey data from the mean value the Fisher-Snedecor test was used. $F_c = 2.119134$ calculated value is lower than the critical value $F_c = F_{\alpha, v1, v2} = F_{0,05; 12, 4} = 5,91$ which indicates that the deviations appear due to the independent variables. The quality of approximation of the mathematical model expressed by the standard error shows the scattering of the experimental values around the regression equation: 84.06 %. The correlation coefficient has the value: $r_{x1x2} = -0.02032$, $r_{x1y} = -0.7756628$ and $r_{x2z} = -0.0429969$. The significance of the simple correlation coefficients is checked using the Student test. The calculated values are: $tc_{x1y} = -4.07604$, $tc_{x2y} = -0.1427366$, $tc_{x1x2} = -0.067393$. The calculated values are lower than the critical table value $t_{\alpha, v} = t_{0,05; 11} = 2,201$ for t_{x1y} and t_{x2y} which indicates that there is no any relationship between variables, $t_{x1x2} = -0.3752093$ so there is some correlation between independent variables The multiple determination coefficient 0.519859 shows that the influence of the two independent variables on the outcome is 51,98 %, the rest being caused by other factors. The response interpretation and search of extremes are more difficult and it preferred to bring the surface into a form more accessible for the analysis using canonical transformation. Allowing a much easier localization of the extreme, the canonical transformation can be seen as an optimization method. The canonical analysis transforms the regression equation in a more simple form and interprets the resulting expression using geometric concepts:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(3)}$$

In this case we have a first degree equation.

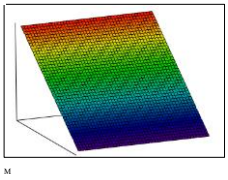


Fig. 1: *The dependence of the goal-function on the independent variables:*

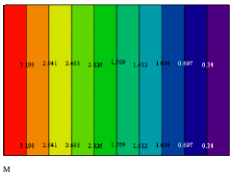


Fig. 2: *Contour curves for various values of Y (weight loss)*

Figure 1 presents the plot which shows the dependence of the goal-function on the two independent variables. The response surface of the regression equation is a plane surface. The constant level curves obtained by cutting the response surface with constant level plans presented in Figure 2 allows the evaluation of the dependent variable *Y*, according to the conditions imposed by the independent variables *x* and *y*. The figure presents contour curves for various values of weight loss, 1.11 to 4.03 between

3.2 Interpretation of the obtained mathematical model technology

By analyzing the expression of the obtained goal function:

$$F(x.y) = 2.256 + (-0.812)x \quad \textbf{(4)}$$

These can be seen: the influence of the two independent parameters, *x* (enzyme concentration) and *y* (treatment time) on the dependent variable *Y* (weight loss) manifests in different way. Only *x* variable (enzyme concentration) influences directly the outcome *Y* (weight loss): the deacreasing of *x* (enzyme concentration) conducts to the increasing of *Y* (weight loss); the influence of variable *x* (enzyme concentration), on *Y* (weight loss) is 31.5 %; the influence of variable y (treatment time), on *Y* (weight loss) is 0 %; the absence of quadratic form for both parameters indicates that the response surface defined by the obtained mathematical model, is not well formed, reinforcing the hypothesis regarding the influence of only one parameter on the outcome.

Figure 3 shows the dependence of the goal-function on one of the two independent variables for all significant values of the parameters, given that the second independent variable is constant. It can be observed how, for a constant value of enzyme concentration, the graph representing the variation of weight loss versus time, indicates for the interval [–1414, 1,414], (between 20–60 minutes) a constant weight loss, which indicates a zero influence of this parameter on the weight loss.

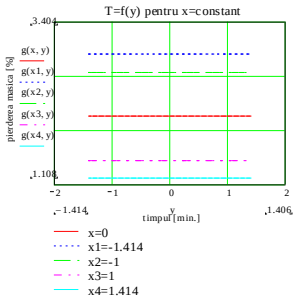


Fig. 3: *The dependence of the goal-function on all significant values of y parameters for x = constant*

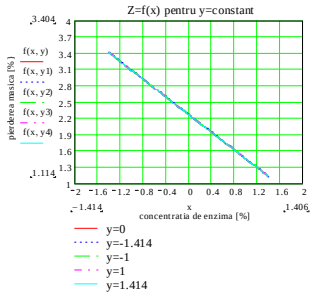


Fig. 4: *The dependence of the goal-function on all significant values of x parameters for y = constant*

Figure 4 shows the dependence of the goal-function of one of the two variables for all significant values of the parameters, given that the second one is constant. From the graph it can be

observed that conducting the experiment with values for variable y between 20–60 minutes will result a linear decrease of weight loss in the same time with the increasing of the enzymes concentration.

4. CONCLUSIONS

It was found that the chosen range of the treatmet parameters (time and concentration) does not influence the process because the enzymatic reaction occurs in less than 20 minutes (as recommended by the producer for 100 % cotton materials). It appears that the behaviour of the 40 % cottonised flax + 60 % cotton fabrics are different from the 40 % hemp + 60 % cotton fabrics [1]. The behaviour of the 40 % cottonised flax + 60 % cotton fabrics is simmilar with 100 % cotton fabrics which can be explained by the fact that previous cottonisation method applied to flax fibers led to fibers with similar characteristics to cotton ones.

ACKNOWLEDGEMENT

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1370

and ''Bast plants - Renewable Strategic Resources for European Economy - BASTEURES'' project, no. 210/2010 POS-CCE - supported by Structural Founds - "Investment in Your Future".

REFERENCES

[1] Q. Wang, X.-R. Fan, Z.-Z. Hua, J. Chen, *"Optimizing bioscouring condition of cotton knitted fabrics with an alkaline pectinase from Bacillus subtilis WSHB04-02 by using response surface methodology"*, Biochemical Engineering Journal, 34, pp. 107–113, 2007.

[2] I. V. Istoc, M. Pustianu, A. Bucevschi, M. A. Dochia and C. Sîrghie, "*Study regarding the optimization of the bioscouring treatment on 100 % cotton materials*", in Advanced in Environmental Technologies, Agriculture, Food and Animal Science. ISSN 2227-4359, ISBN 978-1-61804-188-3. Proceeding of the 2nd International Conference on Energy and Environment Technologies and Equipment (EEETE '13), series 10, Braşov, Romania, 2013.

[3] E.S. Abdel-Halim, H.M. Fahmy, Moustafa M.G. Fouda, "*Bioscouring of linen fabric in comparison with conventional chemical treatment*", Carbohydrate Polymers, 74, pp. 707–711, 2008.

[4] Catalog DyStar Textilfarben GmbH, 2007.

[5] M. Pustianu,M. Dochia, M.S. Pernevan, C.Sîrghie, "*Study regarding the influence of the bioscouring treatment in ultrasound on 60 % cotton+40 % hemp materials, Part 1: Study regarding the optimization of the bioscouring treatment",* in Annals of the University of Oradea, Fascicle of Textiles, Leatherwork, VOLUME XV, No. 1, 2014, pp. 93– 98.

[6] A. Popescu, A. Grigoriu, C. Zaharia, R. Mureşan and A. Mureşan, "*Mathematical modeling and the technological process optimization for the bio-scouring of the cotton textile materials*", Industria Textilă, vol. 61, pp. 70-80, 2010.

[7] R. Butnaru and L. Stoichițescu, "*Special finishing procedures of textiles fabrics*", Editura Gh. Asachi, Iași, 1995.

[8] R. Mihail, "*Introduction to the strategy experimenting with applications in chemical technology*", Ed. Scientific and Encyclopedic, Bucharest, 1976.

[9] S. Akhnazarova and V. Kafarov, "*Experiment optimization in chemistry and chemical engineering*", MIR publ., Moscow, 1982.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

PART II. STUDY REGARDING THE INFLUENCE OF BIOSCOURING TREATMENT ON 60 % COTTON + 40 % COTTONISED FLAX MATERIALS FOLLOWED BY A WHITENING TREATMENT USING ALTERNATIVE METHODS

DOCHIA Mihaela[1], SÎRGHIE Cecilia[1], PUSTIANU Monica[1,2]

[1]"Aurel Vlaicu" University of Arad, Romania, Research Development Innovation in Technical and Natural Science Institute,
Postal address, 310330 Arad, Romania, E-Mail: dochiamihaela@yahoo.com, cecilias1369@yahoo.com, pustianumonica@yahoo.com

[2]"Aurel Vlaicu" University of Arad, Romania, Faculty of Engineering
Postal address, 310330 Arad, Romania, E-Mail: pustianumonica@yahoo.com

Corresponding author: Dochia, Mihaela, E-mail: dochiamihaela@yahoo.com

Abstract: *A comparative study of whitening treatment using various methods for 60 % cotton +40 % flax materials was made. The samples materials were scoured by bioscouring treatment in ultrasound as was described in our previous work (part I). The removal of noncellulosic impurities using the bioscouring treatment was evaluated by weight loss and hydrophilicity of the treated samples. Some of these bio-scoured samples were further bleached using the folowing procedures: Classical procedure with hydrogen peroxide (30 %), bleaching with catalyst and with laccase enzyme.*
Hydrogen peroxide is usually used as oxidative bleaching agent for cotton and cotton blends. A high and stable degree of whiteness is obtained by this treatment. The advantages of the treatment are: low costs, flexibility of application and the possibility of a one-bath (scour/bleach) procedure. But, high temperature of bleaching under alkaline conditions necessitates high energy utilization that can cause considerable fiber damage. Different solutions like the use of enzymes and catalysts have been investigated to overcome such problems. In order to characterize the quality of the enzymatic pretreatment compared to the classical one, the values of the whiteness degree after different type of bleaching (hydrogen peroxide, catalyst and laccase) for the samples treated with the same concentration of enzyme were studied. The tensile strength and elongation at break of treated materials were investigated.

Key words: *cotton, flax, bioscouring treatment with ultrasound, weight loss, alternative whitening methods, whiteness degree*.

1. INTRODUCTION

Hydrogen peroxide is usually used as oxidative bleaching agent for cotton and cotton blends. A high and stable degree of whiteness is obtained by this treatment. The advantages of the treatment are: low cost, flexibility of application and the possibility of a one-bath (scour/bleach) procedure. But, high temperature of bleaching under alkaline conditions necessitates high energy utilization that can cause considerable fiber damage. Different solutions like the use of enzymes and catalysts have been investigated to overcome such problems [1]

After the removal of noncellulosic impurities using the bioscouring treatment, the material becomes much cleaner and hydrophilic with better absorbent properties. By whitening treatment, the whiteness degree it is considerably improved because the chromophore groups of the natural pigments from cotton and flax are destroyed by oxidation reactions. Bleaching may be carried out by using several procedures like classical method with hydrogen peroxide or enzymatic method with different type of enzymes.

2. EXPERIMENTAL PART

The experiments were carried out using samples fabrics treated by bioscouring method presented in the first part. The bioscouring treatment was done with a commercial enzyme called SERA ZYME C-PE in the presence of ultrasound in a multi-frequency ultrasonic cleaning unit; model TI-H-10 from Elma Schmidbauer GmbH, Germany. The energy of sonication applied was 200 W (ultrasonic power effective) and 800 W (ultrasonic peak performance max). The commercial enzyme product contains a Pectate Lyase with the calsiffication E.C. 4.2.2.2. A sequestering agent with the role of binding the metal ions in water was used. The agent was HEPTOL NWS in 2 mL/L concentration. The wetting and scouring agent SULFOLEN 148 of 2 mL/L concentration was added. 10 % of the fleet treatment was pH 7.5 buffer solution (0.1 molar sodium dihydrogen phosphate/disodium hydrogen phosphates). The experiments were conducted in a fabric to liquid ratio 1:10, at the temperature of 55 ^{0}C and a variable time between 20-60 minutes [2].

The bleaching treatments applied to the scoured samples were carried out under the following conditions: [3, 4, 5, 6]

- *Classical procedure*: 3 mL/L hydrogen peroxide (30 %) + 1 g/L NaOH + 4.5 mL/L sodium silicate; fabric to liquid ratio – H - 1:20; Temperature = 90-95 ^{0}C; time = 40 min.
- *Procedure with catalyst*: 3 mL/L of catalyst solution prepared from 1 g of catalyst + 1.5 mL 30 % hydrogen peroxide); fabric to liquid ratio – H - 1:20; Temperature = 60 ^{0}C; time = 40 min.
- *Procedure with laccase enzyme*: 3% o.w.f. (over fiber) commercial Laccase - Lava Zyme LAC, wich is a suitable enzyme for bleaching of cellulosic materials + buffer 0,1 molar acetic acid/sodium acetate (pH = 5); fabric to liquid ratio – H - 1:20; Temperature = 60 ^{0}C; time = 40 min.

The evaluated properties of 60 % cotton + 40 % flax materials bioscoured according to the experimental program [7] presented in the first part are presented in Table 1.

Table 1: *The properties of cotton 60 % + flax 40 % materials after the bioscouring treatment*

Samples	Enzyme concentration (%)	Weight loss (%)	Hydrophilicity (s)	Whiteness degree R (%)
1	1.70	3.04	4.6	43.78
2	2.70	1.59	3.4	46.23
3	1.70	2.85	5.2	47.55
4	2.70	1.25	3.2	45.03
5	1.00	3.55	7.8	46.35
6	3.00	1.11	6.0	45.58
7	2.00	2.06	4.4	46.48
8	2.00	2.18	4.0	46.43
9	2.00	4.03	9.6	46.80
10	2.00	2.57	7.2	45.78
11	2.00	1.4	7.2	47.35
12	2.00	1.39	10.4	45.55
13	2.00	1.89	5.0	44.35

The samples 10, 11, 12 and 13 (pretreated in the same conditions: 2 % enzyme concentration for a time of 40 minutes) were further bleached as described in table 2.

Table 2: *The Corespondence between pretreated samples and bleaching treatments applied.*

No.	Samples	Bleaching type
1.	10	Classical
2.	11	Catalyst
3.	12	Laccase
4.	13	Control

The efficiency of the alternative bleaching treatments compared to the classical one was established by measuring the following characteristics of the treated samples: 1) the whiteness degree R (%), 2) weight loss (%) and 3) hydrophilicity (seconds) as shown in table 3, as well as 4) the tensile strength [N] and 5) elongation at break [%] as shown in the table 4. The values of the whiteness degree were studied after different type of bleaching (hydrogen peroxide, catalyst and laccase) for the samples treated with the same concentration of Pectate Lyase enzyme SERA ZYME C-PE.

Table 3: *Comparative characterization of bleaching treatments on the bioscoured samples*

No	Samples	Type of bleaching	Treatment conditions	Weight loss (%)	Hydrophilicity (seconds)	Whiteness degree R (%)
1.	10	Alkaline bleaching	1:20 fabric to liquid ratio Temperature 90-95^{0}C time - 40 min 3 mL/L H_2O_2 (30 %) 1 g/L NaOH 4.5 mL/L Na_2SiO_3	2.53	2	63.38
2.	11	With Catalyst:	Fabric to liquid ratio H = 1:20 Temperature = 60 ^{0}C time = 40 min 3 mL/L of the catalyst (solution prepared from 1 g catalyst + 1.5 mL 30% H_2O_2	0.75	2	49.33
3.	12	With laccase enzyme	Fabric to liquid ratio H = 1:20 Temperature = 60 ^{0}C pH = 5 of 0.1 molar buffer of acetic acid / sodium acetate time = 40 min 3 % o.w.f. commercial Laccase	0.39	2	47.60
4.	13	Control	Fabric to liquid ratio H = 1:20 Temperature = 60 ^{0}C time = 40 min	0.16	3	46.33

To evaluate and compare the degradation occurred during the enzymatic preatreatment of cellulosic fabrics, before and after bleaching with enzymes, catalyst and classical method, measurements of the tensile strength and elongation at break for the treated 60 % cotton + 40 % flax material were performed. [8]

Table 4 presents the results of tensile strength and elongation at break for the treated sample fabrics.

Table 4: *Determination of the tensile strength after different bleaching treatments*

No.	Samples	Tensile strength [N]	Elongation at break [%]
1.	Classical	498.5	16
2.	Catalyst	619.9	17.9

3.	Laccase	621.2	20.1
4.	Control	673.9	21.1

The alkaline bleaching treatment shows a higher weight loss compared with the other samples treated with catalyst or laccase. For the all samples the hydrophilicity is the same. The whiteness degree obtained after the classical treatment is higher, followed by catalyst treatment and laccase one. According with the values of the tensile strength the tratment with catalyst caused a slight fiber damage comparing with the treatment with laccase.

3. CONCLUSIONS

During the studies carried out it was found that the alternative methods shows a promising and viable ecological solution for bleaching of cellulosic, lignocellulosic fabrics and mixtures of thereof. Moreover, these treatments are more environmentally friendly by less energy consumption and water pollution and less destructive to the fabrics by a small decrease of their tensile properties which means a minimal amount of fiber damage.

ACKNOWLEDGEMENT

This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-1370

and

''Bast plants - Renewable Strategic Resources for European Economy - BASTEURES'' project, no. 210/2010 POS-CCE - supported by Structural Founds - "Investment in Your Future".

REFERENCES

[1] A. Farooq, S. Ali, N. Abbas, G. Alia Fatima, M. Azeem Ashraf, *"Comparative performance evaluation of conventional bleaching and enzymatic bleaching with glucose oxidase on knitted cotton fabric"*, Journal of Cleaner Production, 42, pp. 167-171, 2013.

[2] Catalog DyStar Textilfarben GmbH, 2007.

[3] R. Butnaru and L. Stoichițescu, "*Special finishing procedures of textiles fabrics*", Editura Gh. Asachi, Iași, 1995.

[4] C. Sîrghie, A. Botar, N. Dincă, G. Crăciun, M. Dochia, "*Environmentally friendly bleaching process of natural fibers by catalytic oxidation with polyoxometalates*", patent no. 122728, 2009.

[5] M. Pustianu,M. Dochia, M.S. Pernevan, C.Sîrghie, "*Study regarding the influence of the bioscouring treatment in ultrasound on 60% cotton+40% hemp materials, Part 1: Study regarding the optimization of the bioscouring treatment",* in Annals of the University of Oradea, Fascicle of Textiles, Leatherwork, VOLUME XV, No. 1, 2014, pp. 93– 98.

[6] M. Dochia, C.Sîrghie, M.S. Pernevan, M. Pustianu,"*Study regarding the influence of the bioscouring treatment in ultrasound on 60% cotton+40% hemp materials, Part 2: Study regarding the influence of the bioscouring treatment followed by a whitening treatment using various methods",* in Annals of the University of Oradea, Fascicle of Textiles, Leatherwork, VOLUME XV, No. 1, 2014, pp. 99 – 102.

[7] R. Mihail, "*Introduction to the strategy experimenting with applications in chemical technology*", Ed. Scientific and Encyclopedic, Bucharest, 1976.

[8] AGIR, Textile Engineer's Manual, Ed. AGIR, Bucuresti, 2004.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ANALYSING THE PEEL STRENGTH OF FUSIBLE INTERLINING USED IN WOOL FABRIC WITH ELASTANE

SARICAM Canan[1], KALAOGLU Fatma[1]

[1,] İstanbul Technical University, Faculty of Textile Technologies and Design, Department of Textile Engineering, Inonü Cad. No:65, 34437, İstanbul, Turkey, E-Mail:saricamc@itu.edu.tr

Corresponding author: Sarıçam, Canan, E-mail:saricamc@itu.edu.tr

Abstract: *Fusibles are used to improve the aesthetic and performance characteristics of wool fabrics. The peel strength of fused composites determines the durability of the pressing operation and they are influenced from the process conditions, the characteristics of fusible interlining and the fabric to whom they are sticked to. In this study, it was aimed to analyze the effect of fusible type and process conditions, weave type and different elastane compositions on peel strength. To this aim, two fusible types combined with eight different types of wool fabrics having different amount of elastane were studied. It was found out that only the fusible type and the process conditions are confirmed statistically that they influence the peel strength values. Nonetheless, it was observed as the elastane composition increased, the peel strength values tend to increase for twill type of fabrics and tend to decrease for plain type of fabrics. Moreover, the influence of composition may be in different direction when different type of Fusibles is used to form fusible composites. In conclusion, it can be stated that the dominant mechanism in determination of the peel strength is the selection of fusible type and suitable process conditions for this fusible type and more investigations are necessary if the composition of the material is also influential on the peel strength because of its compatibility with the fusible interlining.*

Key words: *Wool, Fusible Interlining, Peel Strength, Weave Type, Elastane***.**

1. INTRODUCTION

Fusibles are very important auxiliary material especially for use with the wool wfabrics that influences the shape and aesthetic of the garment. The fused composites are obtained by using a point bonding procedure followed with a heat pressing procedure. Other than dimensional stability, fastness to washing and chemical dyeing, peeling strength is an important parameter for determination of the durability of the fusing process. It was stated that since the fused composites involve three separate materials which are fabric, fusible interlining and adhesion material, the characteristics of the material are influenced from these materials. Moreover, it was specifically claimed by, the type and amount of the adhesive are the two important parameters in the peel strength values [1] with the affinitiy of the adhesive material to the fabric and the bonding of the material at all points to the fabric [2]. Nonetheless, the amount of the studies [3,4,5] is limited regarding the analyzing of the peel strength and the influential parameters on them.

In this study, it was aimed to analyze the influence of the fabric, fusible type and processes on the peel strength values on peel strength values. Within this regard, two fusible types were combined with eight wool fabrics that differ in terms of composition and weave type basically. The influence of the fabric, fusible type and process conditions were analysed statistically.

2. MATERIAL AND METHOD

The characteristics of 8 different types of fabrics used as specimen are given in Table 1 below. The standards TS 250EN 1049-2, TS251, TS 244 EN ISO 2060 were used to determine weft and warp densities, fabric weight and yarn counts respectively.

Table 1: *The characteristics of the fabrics used for the study*

Fabric No	Composition	Weave type	Weft density (weft number /cm)	Warp density (warp number /cm)	Weft yarn count (Nm)	Warp yarn count (Nm)	Weight (gr/m^2)
1	100% Wool	TWILL	26	33	28	28	238
2	100% Wool	PLAIN	28	50	30	30	228
3	98% Wool 2% Elastane	TWILL	23	31	32	30	205
4	98% Wool 2% Elastane	PLAIN	22	23	30	30	234
5	96% Wool 4% Elastane	TWILL	23	27	30	30	190
6	96% Wool 4% Elastane	PLAIN	25	25	30	30	226
7	59% Wool 39%PET 2% Elastane	TWILL	23	25	35	35	171
8	59% Wool 39%PET 2% Elastane	PLAIN	23	25	35	35	171

Table 2: *Fusible interlinings and process conditions*

Fusible type	Material	Weight (g/m^2)	Fusing material	Process conditions
Fusible 1	80% Viscose,20% PET	79	Polyamide $12g/m^2$, 17 dots	121-127 C, 2-4 bar, 12-15 second
Fusible 2	100%PET	57	Polyamide $7g/m^2$, 34 dots	121-127 C, 2-4 bar, 12-15 second

Peel strength was tested using Instron Tensile Tester for each three specimen by measuring the tensile force in the process conditions of 10 cm/minute [6].

3. RESULTS

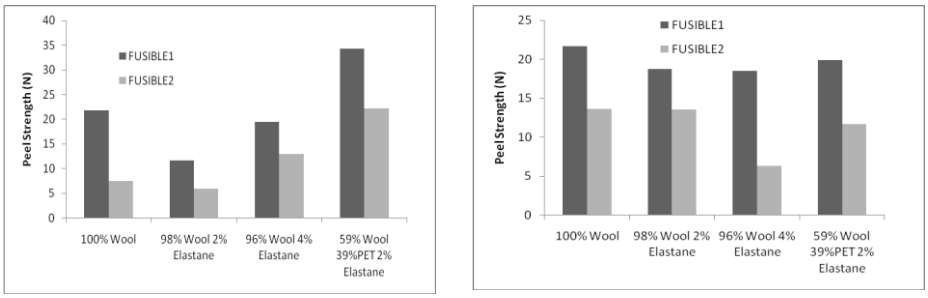
The peel strength of the fused composited that are combined with the Fusible 1 and 2 were given in Table 3 below.

Table 3: *Peel strength of Fusible 1 and 2 in warp and weft direction*

Fabric no	Composition	Peel strength in weft direction (N)	
		Fusible 1	Fusible 2
1	100% Wool	21.83	7.5
2	100% Wool	21.72	13.64
3	98% Wool 2% Elastane	11.67	6.0
4	98% Wool 2% Elastane	18.75	13.54
5	96% Wool 4% Elastane	19.45	12.92
6	96% Wool 4% Elastane	18.51	6.3
7	59% Wool 39%PET 2% Elastane	34.27	22.15
8	59% Wool 39%PET 2% Elastane	19.88	11.7

Within Table 3, it is observed that the peel strength of the Fusible type 1 which is made up of 80% Viscose, 20% of PET is higher than the peel strength of Fusible type 2 which is made up of 100% PET for all the specimen. In fact, the influence of the selection of fusible type and specific process conditions for this fusible type on the peel strength is proven statistically since the independent t-test result (t=3.101; p=0.008).

Figure 1a and Figure 1b shows the relationship between the material type and the peel strength for the twill and plain fabrics respectively.



(a) *(b)*

***Fig. 1**: Peel strength for Fusible 1 and 2 for a) Twill fabrics b) Plain Fabrics*

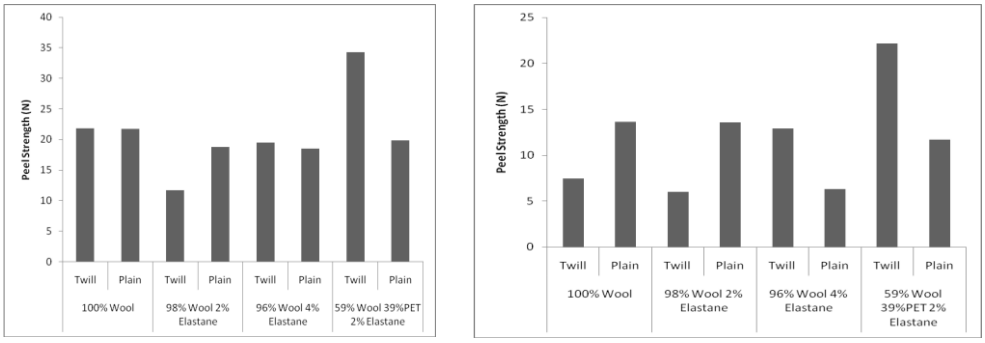
From Figure 1a, it can be seen that the specimen made up of 98% wool and 2% elastane gets the lowest value and the fabric that is composed of 59% wool 39%PET and 2% elastane gets the highest value in terms of peel strength for both Fusible type 1 and 2. Figure 1a also shows that the specimen 100% wool gets lower peel strength value than the specimen 59% wool 39% PET and 2% elastane. On the other hand, if the specimens that are involving only wool or only wool and elastane, it is observed that the peel strength value decreases as the amount of elastane amount increases and then it increases as the amount of elastane further increases for both Fusible types 1 and 2 in twill fabric structure. Figure 1b shows the specimens that are constructed in plain weave. Within Figure 1b, it can be seen that the specimen that is composed of 100% wool gets the highest value in terms of peel strength in both Fusible Type 1 and 2. The specimen that is composed of 98% wool and 2% elastane gets second highest peel strength value for Fusible Type 2 and the specimen that is composed of 59% wool 39%PET and 2% elastane gets the second highest peel strength value for the Fusible type 2.Moreover, the relation about the amount of elastane and the peel strength that was put forward in Figure 1a was not observed in Figure 1b. Thus, there is no apparent relation with the peel strength and the composition of the fabric specimen. Actually, one way ANOVA test results also confirms this because, no statistically significant relationship was observed between material composition and the peel strength values (F=1.363; p=0.301). Nonetheless, although the relation between the composition and the peel strength was not found statistically, considering the findings above, the composition of the material may be influential on the peel strength values indirectly due to its compatibility with the fusible and adhesive material and process conditions.

Figure 2a and 2b shows the peel strength values for specimen that is the same composition but having different weave types for Fusible Type 1 in Figure 2a and Fusible Type 2 in Figure 2b.

According to Figure 2a which shows the values for Fusible type 1, the peel strength values are almost the same in twill and plain structures for the specimen 100% wool and 96% wool and 4%elastane. On the other hand, the specimen that is composed of 98% wool 2% elastane gets lower peel strength value for twill structure whereas the specimen that is composed of 59% wool 39% PET and 2%elastane gets lower peel strength value for the plain structure.

According to Figure 2b which shows the values for Fusible type 2, the peel strength values are higher in plain structure for the specimen 100% wool and 98% wool 2%elastane whereas the

peel strength values are higher in twill structure for the specimen 96% wool 4% elastane and 59% wool 39%PET and 2%elastane. Nonetheless, no statistically significant relation was observed (t=0.390; p=0.702) between the weave type and the peel strength.



(a) *(b)*

Fig. 2: *Peel strength for different material composition and weave structure a)Fusible Type 1 b)Fusible Type 2*

5. CONCLUSIONS

In the study, the fusible type and process conditions and the fabric parameters such as elastane composition and weave type were analyzed to see if they have influence on the peel strength values. It was found out that only the fusible type and the process conditions are confirmed statistically that they influence the peel strength values. Nonetheless, it was observed as the elastane composition increased, the peel strength values tend to increase for twill type of fabrics and tend to decrease for plain type of fabrics. Moreover, the influence of composition may be in different direction when different type of Fusibles is used to form fusible composites.

Considering the results stated above, it can be stated that the dominant mechanism in determination of the peel strength is the selection of fusible type and suitable process conditions for this fusible type and more investigations are necessary if the composition of the material is also influential on the peel strength because of it compatibility with the fusible interlining.

REFERENCES

[1] S. J. Kim, K.H. Kim, D.H. Lee, G.H. Bae, "*Suitability of nonwoven fusible interlining to the thin worsted fabrics"* International Journal of Clothing Science and Technology, vol.10, 3(4), pp.273-282, 1998.

[2] I. Holme, "*Adhesion to textile fibres and fabrics"*, International Journal of Adhesion and Adhesives, vol.19, pp.455-463, 1999.

[3] Lai, SS., "*Optimal Combinations of Face and Fusible Interlining Fabrics"*, International Journal of Clothing Science and Technology, vol.13, 5, pp.322 – 338, 2001.

[4] Shiloh, M. "*The Wrinkling and Bending of Fusible Interlinings",*The Journal of the Textile Institute, vol.63, 10, pp.533-543, 1972.

[5] Morris, PA., Chamberlain, NH. "*The Physical Properties of Textile Laminates Made with Fusible Interlinings",* Clothing Institute Technological Report No.2, 1971.

[6] R. Shishoo, P. H. Klevmar, M. Cednas, B. Oloffson, "*Multilayer Textile Structures Relationship Between the Properties of a Textile Composite and its Components,"* Textile Research Journal, pp.669-679, Aug. 1971.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ESD - FUNCTIONAL CLOTHING

SCARLAT Razvan[1], CARPUS Eftalea[2], DONCIU Codrin[3], POPA Alexandru[4], BARBU Ionel[5]

[1, 2]The National Research and Development Institute for Textile and Leather Bucharest, 16, Lucretiu Patrascanu str., sector 3, Bucharest, Romania, razvan.scarlat@certex.ro

[3]"Gheorghe Asachi" Technical University of Iasi, 76, Bd. Prof. Dimitrie Mangeron, Iasi, Romania, cdonciu@tuiasi.ro

[4,5]"Aurel Vlaicu" University of Arad, 77, Bd. Revolutiei, Arad, Romania, alexpopaarad@yahoo.com

Correspomding author: Scarlat Razvan, e-mail: razvan.scarlat@certex.ro

Abstract: *The functional clothing represents a sustainable development direction of in the field of technical textiles, a bridge between various activity domains, a solution to user's complex requirements. The research and development potential in the field is supported by the new fibers/ yarns generation, the new technologies and the market niches, as well. Protective clothing is now a major part of textile classified under technical textile. Protective clothing refers to the garment and other fabric related items designed to protect the wearer from harsh environmental effects that results in injuries or death. The innovation, as a result of convergence processing technologies, consumer demands and what is viable on the market, defines the personal protective equipment field.*

In this article, we present the work of an ESD protective clothing development. Therefore, it has been applied a modern knitting technology, on 7E and 12E STOLL machines, using cotton and wool yarns as base yarn and conductive yarns for plaiting structures. Also, the optimal parameters establishment and the functional requirements are aspects of the research activity performed. The experimental models have been conducted in order to demonstrate the design concept used and choosing the optimal variant.

The characterization of the developed experimental variants took into account the evaluation of physico-mechanical and electrical characteristics. From the electrical point of view, the variants have been mainly evaluated through "point to point" method in terms of electrical isolation efficiency dimensional changes analysis.

Keywords*: textile, knitted structures, electrostatic discharge, conductive yarn*

1. INTRODUCTION

The EU's priorities are outlined in the Europe 2020 Strategy: focusing on Europe becoming a smart, sustainable and inclusive economy by 2020.

The clothing and textiles sector is a significant part of the world's economy. Textiles and clothing is a diverse sector that plays an important role in the European manufacturing industry, employing 1.7 million people and generating a turnover of EUR 166 billion. The sector has undergone radical change recently to maintain its competitiveness with a move towards products with higher value added [1]. The textile and clothing industry (T/C industry) is a very diverse and heterogeneous industry, covering a wide range of important activities regarding the transforming of

fibers into yarns and yarn into fabrics used for textile products/ systems development meant for all activity domains [2,3]. Years ago, technical textiles were defined as textiles that are other than clothing or home textiles. Advances in the field of textile fibres as well as in the flexible processing systems have assigned to the technical textiles a new definition, namely: "Technical textiles are materials meeting high technical and quality requirements (mechanical, thermal, electrical, durability etc.) giving them the ability to offer technical functions" [4].

The value chain of technical textiles is influenced by political, economical, sociological, tehnological, legal, ecological, cultural and historical factors with environmental and social effects [5].

Functional apparel can therefore be defined as a generic term that include all such types of clothing or assemblies that are specifically engineered to deliver a pre-defined performance or functionality to the user, over above its normal function [6]

Technical textiles represents a multi-disciplinary field with numerous end use applications.

Types of technical textiles [7]:

- mechanical functions: mechanical resistance, reinforcement of materials, elasticity, tenacity;
- exchange functions: filtration, insulation and conductivity, drainage, impermeability, absorption;
- functionalities for living beings: antibacterial, anti dust mites, biocompatibility, (hypoallergenic textiles), biodegradability/ bioresorption;
- protective functions: thermal, fire, mechanical, chemicals, impermeable – breathable, antistatic, particles antirelease, electrical insulation, IR and UV rays, NBC (nuclear, biological and chemical), high visibility, electromagnetic fields etc.

Protective clothing is now a major part of textile classified under technical textile. Protective clothing refers to the garment and other fabric related items designed to protect the wearer from harsh environmental effects that results in injuries or death.

The innovation, as a result of convergence processing technologies, consumer demands and what is viable on the market, defines the personal protective equipment field (fig. 1).

Fig. 1: *The factors convergence influencing the innovation process (http://www.textiletoday.com.bd/transformation-of-the-textile-and-apparel-industry-of-bangladesh-through-innovation/)*

The studies regarding the essential performances of ESD protective garments lead to a number of contradictory requirements when defining the ideal ESD garments: (i) high conductivity to facilitate the dissipation process and to avoid charge accumulation and (ii) high resistivity to

prevent fast dissipation and to limit the energy transfer during discharging [8]. They also must have good shielding properties to reduce the intensity of the electrostatic fields generated under the garment [9] and anti-static properties to not generate electric charge when come in contact with other materials [10]. These requirements can't be met at the same time by a garment, thus a compromise will be considered. In general is aimed to obtain a garment with dissipative properties that, according to Standard EN 1149-5:2008, must possess a half decay time of the electric field strengthunder 4 seconds, shielding factor greater than 0.2 or surface resistance less than 2.5 × 109 Ω [11].

2. EXPERIMENTAL PART

For ESD equipment development was chosen a knitted bilayer structure that can assure good protection from accidental electrical discharges on the dielectric layer and a drainage of accumulated electric loads through conductive layer. In these conditions, the bilayer type approaching allows the delimitation of accidental discharge path from the controlled discharge path of the electrification material.

The knitting was made at SC TANEX SRL on the 7E and 12E STOLL knitting machines, with the possibility of yarn tension adjusting in order to obtain a correct yarn plating.
The experimental matrix comprise the following yarns:

- base yarn: - Nm 50/3, 100% cotton;
  - Nm 30/2, 100% wool;
- plaiting yarn: - conductive yarn 75% cotton + 25% epitropic yarn (Nm 34/1carbon coated polyester);
  - conductive yarn multifilament bi-component core-sheath structure, Nega-Stat P210, 112 dtex 12 f, polyester filament with trilobal core and carbon outer layer;
  - conductive yarn Nega-Stat P190, 155 dtex, 24f, polyester filament with carbon trilobal inner core;
  - conductive yarn filament nylon surface saturated with carbon particles.

Reduced elasticity of the used yarns imposed low speed knitting to 0.65 m/ sec, and the plaiting of knitted fabric was performed in two textures of fabric.

The characterization of experimental variants took into account the evaluation of the physico-mechanical and electrical characteristics. The main tested characteristics are presented in tab. 1:

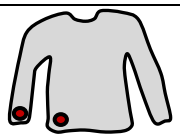
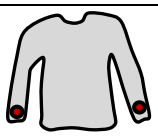
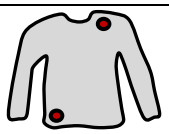
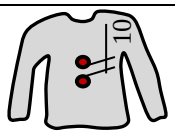
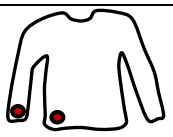
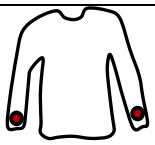
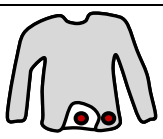
Tab. 1: *The main physico-mechanical and electrical characteristics*

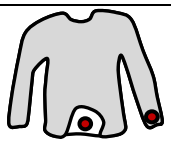
Variant no.	Bilayer structure	Weight [g/m^2]	Density		Thichness, [mm]	Discharging time $t_{1/2}$ (F1)	Discharging time $t_{1/2}$ (F2)	Conductive yarn percentage
			rows/10cm	wales/10cm				
5		470	43	92	1,58	0,0227	0,0228	5
7		487	44	86	1,63	0,0274	0,0246	7
21		521	47	71	1,65	0,0253	0,0282	21
8		705	37	61	3,52	0,026	0,0268	4.5%

The variants have been evaluated through "point to point" method in terms of electrical isolation efficiency according to directions graphically displayed. All samples presents good

electrical isolation properties at the surface. Especially, with very good properties, it stands out the following variants: V7 and V8.

Tab. 2: *Point to point resistance*

Measurement points location	Variant	Point to point resistance	Observations
	V5	96.3 MΩ	Front measurement
	V7	1.5GΩ	
	V8	1.7GΩ	
	V21	23.2MΩ	
	V5	183MΩ	Front measurement
	V7	2GΩ	
	V8	2GΩ	
	V21	36.6MΩ	
	V5	22.5MΩ	Front measurement
	V7	1.2GΩ	
	V8	49MΩ	
	V21	5.35MΩ	
	V5	11.4MΩ	Front measurement
	V7	0.4GΩ	
	V8	0.38GΩ	
	V21	7.7MΩ	
	V5	120MΩ	Back measurement
	V7	1.9GΩ	
	V8	2GΩ	
	V21	20.2MΩ	
	V5	134MΩ	Back measurement
	V7	2GΩ	
	V8	2GΩ	
	V21	37MΩ	
	V5	20.9MΩ	Back measurement
	V7	0.97GΩ	
	V8	0.7GΩ	
	V21	6MΩ	
	V5	8.3MΩ	Back measurement
	V7	0.6GΩ	
	V8	0.5GΩ	
	V21	2.7MΩ	
	V5	2.4MΩ	Measurement from front to back
	V7	0.18GΩ	
	V8	39MΩ	
	V21	0.8MΩ	

	V5	109MΩ	Measurement from front to back
	V7	2GΩ	
	V8	1.85MΩ	
	V21	25MΩ	
	V5	40MΩ	Measurement from front to back
	V7	0.6GΩ	
	V8	1.1GΩ	
	V21	9.1MΩ	
	V5	157MΩ	Measurement from front to back
	V7	2GΩ	
	V8	2GΩ	
	V21	39MΩ	
	V5	99.2MΩ	Measurement from front to back
	V7	1.38GΩ	
	V8	2GΩ	
	V21	23MΩ	

The results of dimensional changes analysis after 1, 5, 10, 15 and 20 washes are presented in tab. 3.

Tab. 3: *Dimensional changes*

Variant no.		**Washing and drying dimensional changes (%)**				
	No. of washes	**1 wash**	**5 washes**	**10 washes**	**15 washes**	**20 washes**
5	Sleeve length	-0.76	-0.91	-1.36	-1.67	-1.97
	Equipment length	-0.90	-1.06	-1.66	-2.04	-1.59
7	Sleeve length	-0.45	-0.75	-1.35	-1.66	-1.66
	Equipment length	-0.38	-0.61	-1.61	-1.92	-1.92
21	Sleeve length	-0.44	-0.74	-1.04	-1.34	-1.34
	Equipment length	-0.38	-0.54	-0.77	-1.23	-1.23
8	Sleeve length	-0.28	-0.57	-0.86	-1.00	-1.29
	Equipment length	-0.52	-0.74	-1.11	-1.34	-1.34

Regression equations representing dimensional change tendency define the interdependence or the link between observed variables in statistic data (tab. 4).

Tab. 4 *Regression equations*

Variant no.	**Dimensional changess**	**Dimensional change tendency equations**	**Dependancy grade, R^2**
5	Equipment length	$y = 0,0258x^3 - 0,2439x^2 + 0,3602x - 0,894$	0,9955
	Sleeve length	$y = 0,0008x^3 + 0,0054x^2 - 0,3555x - 0,852$	0,9901
7	Equipment length	$y = 0,0508x^3 - 0,3939x^2 + 0,4852x - 0,584$	0,9962
	Sleeve length	$y = 0,0817x^3 - 0,6793x^2 + 1,009x - 0,826$	0,9779
21	Equipment length	$y = 0,025x^3 - 0,1821x^2 + 0,0929x - 0,38$	0,9979
	Sleeve length	$y = -0,4x - 0,39$	1
8	Equipment length	$y = 0,0317x^3 - 0,2436x^2 + 0,2748x - 0,58$	0,9989
	Sleeve length	$y = 0,0175x^3 - 0,2039x^2 + 0,2086x - 0,538$	0,9995

3. CONCLUSIONS

- To satisfy the two conditions for the ESD garments (high resistivity and high conductivity) it was opted for a bilayer structure:
• internal layer: best charge dissipation properties;
• external layer: good charge dissipation properties and high surface resistivity.

- When using a rib structure, voluminousness of the fabric will be higher due to the spatial arrangement of the stitch elements, due to an increased amount of incorporated air into the knitted structure. These aspects favour on the one hand a very high thermal comfort and on the other hand an effective air flow, respectively perspiration vapours between body and environment.

- Simple electrical measurements, like two point and four point DC- measurements reveal the good electrical behaviour of the yarn and fabric of the tested samples, when containing carbon covered fibers. The measured resistances are in the MΩ - range and are sufficient to avoid electrical charge build-up in the fabric.

ACKNOWLEDGEMENT

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project PCCA 179 - 2012 "*Haine ESD realizate din fibre cu miez conductor tricotate bistrat*".

REFERENCES

[1] http://ec.europa.eu/growth/sectors/fashion/textiles-clothing/index_en.htm.
[2] http://www.investineu.com/content/textile-industry-european-union.
[3] http://www.ifm.eng.cam.ac.uk/uploads/Resources/Other_Reports/UK_textiles.pdf
[4] [EncyclopediaUniversalis][http://www.tpot.eu/docs/Workshops/ LEITAT_5_Technical_Textiles_1.pdf].
[5] http://www.ifm.eng.cam.ac.uk/uploads/Resources/Other_Reports/UK_textiles.pdf
[6] M. Md. K.Akter, transformation of Textile and Apparel Industry of Bangladesh trough Innovation,www.textiletoday.com.bd.
[7] De. Gupta, Functional clothing – Definition and classification., Indian Journal of Fibre & Textile Research, vol.36, December 2011, pp.322.
[8] J. Paasi, S. Nurmi, T. Kalliohaka, G. Coletti, F. Gustavino, et al.: Electrostatics 2003 Conference (2003), p. 23.
[9] A.S. Ardeleanu, A. Verejan and C. Donciu: Acta Electrotehnica vol. 51 (2010), p. 128.
[10] G. Baumgartner: Consideration for developing ESD garment specifications, ESD TR 05-00Report, ESD Association (2000).
[11] Standard EN 1149-5:2008, Protective clothing - Electrostatic properties - Part 5: Material performance and design requirements (2008).

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE NEED TO RECYCLE TEXTILE WASTES. LEGISLATIVE ASPECTS

TIMOFTE Claudia Simona

University of Oradea, Department of Law and Public Administration, Faculty of Law, 26 Gen. Magheru St., 410048, Oradea, Romania,
E-Mail: clau_timofte@yahoo.com

Corresponding author: Timofte Claudia Simona, E-mail: clau_timofte@yahoo.com

Abstract: *The paper presents arguments and examples regarding the need to reuse, sort, manage and recycle more efficiently the textile wastes. Waste are increasing from a quantitative point of view and represent a major problem in each European country and the textile waste represent 5% of the total quantity of waste at a global level. It is estimated that about 95% of what it reaches the landfill could be reused so that the necessity of recycling is obvious.*
The constant need of transforming the wastes into by-products represents a priority because the textile waste have a special characteristic in the way that they can be reused or even repurposed.
The paper also syhthesizes the legislation that makes reference to the textile waste, their classification and the obligations of the local community members, natural or legal persons.
It is also presents the current situation of the textile waste with respect to Romania and Bihor county, but there are also presented other numerous cases, examples and situations in which the waste is recovered/collected properly. *The examples have the role of showing and emphasizing the concerns of some companies, brands, institutions or local authorities, specialists and specialized personnel within the agencies of environmental protection to encourage recycling or reuse of the textile products that are inappropriately considered as wastes.*
The information for this paper was collected from literature, from the Agency of Environmental Protection Bihor and on the Internet.

Key words: *reusage, by-product, legislation, codes, valorisation*

1. INTRODUCTION

Waste is any substance or object which the holder throws or intends or is required to discard under Directive EP and Council 98/2008 on waste regime.

At the moment, the waste management is based on the provisions of the Environmental Law no. 195/2005 as amended, Law no. 211/2011 on waste regime and subsequent legislation, that transposes the EU legislation, namely Directive EP and Council 98/2008 on waste regime and abolition of the Directive 12/2006. Processing and reporting of data on waste management has in view the EC Regulation no. 2150/2002 of the EP and of Council on waste statistics, Commission Decision nr. 2011/753 / EU notified under the document no. C (2011) 8165. The following principle is also applied: “the polluter pays”, extended responsibility of the generator, economic profitability of recycling and waste hierarchy.

According to Law no. 211/2011, Art. 4, the waste hierarchy is applied according to prioritization in legislation and policy on the prevention of waste generation and management, as follows:

a) prevention; b) preparation for reuse; c) recycling; d) other recovery operations, e.g. energy recovery; e) removal.

Textile waste are among the main groups of waste that is suitable for recycling and recovery processes, along with waste glass, plastic, scrap metal, paper, cardboard and wood (Law 465/2001 which classifies waste). Globally, textile waste represents 5% of the total waste [1]. The same source shows that, according to the American Environmental Protection Agency, there are reused only 15% of the textile waste, although 95% of what reaches the landfill could be valorised [2].

2. SITUAŢIA ACTUALĂ A DEŞEURILOR TEXTILE ÎN ROMÂNIA ŞI JUD. BIHOR

In Romania the central authority for environmental protection promoted those legislative measures aimed at meeting the minimum obligations but mandatory for all EU Member States.

Thus the Integrated Environmental System was established and optimized that allows / will allow the active participation of society, economic operators and citizens that can communicate online interactively with the environmental institutions in Romania; thus, they could participate in the formation of databases on areas of national interest.

The waste generators who hold an environmental permit were provided in the environmental permit for operation with the obligation of reporting statistical data yearly basis in a format established by the competent environmental authority. Operators registered in SIM conformed themselves; therefore they requested the access approval in SIM on Waste / Waste Statistics.

The main issue here is the participation / acceptance of economic agents in SIM registration and reporting, compliance with the reporting session duration, technical barrier and adaptation to the rigour / accuracy of data provision.

AEP (Agency of Environmental Protection Bihor) develops activities in waste management under NAEP Bucharest and MAWF coordination, where appropriate, taking into account the provisions of the national law.

AEP Bihor submits annually in the first semester the yearbook on the Status of environmental factors in Bihor County. Herein (Chapter Waste), there are found data on waste management structured according to data provided by NAEP guideline or by the Minister Order of Environment.

In GD. 856/2002 on the evidence of waste management and for approving the list of waste, including hazardous waste, industrial waste codes are specified. Textile waste can be found in category 04. Waste from leather, fur and textile industries or subcategory 04 02 waste from the textile industry. Their specific waste codes are:

04 02 09 wastes from composite materials
04 02 14* wastes from finishing containing organic solvents (* hazardous waste)
04 02 16* dyestuffs and pigments containing dangerous substances
04 02 17 dyestuffs and pigments other than those specified at 04 02 16
04 02 21 unprocessed textile fiber waste
04 02 22 processed textile fiber waste
04 02 99 other unspecified waste

In category 20, subcategory 20 01 separately collected fractions, no waste code clothing and January 20 10 January 20 11 textile waste code. For this code there weren't reported quantitative data on selective collection in Bihor. In urban areas, the municipal waste is collected selectively, the

combustible fraction of the municipal waste is directed towards co-incineration/ heat power recovery. But it is estimated the percentage mass composition of the mixed municipal waste collected from the environment in Table 1.

Table 1:*The percentage mass composition of the collected mixed municipal waste (AEP Bihor [3])*

Composition of municipal wastes RURAL 2014	Kg	**%**
Textiles	**37.6**	**3.94**
Paper / Cardboard	25.6	2.68
Plastic	46.6	4.89
Wood	13.3	1.39
Glass	20.3	2.13
Metals	7.5	0.78
Wastes from constructions	14.3	1.50
Biodegradable	447.3	46.90
Other	330.3	34.69
Unprocessed quantity input	952	100

Selective collection at source is carried out only in the premises of the economic operators, under the afore-mentioned codes. There have not been received reports from institutions and operators on disposing of bedding cassation or textile / knitting /garment. Textiles / clothing collected from households were also not reported under the waste code 20 01 11 and 20 01 10 for reasons of storage due to the outdated procedures of the present situation in waste management when it is requested to pay for the waste management and not to be awarded for providing the waste

These wastes are managed under the form of services by applying the principle of extended responsibility of the generator and the principle “polluter pays”. Management reporting is stipulated in the environmental permit of the licensed operators. Collecting for the reuse of textiles was authorized for AEP Bihor for Roxana Textil Colect SRL Oşorhei - AM no. 52 / 15.03.2010; point of collection / recovery of recyclable non-metallic waste Oşorhei no. 66.

In 2011 they reported to the collection and recovery of 48 tons waste under the waste code 04 02 21 and 1.8 tons under the waste code 04 02 22 in Popesti Leordeni.

If the operator from Bihor / Oradea works in Lohn system, it returns the waste materials to the provider especially for the fibers / natural materials. The non-recyclable waste in Bihor / Oradea are routed to disposal facilities or thermal utilization in the form of an authorized combustible stream under the code 19 12 10; and code 19 12 12;; respectively to Chișcădaga/ CarpatCement or Holcim / Ecovalor Chistag. In rare cases the waste reaches SC Minet Rm Valcea.

In Romania a large quantity of used clothes are brought. It was a period between 1990-1996 when the import of second-hand clothes exploded and in the recent years a new growth is observed. Many Romanians buy these products both in shops and in markets, bazaars and fairs. In Oradea, in Ocska market a large amount of second-hand clothing and footwear products are now traded, thanks to the very affordable price and their good quality. However, there is some degree of wear and much of these products will not ever sell. Like in the sale of second-hand cars, Romania became a small "warehouse" for these products. Europeans 'are getting rid off' of old, old-fashioned, worn, useless things. Leaving aside the topic of selling second-hand cars, we may say that the market Ocska in Oradea is covered by approx. 40%, by these products which is a lot and showing a sad aspect of this situation.

Among the counties that own modern waste sorting stations, in Buzau a station aligned with European requirements in place was inaugurated in Stânceşti, Buzau. In addition to the groups of waste that are collected selectively across the country, here are also recycled waste textiles, altogether

with recyclable waste collected selectively from the population, economic agents from the containers intended for selective collection on public land and from the " yellow bag ". SC RER Ecologic Service S.A. Buzau is the only textile waste collector from Buzau county, built inside the Regional Deposit of non-hazardous waste [4].

3. THE NECESSITY OF WASTE CONSTANT TRANSFORMATION INTO BY-PRODUCTS

In general, the waste is growing in terms of quantity and is a major issue in every European country. In the industrial sector we talk more about Rational, clean or environmental technologies or eco-technologies [5].

According to the waste hierarchy it is recommended the prevention / reduction of waste production or their preparation for re-use; recycling, recovery and disposal should be avoided in terms of the waste hierarchy. Also the Law no. 211 of 15 November 2011 defines the By-product as "a substance or object resulting from a production process whose main objective is not to produce it" and that cumulatively fulfills several conditions, including that "it meets all relevant requirements for the product, environmental protection and health protection for its specific use and will not lead to overall adverse environmental or human health "[6].

Among the main groups of waste, textile waste can easily be subjected to recovery processes.

For a proper reuse, it is necessary the sorting of textile waste:

- natural or synthetic;
- according to their ecological impact: very polluting, polluting or non-polluting;
- according to the degree of workability/processability in: processed by complete textile processes, processed by incomplete textile processes or unprocessed by textile processes.

To show why reuse or recycling of textile waste are important or what are the negative effects of the textile waste, some examples are given:

- In November 2015 the European Union announced an investment of 3.6 million euros in a program to reduce carbon emissions and water consumption in the European textile industry. It will be implemented in 11 countries, including Romania and this program is intended to reduce by 90,000 tons of textile waste that reaches the landfill, by 2019 [1]. One of the main objectives is that waste to be recovered from the production line.
- There are brands and companies (organization I: Collect, for example) which have developed a global network of waste collection textiles in collaboration with major companies (H & M, Puma, Levi Strauss & Co., American Eagle Outfitters and others) that collects the textile waste from households. Thus, in the city of San Francisco there is a municipal program designed to prevent storage or textile waste incineration [2].
- Recycling saves raw materials, electricity (using dozens of cars in a technological flow), time, resources (use of enormous amounts of water and other substances: quantities of dye, chemicals, fixing agents etc.), it pollutes the environment less (using dyes, chemicals), decrease of costs for finished goods;
- Are in an overwhelming proportion; over 90% of the textile waste may be reused in the same form, or as a raw material for various items of clothing;
- Textile waste have a special feature, meaning that some of them may even re-used by collecting donations for the needy, or in the form of charity actions;
- There are companies concerned to expand their services in waste collection. For example, the company GREEN GLOBAL FUTURE S.R.L ensures the collection of textile waste from the special collection centers and their transportation to the recycling plants, where they are treated and ready to be put under any form, again in use [7];

- In Covasna county there are produced approx. 600 tonnes of textile waste per year and there are 14 textile factories, one of which gather in a month about two tons of textile waste. The members of a business cluster in Sfântu Gheorghe, together with specialists from Transilvania University from Braşov and Gheorghe Asachi from Iasi were able to make plates for insulation from the remains of textile materials, as replacements for the polystyrene plates which are readily degraded in time [8].

- Regarding the waste reuse and recover of textiles, RER Buzau sends them to Lafarge company that uses them in the cement production [9]

4. CONCLUSIONS AND RECCOMMENDATIONS

Sorting and recycling of textiles is highly appreciated in Romania. A small part of the waste resulted in the manufacture of garments and textiles are recovered and are reintroduced into the production process, and part of it is largely unrecoverable waste that is incinerated or ends up in landfills. Internationally, there are many ways and initiatives that take away textiles from landfills.

Targets and objectives set in national and European legislation are required, but each Member State may establish additional objectives and targets, more ambitious legislation of its own.

Romanian economic operators report generally non- hazardous waste generated by light industry under the codes: 04 02 09, 04 02 21, 04 02 22. Part of this waste reach incineration and the other part is removed through final disposal. There are also operators that eliminate this waste under the waste code 20 03 01 mixed municipal assimilated wastes. In the regulatory and monitoring waste activity, the waste stream is necessary to respect the hierarchy of waste.

Institutions of Bihor county (state / public) are imposed to follow the 'cassation procedure' to sell / assign a value to the objects proposed for cassation, regardless of their condition. It is an example of preparation for reuse.

By Law 211/2011, the industry proposed to conduct an audit of waste management operators who have implemented management systems voluntarily. Anyway, we have examples of target, minimizing hazardous waste, waste minimization, constantly transforming waste products.

GD 349/2005 sets maximum term of operation of landfills for non-hazardous municipal-industrial waste in accordance with the timetable for compliance. Legislation does not allow the mixed storage of waste under the code 20 03 01. The legislation obliges to reduce to 35% the amount of biodegradable waste landfilled compared with 1995, other and other restrictions, including the environmental tax pay per deposited ton under GEO 196/2005 as amended, including by OM / 2015.

As regards the population, it is desired a reduction in wasted materials and energy, to save raw materials and reduce air, soil and water pollution. Needed awareness campaigns for recovering, sorting and recycling of waste properly are required. At present, textile waste is not yet part of the public awareness actions in our country.

In Romania selective collection of textile waste is still not promoted, neither nationally nor locally. Tossing them into landfills is currently a widely-spread practice. It is known that some components / materials are harmful to the environment, meaning it does not decompose or break down very hard (Synthetic fibers) or directly pollute the environment through decomposition (methane producing woolen clothes).

Certainly, in not too far future, in addition to the large groups of recyclable waste (plastic, paper, cardboard, glass and metal), as it is the case for Oradea municipality, the waste textiles will be introduced with the obligation of the members of local communities to sort them. Beginning with 2016, the new regulations for the operation of sanitation services provide as liability for both individuals and legal entities, as an obligation "to provide pre-collection separately in containers provided by the operator of the service, distinctly marked and placed in dedicated facilities, of the

waste that they generated in their own household or because of the lucrative activities they carry out"[10].

REFERENCES

[1] http://www.green-report.ro/cum-ne-va-ajuta-ue-sa-reducem-deseurile-textile/
[2] http://www.ecoteca.ro/deseurile-textile.html
[3] APM Bihor
[4] http://www.sansanews.ro/stiri/actualitate/buzau/ne-aliniem-cerintelor-europene-statie-de-sortare-a-deseurilor-reciclabile-inaugurata-astazi-la-buzau.html
[5] http://www.mdrl.ro/euroimm/index.php?id2=050401
[6] LEGE nr. 211 din 15 noiembrie 2011 - Ierarhia deşeurilor
[7] https://www.greenglobal.ro/colectare-deseuri-textile/
[8] http://www.digi24.ro/Stiri/Regional/Digi24+Brasov/Stiri/Deseuri+textile+folosite+pentru+termoizolare
[9] (http://opiniabuzau.ro/ce-se-nt-mpl-cu-de-eurile-textile)
[10] http://www.ipp.ro/deseuri/3-lege

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

SILK FIBRE DEGRADATION AND ANALYSIS BY PROTEOMICS

YUKSELOGLU S.Muge[1], CANOGLU Suat[2]

[1]Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe Campus, 34722, Istanbul, Turkey, E-Mail: myukseloglu@marmara.edu.tr

[2]Marmara University, Faculty of Technology, Department of Textile Engineering, Goztepe Campus, 34722, Istanbul, Turkey, E-Mail: scanoglu@marmara.edu.tr

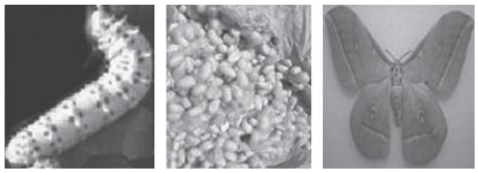
Corresponding author: Yukseloglu, ,S.Muge, E-mail: myukseloglu@marmara.edu.tr

Abstract: *Silk is one of the promising natural fibres* and *has a long established history in textile production throughout the centuries. Silk is produced by cultured silk worms, spiders, scorpions, mites and flies. It is extracellular proteinaceous fibres which consist of highly crystalline and insoluble proteins, the fibroins glued with sericin and an amourphous protein. On the other hand, understanding and controlling the degradation of protein materials are important for determining quality and the value of appearance retention in textiles. Hence, for silk textiles, appearance retention is critical value for the quality. And this is one of the key properties directly related to the degree and nature of protein degradation. It is therefore necessary to understand the silk composition and damage to obtain good conservation treatments and long-term preservation especially for the historical silk fabrics. In this study, silk fibre and its properties are briefly introduced along with images on their fibre damages. Additionally, proteomics method which helps to understand the degradation at the molecular level in textiles is introduced. Finally, proteomic evaluation of silk is summarized according to the researchers carried out in the literature.*

Key words: *Silk, Properties, Damage, Proteomics, Mass spectrometry*

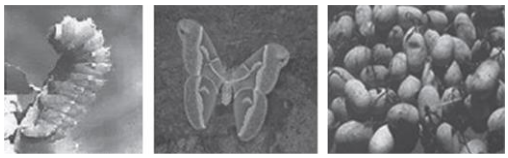
1. INTRODUCTION

Silk is an ancient and the only natural filament fibre which is used for thousands of years and nowadays the major producers are China, India and Japan. Silk is a fine, strong continuous fibroin filament with its lustre and excellent mechanical properties. It is produced by cultured silkworms and is a fibrous protein synthesized in specialized epithelial cells that line glands in the class of *Arachnida* and in several worms of the *Lepidoptera* larvae such as silkworms and insects as spiders, scorpions, mites and flies [1]. Some types of silk are suitable for commercial textiles due to the amount of silk that can be produced. These insects include the domesticated silkworm (*Bombyx mori*) and the wild silk worm i.e. *Eri* (Figure 1), *Tasar (Figure 2)* and *Muga (Figure 3)* [2].



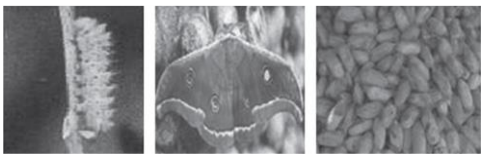
(a) (b) (c)

Fig.1: *Eri silk: (a) worm, (b) cocoons and (c) moth*



a) (b) (c)

Fig. 2: *Tasar silk: (a) worm, (b) moth and (c) cocoons*



a) (b) (c)

Fig. 3: *Muga silk: (a) worm, (b) moth and (c) cocoons*

The silk fibres of the *B.mori* silkworm are composed of a fibrous core twin thread of protein fibroin (70-80%) with sericin (20-30%) along with other impurities such as wax, colour pigments and inorganic components [3]. Whereas wild silk has higher fibroin content (80-90%) and lower sericin content (10-20%) than domesticated silk. Fibroin is the protein that forms the filaments of silkworm silk and gives unique physical and chemical properties to the fibre. On the other hand, sericin is consisting of group proteins which bring the fibroin filaments together and imparts strength to the cocoons. Silk sericin and other impurities cause hardness, coarseness and cover the lustre of silk fibroin. Hence, removing of sericin and other impurities is necessary because it provides soft, shiny and whitened silk fibres ready to be dyed.

For the silk textiles, appearance retention is critical value for the quality which is one of the key properties directly related to the degree and nature of protein degradation. It is therefore necessary to understand both silk properties and degradation which leads to a better conservation treatments and long-term preservation especially for the historical silk fabrics.

2. PROPERTIES OF SILK

As mentioned earlier, there are two main types of silk fibre: cultivated and wild. Both differ in diameter, cross-sectional shape and in fine structure. Its length is about 300-700 m; but generally is 300 m. and it has a fine diameter of 12-30 μm [4]. Because of its beauty, its handling and its high cost, silk is also known as a luxury fibre. Hence it remains its use both in various textiles i.e. fabrics, underwear, robes, socks, leggings, shirts, ties, blouses, formal dresses, high fashion clothes, folk costumes, furnishing applications, upholstery, rugs, beddings and more recently surgical sutures and etc. In the past, one of the elegant silk textiles was also used in caftans (see Figure 4) by several cultures in the world and these historical chic textiles must be well preserved for the next generations. And this can be achieved by understanding the fibre damages in textiles and advents of analysis methods, i.e. proteomics, for the degradation. Prior to the advent of proteomics method let's give a summary on the properties of silk, first.

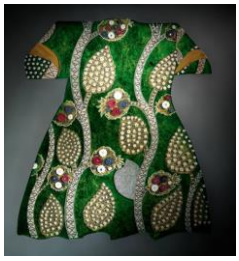


Fig. 4: *A silk caftan worn by Ottoman Sultan Süleyman [5]*

Silk fibres from the *B.mori* silkworm have a more or less irregular triangle cross-section with rounded corners (5–10 μm wide) and the density of *B.mori* silk is between 1.30-1.37 g/cm^3 [6]. Silk is more hygroscopic than cotton and can absorb up to 30% of its mass. Also, silk is one of the best natural fibres for its high strength and elongation at break result in higher fracture energy. It shows large initial modulus higher than that of nylon and wool but less than flax, polyester and aramid [7]. Although silk is a strong natural fibre, it loses up to 20% of its strength when wet. It has a good moisture regain of 11%. It can be weakened if exposed to too much sunlight and may also be attacked by insects, especially if left dirty. Silk is a poor conductor of electricity and thus susceptible to static cling. On the other hand, silk proteins consists of chain of amino acids, each of which is built of four groups: an amine group (-NH_2), a carboxyl group (-COOH), a hydrogen group (-H). These groups are bound to a carbon molecule designated as the α-carbon. The fourth group of each amino acid, the "R" group varies. The diversity of silk proteins is derived from these distinctive "R" groups [8]. Although acids and alkalis decompose warm silk easily, diluted acids revive the colour and increase the crispness of the silk. Diluted organic acids, tartaric acid and citric acid are used in finishing silk fabrics, whereas concentrated acids destroy silk. The concentrated solution of certain organic acids (i.e. formic acid) and 37% hydrochloric acid can cause dissolution and damage in proteins [9]. The sericin is soluble in hot soapy water or slightly alkaline solution while fibroin is insoluble. When silk fibre being heat-treated, it looses its weight gradually at 175^{o}C and its colour changes to black at 250^{o}C [10]. Silk is tolerant to burning, emitting a smell of burnt horn and leaving a black carbon residue. Silk resists heat better than wool and is a good thermal insulator.

3. SILK DEGRADATION

Understanding and controlling the degradation of protein materials are important for determining quality and the value of appearance retention in textiles such as silk materials. Protein oxidative damage is implication of decreased performance and degradation in proteinaceous materials such as silk, wool, even in reduced food quality, loss of enzyme activity etc [11-12]. For proteins, oxidative damage is generally attributable to the generation and attack of reactive oxygen species on both amino acid residue side chains and the protein backbone itself. Therefore for silk textiles, in particular the colour and mechanical properties of the material are critically influenced by the oxidative damage at the molecular level. Especially, both archaeological and historic silk fabrics that have survived to nowadays have been undergone some modifications in their physical appearance and chemical structure. Even though the damage cannot be entirely stopped, a good understanding of the textile composition and degradation can conduct to better conservation treatments and long-term preservation.

As silk is made of protein, it is at risk to damage by heat, humidity, light, microorganisms, chemicals and pollutants. And the processing of silk textiles involves degumming, weighting, dyeing and finishing which all these agents may break polymer molecules or cause other changes in their structure. Thus, all these processes weaken and degrade the fibre itself. Furthermore, fibre damage

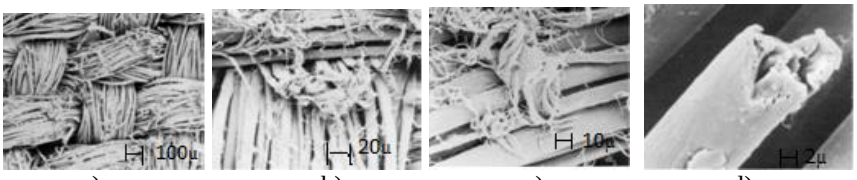
can be caused by light and other environmental factors as well. Microorganisms are also another problem for the archaeological silk textiles which must be understood to correlate damage of the fibre where it has been buried. Insects have also been a problem in museums and must be carefully monitored.

3.1 Examples on Degraded Fibres

As mentioned earlier that natural textile fibres are vulnerable to damage and degradation. Therefore, it is not surprising that in many archaeological contexts textiles do not survive. Fortunately attack by the majority of biological opponent is nearly eliminated if one or more of the following conditions endure: (1) absence of water; (2) temperature less than 5°C and (3) absence of air. Most of the significant collections of archaeological textiles have been preserved by such conditions. As a consequence, textiles rarely survive their useful lifetime. Even though, those textile collections in museums, where despite careful attention being taken are yet continue to degrade; because of on display they suffer photo-degradation and even suffer from insect damage. And in today's cities they become progressively more acidic.

In this section, fibres are in varying degrees subject to attack by light, heat and chemicals. So, differing forms of damage produce changes in morphology which are given below as some examples recognized by SEM images for fibre degradation.

In silk; the tensile strength, fibre cross-section and cocoon length are all influenced by the production condition and diet of the silk larva, and problems with either of these result in short cocoons and 'thin' filaments. Figure 5 shows wear damage in silk dress after 60 years; a) crown breakdown, b) fatigue breaks in weave, c) pilling and fibrillation, d) fibre fracture and rounding off.



a) b) c) d)

Fig. 5: *Wear damage in silk dress after 60 years [13]*

Some different archaeological environment has consistently surrendered with well-preserved textiles. The most widespread discovers have come from desert conditions, i.e. Egypt and Sudan, where the absence of water has prevented biological attack from the textile materials. The Northern European acid peat marshland has preserved many organic remains, including wood, animal and human cadavers, and textiles. Unfortunately acid conditions lead to acid-catalysed hydrolysis of cellulose, which eventually dissolves however consequently wool and silk survive, while linen, cotton, nettle and jute vanish [13].

4. PROTEOMIC EVALUATION OF SILK

In recent years “OMICS” technologies are one of the developing fields; before discussing proteomic method let us mention in brief what proteomics is: Genomics is a total practice for the description of information about genome and genes. Genomics studies provide assessment and interpretation of total genome of any cell or tissue. Proteomics is a discipline which obtains total information of proteins and its history goes back to 1975s. On the other hand, Marc Wilkins is the first PhD student who is working on the concept and suggested to use the “*Proteom”* term in a symposium in 1990’s and later he and his collegues [14] announced their work to scientists. The

word PROTEOM is a portmanteau of *protein* and *genome*. It can be defined as the entire set of proteins which are produced or modified by an organism or system. Proteomics is an interdisciplinary domain that has benefited greatly from the genetic information of the Human Genome Project [15]. While proteomics generally refers to the large range of experimental analysis of proteins, it is often and on the whole used for protein purification and mass spectrometry.

Silk degradation, especially photo-degradation has been studied for many years; however at the present the advent of the proteomic methods allows to examine the degradation in molecular level. Traditionally, fluorescence mapping and protein extractability [16] have been used to understand the silk degradation. But today, with the development and application of powerful new proteomic tools (i.e. mass spectrometry-MS) the protein photo-oxidation can be examined.

Proteomics, are known as an emerging field of life science research and can display, identify or characterize all the proteins in a given cell, tissue or organism. However in textiles, there are various researchers on proteomics; one which is Katagata [17] who separated the crystalline regions of fibroin by precipitation and digestion with α-chymotrypsin; 55% of the crystalline regions precipitate while the 45% remained in solution. Inoue et.al [18] characterized the glycoprotein P25 by SDS-PAGE (which is a technique to separate proteins by their molecular weight), Figure 6 shows the molecular markers in the left lane. In their work two bands were identified at 27 kDA and 24 kDa depending on the degree of glycosylation and N-linked oligosaccharide chains which were detected. When it was degummed, the heavy (350 kDa) and light fibroin (25 kDa) bands disappeared, showing only a smear at 100kDa. This indicates that degumming process damages the both heavy and light chains.

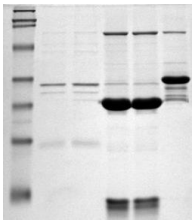


Fig.6: *Picture of an SDS (sodium dodecly sulfate)-PAGE (polyacrylamide gel electrophoresis) [19]*

MS techniques provide highly sensitive and powerful means to profile redox modifications at the molecular level within silk samples. MS has a distinct advantage over traditional tools. As a result; a redox proteomic approach consists of the following [20]:

- Digestion with a proteolytic enzyme to produce peptides,
- Separation of the peptides with appropriate liquid chromatography,
- Tandem mass spectrometric peptide fragmentation,
- Targeted bioinformatics evaluation for key redox products can provide detailed identification and localization of modification throughout the silk proteome.

In this way, oxidatively modified amino acid residues within the proteins can be accurately characterized through comparison of MS/MS data between native and degraded peptides.

5. CONCLUSION

The development and application of new technologies i.e. proteomic tools, may allow for identifying, mapping and tracking oxidative degradation at the protein amino acid residue level of the samples. Hence, implements in proteomics offer a better understanding of silk damage and degradation. We believe that, both with new technologies and advent of proteomics, textile fibres such as silk and other historical textile materials can be studied for their ageing and can help to identify their degradation.

REFERENCES

[1] D. L. Kaplan, S. M. Mello, S. Arcidiacono, S. Fossey and K.W. M. Senecal, "*Protein Based Materials"*, Birkhauser, Boston, 1998.

[2] B. B. Mandal and S. C. Kundu, *"Biospinning by silkworms: silk fiber matrices for tissue engineering applications*", Acta Biomaterial, 6, 2, pp.360-371, 2010.

[3] B. C. Dash, B. B. Mandal and S. C. Kundu, *"Silk gland sericin protein membranes: fabrication and characterization for potential biotechnological applications",* J. Biotechnology, 144, 4 , pp.321-329, 2009.

[4] Y. Li and X-Q Dai, "*Biomechanical engineering of textiles and clothing"*, Woodhead Publishing in Textiles, Cambridge, U.K., 2006

[5]Available:http://www.trendus.com/images/news/orjinal/sultan-suleymaninkaftani_09052011125858.jpg

[6] Available: https://en.wikipedia.org/wiki/Silk

[7] E. Lizuka and H. Itoh, "*Physical Properties of Eri Silk"*, International Journal of Wild Silkmoth Silk , 3 , pp.37-42, 1997.

[8] S. Warner, "*Fiber Science",* Prentice Hall, New Jersey, US, 1995.

[9] P. P. Viktorov and Z. S. Bloch, "*Text Prom.*" ,43, 11, 1933.

[10] R. Somashekar and U. Gopalakrishna, "*Polymer"* , 36, 10, pp.2007-2011, 1995.

[11] P. Zhang, K. Yamamoto, Y. Wang, Y. Banno, H. Fujii, F. Miake, N. Kashige and Y. Aso, *"Utility of dry gel from two-dimensional electrophoresis for peptide mass fingerprinting analysis of silkworm proteins*", Bioscience, Biotechnology and Biochemistry, 68,10, pp.2148-2154, 2004.

[12] M. G. O'Sullivan and J. P. Kerry, *"Sensory and quality properties of packaged meat, Improving the sensory and nutritional quality of fresh meat"*, Ed. J.P. Kerry and D. Ledward, Cambridge, UK, Woodhead Publishing Limited, 2009.

[13] J. W. S. Hearle, B. Lomas and W. D. Cooke, "*Atlas of Fibre Fracture and Damage to Textiles"*, 2nd Edition, CRC Press LLC, USA, 2000.

[14] M.R. Wilkins, C. Pasquali, R. D. Appel, K. Ou, O. Golaz, J.C. Sanchez, J.X.Yan, A. A. Gooley, G. Hughes, I. H. Smith, K.L. Williams and D.F. Hochstrasser, *"From Proteins to Proteomes: Large Scale Protein Identification by Two-Dimensional Electrophoresis and Arnino Acid Analysis",* Nature Biotechnology, 14, 1, pp.61-65,1996.

[15] L. Hood and L. Rowen, "*The human genome project: big science transforms biology and medicine",* Genome Medicine 5, 9, 2013.

[16] S. Tokutake, "*Isolation of the smallest component of silk protein*", Biochemical Journal, 187, 2, pp.413-4171980.

[17] Y. Katagata, A. Kikuchi and K. Shimura, *"Characterization of the crystalline-region peptides prepared from the posterior silk gland fibroin",* Journal of Sericultural Science of Japan, 53, pp.165-174, 1984.

[18] S. Inoue, K. Tanaka, F. Arisaka, S. Kimura, K. Ohtomo and S. Mizuna, "*Silk fibroin of Bombyx mori is secreted, assembling a high molecular mass elementary unit consisting of H-chain, L-chain, and P25, with a 6:6:1 molar ratio*", The Journal of Biological Chemistry, 275, 51, pp.40517-40528, 2000.

[19] Available: https://en.wiki2.org/wiki/SDS-PAGE

[20] J. M. Dyer, S. D. Bringans and W. G. Bryson, *"Determination of phot-oxidation products within photoyellowed bleached wool proteins"*, Photochemistry and Photobiology, 82, 2, pp.551-557, 2006.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

HYDROGELS AND THEIR APLICATION AREAS

AÇIKEL Safiye Meriç[1], ASLAN Ahmet[2]

[1] İstanbul University, Technical Sciences Vocational School, Leather Technology 34320, İstanbul, Turkey,
E-Mail: mericgokalp@gmail.com

[2] Ege University, Engineering Faculty, Leather Engineering Department, 35100, İzmir, Turkey,
E-Mail: ahmetaslan@gmail.com

Corresponding author: AÇIKEL, Safiye Meriç, E-mail: mericgokalp@gmail.com

Abstract: *Hydrogels, being polymeric material,are named "Hydrophilic Polymer" because of their capable of holding large amounts of water in their three-dimensional networks. Hydrogels is not solved in water; however they have been swollen to their balace volume. Because of this swell behavior, they can adsorb big quantity of water in this structure. So they can term of "three sized polymers" due to protect their existing shape. Their cross linked bound structures are able to covalent or ionic and also one polymer which can for use of hydrogel polymer, must have hydrophilic groups such as carboxyl, carbonyl, amine and amide in main chains or side chains, and because of these groups water bound the polymer and polymer start to swell with rising volume and mass. Swell behavior of hydrogel is interested in quantity of hydrophilic groups. Hydrogels can use in different industrial and environmental areas with this high amount water holding capacity. They are used in food industry, biomedical, bioengineering, biotechnology, veterinary, pharmacist, agriculture, telecommunication, etc. Especially in current life, baby nappy has been including inside hydrogel beads. Also they used in contact lens, artificial cornea, synthetic cartilage and gullet, controlled medicine release, surgery yarns. This article general inform about usage area of hydrogels.*

Key words: *Hydrogels, Leather, Hydrophilic Polymers, three-dimensional networks*

1. INTRODUCTION

Polymers are known that compounds of high molecular weight or macromolecules, which is a very large, chain-like molecule made up of monomers. They are derived by the condensation of monomers or polymerization reaction. Polymers can be classified two types according to monomer structure. If polymer consist of same monomers, polymer term of homopolymer or if the polymer is consist of different monomers, they are qualified as copolymer. Polymer according to polymerization reaction can be linear, branched or cross-linked [1]. Cross-linked polymers can not be solved any solvent and if the polymer keep waiting in any solvent, polymer start to swell because of three-sized networks and being covalent bounding. These types of polymers are named in xerogels. Xerogels which has got the swelling ability, take inside the solvent more than % 20 of gel mass [2]. If the solvent is water, this cross-linked structure is named hydrogel. A hydrogel is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium. Hydrogels are highly absorbent (they can contain over 90% water) natural or synthetic polymeric networks [3], [4].Hydrogels term first was in scientific literature as colloidal gel of inorganic salts in 1894 [5]. However poly (2-hydroxyethyl methacrylate) p (HEMA) hydrogel which has got the cross-linked macromolecular network structure and can swell in the water, is today use as contact lens, was found by Wichterle and Lim in 1954 [6]. In 1958 poly vinyl acrylate p

(PVA) hydrogel was produced by Gam radiation and cross-linked poly (ethylene glycol) (PEG) was produced in 1970 by Gama radiation [7], [8]. Pluronic hydrogels which product for drug release, used for the first time in 1972 [9]. Polyethylene glycol–polylactic acid (PEG–PLA) hydrogel was produced in 1993 by photo polymerization method and thermal characterization of same hydrogel was researched in 1997 [10]. Hybrid hydrogel combination of synthetic and natural polymers was searched in 1993 [11], [12]. First commercial gel which is named "Smart Gel", which was launched to market in 1996, was soft and flexible and also was hardened in body temperature [13].This smart gel has been especially used for foot comfort and support inside footwear (Fig. 1:).

Fig.1: *a) Contact Lens [29] b) Smart Gel [30]*

2. GENERAL INFORMATION

2.1 Water Position in Hydrogels and Swell Behaviour

A polymer which has got the polar and hydrophilic function groups as –OH, -NH2,-COOH, -COOR, describe a hydrogel. These groups are interacted with the water by the hydrogen bounding [14]. Volume and mass of hydrogel polymer increase with this bounding water in hydrogel and gel start to swell. Also quantities of hydrophilic groups have raised the swell effect. Swell is characteristic feature of polymeric network structure and it is sudden change of volume in polymer. According to cross linked quantity, polymeric network can adsorb high quantity liquid without solved. Swell feature of a polymeric gel is determined interaction of functional groups with each other and with diluent [15]Push and pull effect between chains, electrostatic interactions that are not covalent, Van der Waals; are not influenced from hydrogen bounding. Hydrophobic interactions are this type of physical cross linked interactions and this situation is affected of swell behavior [16] (Fig. 2).

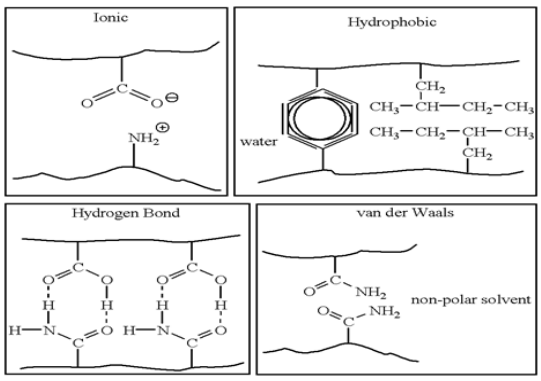


Fig. 2: *Molecular Interactions in Hydrogels* [15]

In figure 3 show a swelled hydrogel and hydrogel is found three type of water molecule. Bounding water molecule is attached to polar groups of polymer by hydrogen bounding. Free water molecule fill in the pore of the polymer. It behaves like normal water and it does not interact with the polymer. Interface water molecule swarm around the hydrophobic groups of polymer and Bounding of this molecule is not powerful interaction [15]

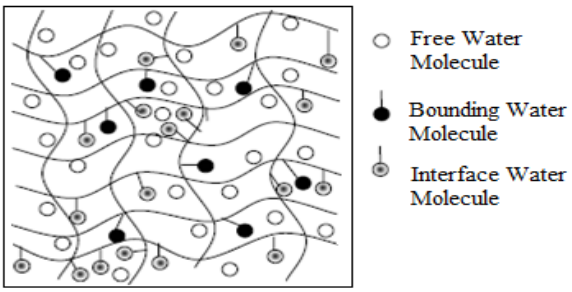


Fig. 3: *Schematic View of Swelled Hydrogel* [15]

2.2 Types of Hydrogels

2.2.1 Homopolymer Hydrogels

Homopolymer hydrogels occur from one type of monomers. These types of hydrogels are used for important application area like contact lens or drug release. poly (2-hydroxyethyl methacrylate) p(HEMA), poly (1-glycerol methacrylate), poly(hydroxypropyl methacrylate can give sample for common usage homopolymer hydrogels [17], [18].

2.2.2 Copolymer Hydrogels

Copolymer hydrogels have been prepared by cross linked of two comonomers. However at least one monomer has to be hydrophilic structure. Cross-linked of copolymer hydrogels occur by covalent or ionic interactions. poly(HEMA-co-acrylic acid) p(HEMA-ko-AA) and poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) poly (HEMA-co-MMA) are most common used copolymer hydrogels [19],[20].

2.2.3 Non Ionic Hydrogels

Ionic hydrogels are homopolymeric and copolymeric neuter hydrogels without including load groups. Swell and shrinkage properties of these hydrogels generally occur that a result of changing of environmental temperature [21]

2.2.4 Ionic Hydrogels

Ionic hydrogels, also known polyelectrolytes, is prepared from ionic monomers. This type of hydrogels can be cationic or anionic hydrogels according to positive or negative monomers. Also ionic hydrogel is term of polyampholytic hydrogels, if hydrogel polymer keeps together both anions and cations. Loading groups, being located in main chain of ionic hydrogels, increase susceptibility to warning. These ionic network structures include both acidic and basic groups. These groups ionized in suitable pH and ionic conditions and constant loads are occurred in hydrogel. Because of electrostatic repulse power of these ions, much more dilute can go inside network structure and in this way swell effect degree increase [22], [23].

2.3 Hydrogel Synthesis

2.3.1 Bulk Polymerization

Bulk hydrogels can be formed with one or more types of monomers. Usually, a small amount of cross-linking agent is added in any hydrogel formulation. The polymerization reaction is normally initiated with radiation, ultraviolet, or chemical catalysts. The choice of a suitable initiator depends upon the type of monomers and solvents being used. The wide variety monomer can use in order to obtain desired hydrogel for a given application. The polymerized hydrogel may be produced in a wide variety of forms including films and membranes, rods, particles, and emulsions [24].

2.3.2 Solution Copolymerization with Cross-linking

In this reaction, can use mixing of ionic or neutral monomers with the multifunctional crosslinking agent. The polymerization is initiated thermally by UV-irradiation or by a redox initiator system. The prepared hydrogels need to be washed with distilled water to remove the monomers. Typical solvents used for solution polymerization of hydrogels include water, ethanol, water–ethanol mixtures, and benzyl alcohol. The synthesis solvent may then be removed after formation of the gel by swelling the hydrogels in water [3].

2.3.3 Suspension Polymerization

Dispersion polymerization is used in order to obtain microspheres (beads). In this technique, the monomers and initiator are dispersed in the hydrocarbon phase as a homogenous mixture. The viscosity of the monomer solution, agitation speed, rotor design, and dispersant type mainly governs the resin particle size and shape [25],[26].

2.3.4 Polymerization by Irradiation

Ionizing high energy radiation, like gamma rays and electron beams, has been used as an initiator to prepare the hydrogels of unsaturated compounds. Examples of polymers crosslinked by the radiation method are poly (vinyl alcohol), poly(ethylene glycol), and poly(acrylic acid). The major advantage of the radiation initiation over the chemical initiation is the production of relatively pure and initiator-free hydrogels [18]

2.4 Usage Areas of Hydrogels

Hydrogels have got lots of application areas because of high capacity swelling property in water solution [8]. They are used in food industry, biomedical, bioengineering, biotechnology, veterinary, pharmacist, agriculture, telecommunication, etc. Especially in current life, baby nappy has been including inside hydrogel beads [27], [28]. Also they used in contact lens, artificial cornea, synthetic cartilage and gullet, controlled medicine release, surgery yarns (Fig. 4 ve Fig. 5).

Fig. 4: Hydrojel Beads [31], [32]

5. CONCLUSIONS

Nowadays, hydrogels are used more different application areas such as industry, environmental, medicine, healthy, etc because of the high capacity water uptake. Especially this important property is chosen in order to remove dye or heavy metal adsorption from waste waters. In this purpose loss of polymers and their combinations are utilised, and adsorption labours have made real according to target material which is wanted to adsorb.

REFERENCES

[1]R. S. Wayne, S. Wilfred, T. W. Campbell, *"Preparative methods of polymer chemistry*", Wiley-Interscience, 2001,pp. 488.

[2] W.R. Sorenson, W. F. Sweeny and T.W. Campbell, *"Preparative Methods of Polymer Chemistry"*, John Wiley & Sons Inc., Us, 2001.

[3] E.M. Ahmed*, "Hydrogel: Preparation, characterization, and applications: A review",* JARE, Vol. 6(2), pp. 105–121, 2015.

[4] Y. Osada, Y. and A.R. Khoklov*, "Polymer Gels and Networks"*, Marcel, Dekker Inc., New York,2001.

[5] K.H. Syed, I. Gulrez and A. Saphwan, *"Hydrogels: Methods of Preparation, Characterisation and Applications"*,pp1-35, Available: http://www.intechopen.com/books/progress-in-molecular-and-environmental-bioengineering-from-analysis-and-modeling-to-technology-applications/hydrogels-methods-of-preparation-characterisation-and-applications.

[6] J.M. Van Bemmelen, *"Der Hydrogel und das kristallinische Hydrat des Kupferoxydes"*, Z. Anorg. Chem. Vol. 5, p.466, 1894.

[7] A. Danno, *"Gel formation of aqueous solution of polyvinyl alcohol irradiated by gamma rays from cobalt-60"*, J. Phys. Soc. Jpn. Vol. 13, 1958, pp. 722–727, 1958.

[8] O. Wichterle and D. Lím, *"Hydrophilic gels for biological use"*, Nature, 185, pp. 117–118, 1960.

[9] P.A. King, P.A. and J.A. Ward*, "Radiation chemistry of aqueous poly(ethylene oxide) solutions"*. I, J. Polym. Sci. A Polym. Chem, vol. 8, pp. 253–262, 1970.

[10] R.M. Nalbandian, R.L. Henry, H.S. Wilks, *"Artificial skin. II. Pluronic F-127 Silver nitrate or silver lactate gel in the treatment of thermal burns"*, J. Biomed. Mater. Res, vol. 6, pp.583–590, 1972.

[11] A.S. Sawhney, C.P. Pathak, J.A. Hubbell*, "Bioerodible hydrogels based on photopolymerized poly (ethylene glycol)–co-poly (α-hydroxy acid) diacrylate macromers"*, Macromolecules, vol. 26 ,pp.581–587, 1993.

[12] B. Jeong, Y.H. Bae, D.S. Lee, S.W. Kim, *"Biodegradable block copolymers as injectable drug-delivery systems"*, Nature, vol. 388, pp.860–862, 1997.

[13] M.G. Cascone, B. Sim, D. Sandra, *"Blends of synthetic and natural polymers as drug delivery systems for growth hormone"*, Biomaterials, vol. 16, pp.569–574, 1995.

[14] W.E. Hennink, C.F. Van Nostrum, *"Novel crosslinking methods to design hydrogels",* Adv. Drug Deliver. Rev., vol. 54, pp.13-36, 2002.

[15] H.İ. Özgündüz*, "Swelling properties of semi-IPN type hydrogels containing acrylic acid-acrylamide- poly(vinyl alcohol) and lipase release behaviors"*, M.Sc. Thesis, Department Of Chemistry, Gazi University, pp. 1-94, 2006.

[16] M. A. Atta and K.F. Arndt., *"New crosslinkers to synthesize pH and temperature-sensitive ionic hydrogels",* Macromolecules, vol. 14, pp. 671-674, 1994.

[17] A.S. Hoffman, *"Hydrogels for biomedical applications"*, Adv Drug Deliv Rev., 43, pp.3-12, 2002.

[18] S.N. Swami, *"Radiation synthesis of polymeric hydrogels for swellingcontrolled drug release studies"*, Doctor of Philosophy, University of Western Sydney, New South Wales, Australia, pp. 120-149, 2004.

[19] C.S. Brazel and N.A. Peppas, *"Mechanisms of solute and drug transport in relaxing, swellable, hydrophilic glassy polymers"* Polymer, vol. 40, pp. 3383-3398, 1999.

[20] M.T. Ende and N.A. Peppas, "*Transport of ionizable drugs and proteins in crosslinked poly(acrylic acid) and poly(acrylic acid-co-2-hydroxyethyl methacrylate) hydrogels 2diffusion and release studies*". J. Control. Release, vol. 48, pp.47-56, 1997.

[21] J. Ostroha, P.M., Lowman and N. Dan, *"Controlling the collapse /swelling transition in charged hydrogels"*, Biomaterials, vol. 25, pp. 4345-4353, 2004.

[22] K. Sutani, K. I. Uchida and Y. Matsubara, *"Stimulus responsive drug release from polymer gel.-Controlled release of ionic drug from polyampholyte gel"*, Radiat Phys Chem, vol. 64, pp.331-336, 2002.

[23] A.E. English, T. Tanaka and E.R. Edelman, *"Polimer and solution ion shielding in polyampholytic hydrogels".* Polymer, vol. 39, pp.5893-5897, 1998.

[24] K. Suda, *"Superabsorbent polymers and superabsorbent polymer composites"*., Science Asia, 33(1), pp. 39–43, 2007.

[25] D. Hunkeler, *"Synthesis and characterization of high molecular weight water-soluble polymers",* Polym Int, vol. 27, pp. 23–33, 1992.

[26] N. Watanabe, Y. Hosoya, A. Tamura, H. Kosuge, *"Characteristics of water-absorbent polymer emulsions"*, Polym Int, 30, pp. 525–531, 1993.

[27] İ. Bayraktar, Synthesis, *"Characterization And Investigation of Adsorption Properties Of Magnetic Hydrogels",* M.Sc. Thesis, Department Of Chemistry, Adnan Menderes University, 2013.

[28] T.R. Hoarea, D. S. Kohaneb*,"Hydrogels in drug delivery: Progress and challenges*", Polymer, vol. 49(8), pp. 1993–2007, 2008.

[29] Contact Lens Imagine, http://www.medikalakademi.com.tr/goz-kontakt-lens-bagli-komplikasyon-mikrobiyal-keratitler/

[30] Smart Gel Imagine, http://m.aliexpress.com/popular/male-height.html

[31] Hydrogel Bead, http://tr.123rf.com/photo_15536845_kahverengi-hidrojel-toplar-s%C3%BCper-emici-polimer-bir-bardak-pothos-the-devil-s-ivy.html

[32]http://www.cosmoactive.com/?portfolio=3-custom-post-types

[33] Hydrogel Adhesive Plaster, http://tr.hartmann.info/images/5-Dermaplast_Hydro.pdf

[34] Smart Hydrogel Surgery Plaster http://www.webmasto.com/mit-muhendisleri-akilli-yara-bandi-gelistirdi

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

EVALUATION OF LEATHER QUALITY AND ECOTOXICITY IN SIMULATED TANNERY WASTEWATERS USING MIMOSA TANNIN

ÇELİK Cem[1*], MERİÇ Süreyya[2]

[1] İstanbul University, Leather Technology Program, Vocational School, Avcılar, Turkey, E-mail: celik44@gmail.com

[2] Namik Kemal University, Çorlu Engineering Faculty, Environmental Engineering Department, Çorlu 59860, Tekirdağ, Turkey, E-Mail: smeric@nku.edu.tr

* Corresponding author: Çelik, Cem, E-mail: celik44@gmail.com

Abstract: *The leather tanning industry is characterized by the production of different kinds of effluents, generated in each step of leather processing. These effluents have various chemical compounds which may cause toxicity and endocrine disruption and are thus known as endocrine disrupting chemicals (EDC). Tanning stabilizes the protein structure of the hide and imparts heat stability, enhanced tensile properties, and resistance to microbial degradation. Currently most high quality leather is "chrome-tanned," produced by treatment of the hide with salts of the mineral chromium. In this study, the wastewater characteristics and ecotoxicity before and after tanning and retanning processes using mimosa tannin are assessed. Vegetable leather production procedure was followed using one dose mimosa tannin. Leather quality was evaluated according to standard methods. Wastewater characteristics showed that mimosa contributed high organic content to the wastewater. Although vegetable tannin was used the effluent toxicity was observed in tanning and retanning effluents. The preliminary results also showed that leather quality tests failed or at minimum level to comply with the standard values indicating that there is still a need to optimize the procedure including mimosa dose. This study was designed to produce eco-friendly leather using mimosa in tanning and retanning processes. Leather quality and the ecotoxicity of each process during leather production was assessed according to standard methods.*

Key words: *Vegetable tannin, mimosa, wastewater, ecotoxicity, polyphenols*

1. INTRODUCTION

The leather tanning industry is characterized by the production of different kinds of effluents, generated in each step of leather processing. These effluents have various chemical compounds which may cause toxicity and endocrine disruption and are thus known as endocrine disrupting chemicals (EDC) [1]. Tanning stabilizes the protein structure of the hide and imparts heat stability, enhanced tensile properties, and resistance to microbial degradation. Currently most high quality leather is "chrome-tanned," produced by treatment of the hide with salts of the mineral chromium [2]. Because of environmental considerations, and customer preference, there is interest in developing new chrome-free tannages [3, 4]. Thus, alternative tanning chemicals to the chromium tanning process have been evaluated during recent years to produce eco-leather [5]. The most important one among these methods is the vegetable tanning which is performed with vegetable tannins [6]. However, environmental effects of tannins should be addressed well [7, 8, 9] since

During processing, only 40–50% of the applied tannins have been taken up, and the remaining 50–60% has been released as unspent along with the wastewater. The presence of unspent tannins poses challenge to the wastewater treatment processes, due to their recalcitrant nature. In addition, the biological treatments are less effective in degrading the tannins, due to reduced organic content and xenobiotic nature [10]. This study was designed to produce eco-friendly leather using mimosa in tanning and retanning processes. Leather quality and the ecotoxicity of each process during leather production was assessed according to standard methods.

2. MATERIAL AND METHODS

2.1. Leather processing

Raw leather was provided from a leather provider factory to process it with the required chemicals according to standardized procedures [11]. The processes applied on pelts are given in Table 1.

Table 1: *Water and chemicals use during leather processing in this study (leather sample weight: 6.202 gr).*

Processes/Time	Water consumption (v/w leather)	Chemicals used	Consumption (w/w leather)	pH
Deliming (60 min)	100%	Deliming chemicals	3,30%	8,2
Bating (40 min)	100%	Enzyme	0,50%	8,2
Washing+Pickling (180 min)	80%	Formic acid	1,60%	3,4
		Sulphuric acid	0,20%	
Vegetable tanning (120 min)	**80%**	**Mimosa tannin**	**15%**	**3,8**
Retanning step				
Bleaching (80 min)	200%	EDTA	0,50%	
Washing+Neutralization (70 min)	150%	Sodium formate	2%	5,5
Washing+Vegetable retanning (150 min)	**250%**	**Mimosa tannin**	**8%**	
Softening and degreasing (170 min)	100%	Natural and synthetic oils	14%	

Leather samples were taken according to TS EN ISO 2418 (2006) method as detailed in **Fig.1.** Accordingly, the finished leather was submitted to leather quality evaluation tests following standard methods as explained elsewhere [11]. The details of preparation of leather for leather quality testing and samples taken from vertical and parallel to the back bone.

2.2. Wastewater analyses

The wastewater samples originated from pickling, tanning and retanning procedures were analysed for their COD, TOC (Schimadzu, TOC-LCPH/CPN),TSS, nitrogen (TKN and ammonia, Gerhardt, Vapodes VAP 20s) parameters according to Standard Methods (1998) as well as for absorbance (Schimadzu Lambda 1800), electroconductivity, pH, settling properties which are typical parameters and indicators for leather tannery wastewater. Furthermore, polyphenol contents (arbutrine and gallic acids) of the samples were scanned by HPLC (Prominence Modular LC20A) following the method given by Lopez-Velez et al. [12].

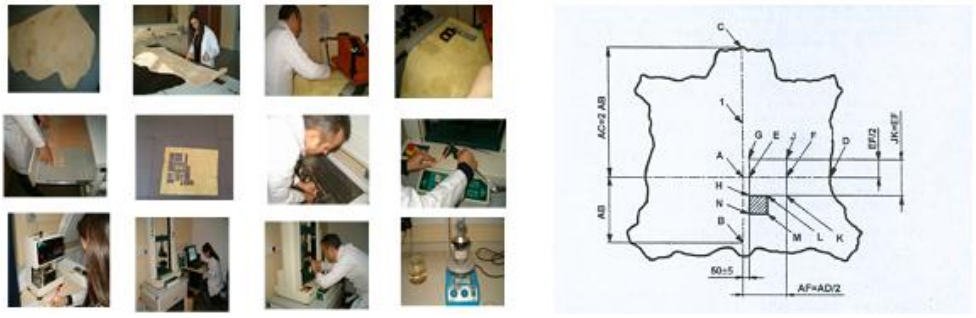


Fig. 1: *Vegetable tanning and retanning steps*

2.3. Toxicity

New born (<24 h) daphnids were exposed to the samples (after 30 min of sedimentation) for 24 and 48 h at different dilution rates to evaluate their toxicity [3, 13].

3. RESULTS AND DISCUSSION

3.1. Water consumption

As seen in Table 1, the ratio between tanning used in tannin and retanning processes is 15/8=1,87 while the ratio of water consumption between two process is 80/250=0.32. This result indicates that tanning process effluents should be more concentrated than retanning process.

3.2. Wastewater characteristics

Table 2 shows the characteristics of samples tested in this work. COD and TOC values increased in tanning and retanning effluent samples conforming the contribution of unspent organic chemicals [14]. As seen in Table 1, the water consumption was higher while the amount of chemicals used in retanning process were higher than tanning process. Accordinggly, the ratio between amount of chemicals used and water consumption in tanning and retanning processes is assess to be more than 2. Drastic decrease in TOC in the retanning effluent indicates the organic content contribution of higher mimosa tannin use in the tanning process as 1 gram of mimosa tannin yields 1,153 g COD; 0,47g TOC (98% of TC); 0,576 g TKN and 0,0017 g NH_3 (unpublished data). This drastic decrease in TKN concentration was also observed in retanning effluent. The presence of organics was followed by UV profiles as shown in **Fig.2.** No absorbance peaks were observed (200-300 nm) in pickling wastewater (PW) indicating that no organics were present in the effluent. As explained above, the organics were lesser in retanning process effluent than tanning process since lesser amount of water and chemicals were used in retanning process.

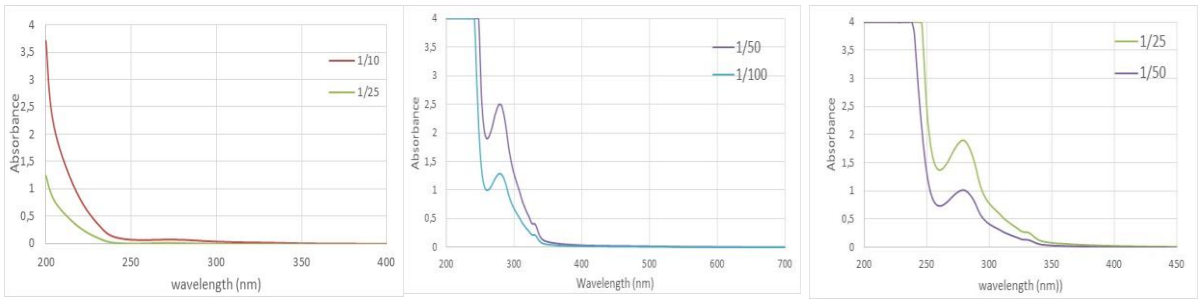
Table 2: *Characteristics of vegetable tanning process wastewaters*

Sample names and codes	COD (mg/L)	TSS (mg/L)	TOC (mg/L)	TKN (mg/L)	Ammonia (mg/L)	UV_{254} (nm)[1]	UV_{280} (nm)[1]
Pickling effluent	3180	405	3030	25,8	25,6	0,001	0,008
Mimosa tanning effluent	19145	330	18030	193	109	>4	>4
Mimosa retanning effluent	8360	280	4325	21,1	6,2	1,68	1,895

3.3.Polyphenols

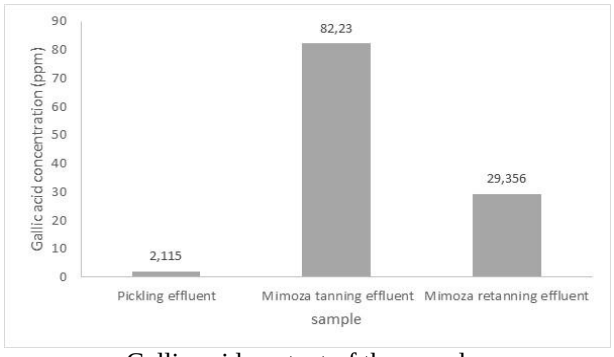
No arbutin was detected in both pickling and tanning processes effluents while Gallic acid (GA) was detected significantly higher in both wastewaters samples than pickling effleunts as seen

in **Fig. 3.** High GA concentration (**Fig.3**) was found to be paralel to higher COD and TOC results (Table 2) and UV absorbances (Table 2, **Fig.3**) in tanning and retanning effluent samples**.** As seen in Table 2, UV_{254} and UV_{280} values that indicate aromatic structure and double bound in the organic content, decreased in parallel to COD and TOC parameters.

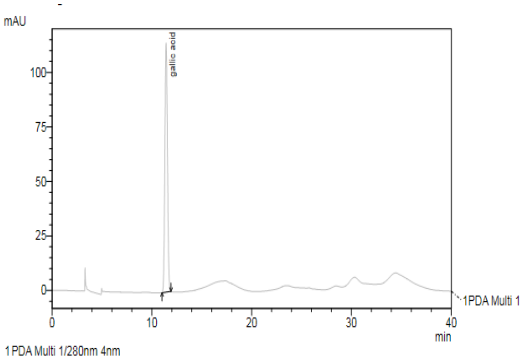


Pickling effluent | Mimosa tanning effluent | Mimosa retanning effluent

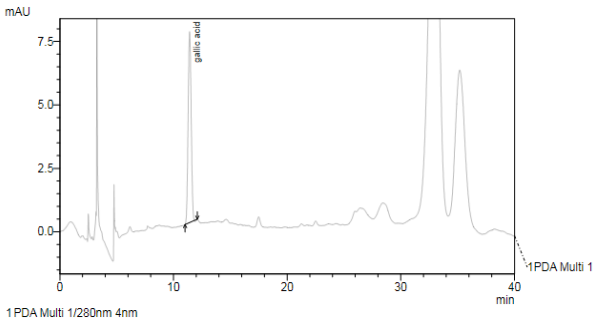
Fig.2: *UV profiles of the samples*



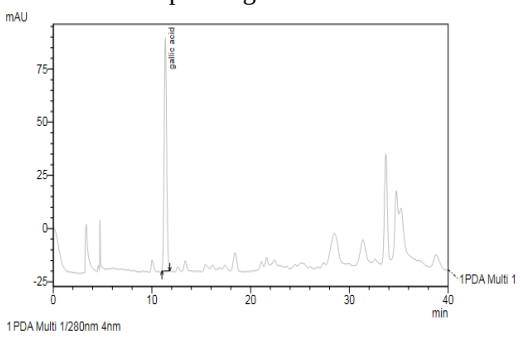
Gallic acid content of the samples



pickling effluent



Mimosa tanning effleunt



Mimosa retanning effluent

Fig. 3*: Gallic acid evolution and HPLC profiles in the samples*

3.4.Toxicity

As seen in **Fig.4**, all samples (pickling, mimosa tanning and mimosa retanning effluents) resulted in 100% toxic to *Daphnia magna* when exposed to non diluted samples. When samples were tested at 50% diluted both mimosa tanning and retanning effluents exhibited higher toxicity than pickling effluent due to higher vegetable tannen content which was explained to be toxic to

different species at hihher doses [7,8]. Toxicity of wastewater can be also confirmed with higher gallic acids content as seen in **Fig.3.**

3.5.Leather quality

Table 3 shows the leather quality tests results. Leather quality by means of the resistance coefficient for pulling was obtained significantly higher than standard values. Whereas strengthness and streching resistance were below the stnadrad values indicating that there is still need to imporve the tanning and retanning procedures including the amount of mimosa to be used. Other tests regarding curving resistance measured by Pheleksometer metod, or streching temperature definition tests were in accordance with the standard requirements.

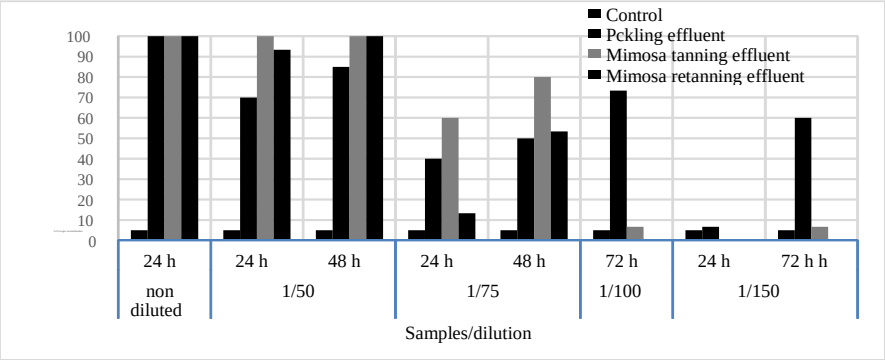


Fig.4: *Toxicity evolution in the effluents of pickling, mimosa tanning and retanning processes.*

Table 3*: Leather quality results obtained according to standart methods*

Tensile strength (N/mm2)		**Elongation at break (%)**		**Tearing Load (N/mm)**		**Flexing resistance (80000 Flexing)**		**Shrinkage Temperature (^{o}C)**	
Vertical	**Parallel**	**Vertical**	**Parallel**	**Vertical**	**Parallel**	**Vertical**	**Parallel**	**Vertical**	**Parallel**
16,18	21,09	63,3	65,7	72,1	64,6	no effect oberved.	no effect observed.	82	82
EN ISO 3376: 2011 (EN): Nisan 2012				**TS 4118–2 EN ISO 3377–2: 2005**		**TS 4132 EN ISO 5402: 2005**		**TS 4120 EN ISO 3380: 2005**	
> 25 N/mm2		**>40 %**		**>100 N/mm**					

4. CONCLUSIONS

All over the abovementioned results vegetable tanning agents can be used for producing ecological high qualiity leather by means of leather quality tests and chromium free wastewater. On the other hand the adverse effect of mimosa tannin of which the amount is still to be optimized for strengther leather product and higher biodegradable wastewater content, is to be better evaluated for safer effluents to protect environment.

ACKNOWLEDGEMENTS

This study has been performed by the support of Namik Kemal University, Scientific Research Projects Fund (NKUBAP.00.17.YL.13.06). Technical assistance of Oguz Kizek and Fethiye Meraci are appreciated. The authors would like to thank Güçlü Leather LTD. for providing

leather, Özşen Leather Factory for processing leather sample before tanning process, Stahl Company for providing tannin and other chemicals, and TASEV laboratory for supporting leather quality tests.

REFERENCES

[1] V. Kumara, C. Majumdar, P. Roya, "*Effects of endocrine disrupting chemicals from leather industry effluents on male reproductive system*", Journal of Steroid Biochemistry & Molecular Biology, vol. 111, pp. 208–216, 2008.

[2] S. M. Mavlyanov, Sh. Yu. Islambekov, A. I. Ismailov, D. N. Dalimov, and N. G. Abdulladzhanova, "*Vegetable tanning agents*", Chemistry of Natural Compounds, Vol. 37, No. 1, 2001.

[3] E. De Nicola, S. Meric¸ C. Della Rocca, M. Gallo, M. Iaccarino, P. Manini, D. Petruzzelli, V. Belgiorno, M. Cheggour, A. Di Gennaro, A. Moukrim, O. Tünay, G. Pagano. ""*Wastewater Toxicity of Tannin-Versus Chromium-Based Leather Tanneries in Marrakesh, Morocco*"",. Arch Environ Contam Toxicol, vol.53, pp. 321–328, 2007a.

[4] S. R. Tariq, M. H. Shah, N. Shaheen, "*Comparative statistical analysis of chrome and vegetable tanning effluents and their effects on related soil*", Journal of Hazardous Materials, vol. 169, pp.285–290, 2009.

[5] S. Saravanabhavan, P. Thanikaivelan, J. Raghava Rao, B. Unni Air, T. Riramasami, "*Natural Leathers from Natural Materials: Progressing toward a New Arena in Leather Processing",* Environ. Sci. Technol., vol. 38, pp. 871-879, 2004.

[6] R. Marín-Martinez, R. Veloz-García, R. Veloz-Rodríguez, S.H. Guzmán-Maldonado, G. Loarca-Pina, A. Cardador-Martinez, L.Guevara-Olvera, R. Miranda-López b, I. Torres-Pacheco, C. Pérez Pérez, G. Herrera-Hernández, F. Villaseñor-Ortega, M. González-Chavira, R.G. Guevara-Gonzalez, "*Antimutagenic and antioxidant activities of quebracho phenolics (Schinopsis balansae) recovered from tannery wastewaters*", Bioresource Technology, vol.100, pp.434–439, 2009.

[7] E. De Nicola, M. Gallo, M. Iaccarino, S. Meric¸, R. Oral, T. Russo, T. Sorrentino, O. Tunay, E. Vuttariello, M. Warnau, G. Pagano, "*Hormetic Versus Toxic Effects of Vegetable Tannin in a Multitest Study*", Arch. Environ. Contam. Toxicol., vol.46, pp.336–344, 2004.

[8] E. De Nicola, S. Meriç, M. Gallo, M. Iaccarino, C. Della Rocca, G. Lofrano, "*Vegetable and synthetic tannins induce hormesis/toxicity in sea urchin early development and in algal growth*", Environ Pollut, vol. 146, pp. 46–54, 2007b.

[9] G. Libralato, F. Avezzù, A. Volpi Ghirardini, "*Lignin and tannin toxicity to Phaeodactylum tricornutum (Bohlin)*", Journal of Hazardous Materials, vol. 194, pp. 435-439, 2011.

[10] G. Lofrano, S. Meriç, G.E. Zengin, D. Orhon, "*Chemical and Biological treatment technologies for leather tannery chemicals and wastewaters: A review*", Science of the Total Environment, vol. *461*, pp. 265-281, 2013.

[11] C. Çelik, "*Vegetable Tannin Leather Processing Technology and Environmental Effects Research*", Master Thesis, NKU, Applied Sciences Institute, 2014.

[12] M. López-Vélez, J.A. Delgado-Prado, E. Gómez-García, F. Martínez-Martínez, "*HPLC-Analysıs of Polyphenolic Compounds in Spanish Red Wines and etermination of Their Antioxidant Activity by Radical Scavenging Assay*". Food Onnova, Spain 2010.

[13] International Organization for Standardisation Water Quality: Determination of the Inhibition of the Mobility of *Daphnia magna* Straus (Cladocera, Crustacea)-Acute Toxicity Test, ISO 6341 (2012) Geneva, Switzerland.

[14] G. Lofrano, E. Aydin, F. Russo, M. Guida, V. Belgiorno, S. Meric, "*Characterization, fluxes and toxicity of leather tanning bath chemicals in a large tanning district area (IT)*", Water, Air, & Soil Pollution: Focus, vol. *8*(5-6), pp. 529-542, 2008.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

3D MODELLING OF PROPHYLACTIC FOOTWEAR FOR A HIGH ARCHED FOOT

COSTEA Mariana[1], MIHAI Aura[1]

[1]"Gheorghe Asachi" Technical University of Iasi, Faculty of Textiles, Leather and Industrial Management, 28, D. Mangeron str., 70050 Iaşi, Romania, e-mail: mpastina@tex.tuiasi.ro

Corresponding author: Mihai Aura amihai@tex.tuiasi.ro

Abstract: *This article approaches the methodology of designing customized footwear for high arched foot. The authors propose to reconsider the classical structure of footwear bottom components for people with high arched foot and recommend incorporating custom components, with the role of compensation or adjustment. This study continues the authors' research, starting from a foot's 3D shape obtained by 3D scanning, the anthropometrical and biomechanical parameters, shoe lasts' 3D modelling and continuing with 3D footwear design. Including customized orthosis can help to stop the evolution of abnormalities, diminishes sensations of pain during walking and improves performance in various physical activities carried out during the day, walking, running, and standing. The prophylactic footwear has to meet four main requirements: to protect the foot and ankle during walking and static; to ensure the normal resistance systems (bones), muscle and joint of the foot; to prevent the installation of irreversible structural changes by reducing stress on the foot; to contribute to increased performance in conducting regular physical activity. It is presented the steps of modelling an orthosis, a virtual simulation of its cutting process, followed by the integration and development of the insole, filling and sole for a customized shoe. Delcam Crispin CAD system and its applications for orthopaedics are used to design the bottom components of prophylactic footwear for a high arched foot.*

Key words: *Prophylactic footwear, 3D CAD, virtual prototype, orthosis, footwear bottom components*

1. INTRODUCTION

It is widely accepted the hypothesis that foot comfort, while wearing a footwear product, is directly influenced by the shape and interior dimensions of the shoe, the materials' properties, the manufacturing technology. From this point of view, prophylactic footwear is defined as one that provides the greatest comfort of the foot. If the footwear doesn't maintain the anatomical structure and normal physiology of the foot, in time, it can be a contributing factor to the appearance and development of foot abnormalities. A series of criteria, deriving from the functions that it must satisfy: esthetical, functional, economical and technological, have to be respected during modelling and design stages [1].

The fundaments of 3D modelling of prophylactic footwear are consisted in a series of conclusions from the reported findings in studies and research carried out nationally or internationally [2, 3], such as:

- Elements like toe shape, sole shape and thickness in the arch area, heel height and shape have to be considered to solve foot pathology during orthostatic position or gait;

- The sole configuration in the arch area has an important role in foot biomechanics.

2. METHOD

This paper continues the authors' research, using the foot's 3D shape obtained by 3D scanning, the anthropometrical and biomechanical parameters, shoe lasts' 3D modelling [4, 5, 6]. With a 3D shoe last for a high arched representative foot and Delcam Crispin Shoemaker software, a women footwear product was proposed (figure 1).

Fig.1: *3D design of a women prophylactic shoe*

3. RESULTS AND DISCUSSIONS

3.1. 3D modelling of a foot orthosis

Foot orthosis is a medical device that can be introduced inside the shoe and designed so that it can modify the value and evolution of the reaction forces acting on the foot. Using the previous scanned foot [4], biomechanical parameters [7] and Delcam Crispin OrthoModel software, a foot orthosis for a high arched foot is designed [8, 9], the main stages being presented below, figure 2÷3.

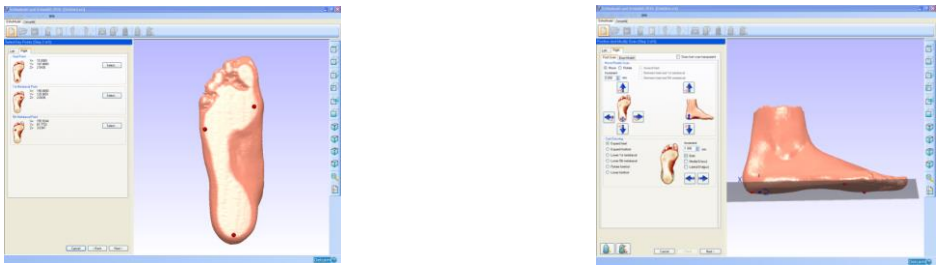


Fig. 2: *Establishing orthosis main points*

Fig. 3: *Virtual model of foot orthosis adapted to a high arched foot*

After the orthosis is designed it can be sent to a CNC machine in order to be produced, figures 4÷6. Delcam OrthoMill module allows simulating the cutting process. The advantages of using this system: reduced number of wastes; special devices for soft materials, like EVA; reduced working time.

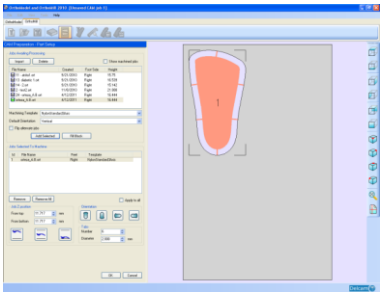


Fig. 4: *Positioning the orthosis on the cutting surface*

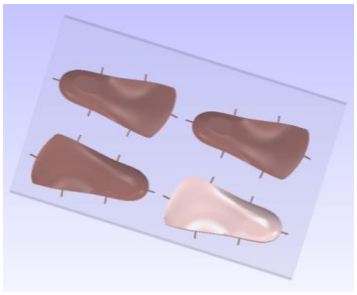


Fig. 5: *Multiplying the orthosis*

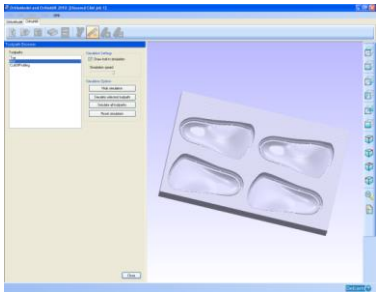


Fig. 6: *The cutting process*

3.2. 3D modelling of an insole, sole and filling by adapting to the orthosis

From a functional perspective, prophylactic footwear meets the four main requirements: protects the foot and ankle during walking and static; ensures the normal resistance systems (bones), muscle and joint of the foot; prevents the installation of irreversible structural changes by reducing stress on the foot; contributes to increased performance in conducting regular physical activity.

In order to obtain all footwear bottom components of for a high arched foot: sole, insole, filling, orthotics, Delcam PowerSHAPE software is used [10], figure 7÷10.

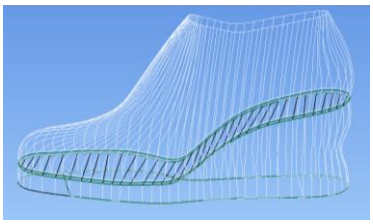


Fig. 7: *Insole lateral lines design*

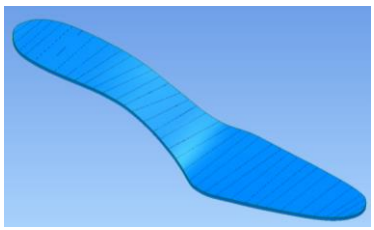


Fig. 8: *Insole surfaces design*

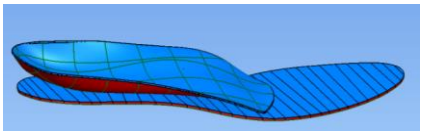


Fig. 9: *Positioning the orthosis on the insole*

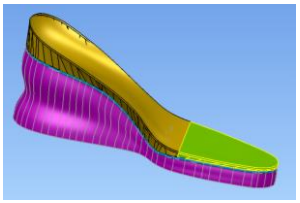


Fig. 10: *3D footwear bottom components: orthotics, filling, insole, sole*

4. CONCLUSIONS

Through this study, the authors propose to reconsider the classical structure of the footwear bottom components for people with high arched foot and recommends incorporating custom components, with the role of compensation or adjustment. Including customized orthosis can help to stop the evolution of anomalies, diminishes sensations of pain during walking and improves performance in various physical activities carried out during the day (eg. walking, running, standing

and so on). The research may continue in this direction, requiring to be extended to large selections of subjects, tested in practice by wearing samples and validated by technological transfer. The validation of these findings may change the classical structure of shoe's bottom components.

ACKNOWLEDGEMENT

This work was supported by UEFSCDI Bucharest under the Partnership Programme project MOBILITY: Preventing gait deficiencies and improving biomechanical parameters for the elderly population by designing and developing customized footwear – code PN-II-II-PT-PCCA 2013-4, contract 122/2014.

REFERENCES

[1]. Mihai A., Curteza A., *DESIGN-Designul produselor din piele*, Performantica, Iasi, 2005, ISBN: 9737300610

[2]. Alcántara E., Artacho M.A., González J.C., García A.C., *Application of product semantics to footwear design. Part I—Identification of footwear semantic space applying diferential semantics*, International Journal of Industrial Ergonomics, vol. 35, nr. 8, 2005, pg. 713-725, ISSN 0169-8141, http://www.sciencedirect.com

[3]. Hung Q. L., Alaoui A., Erlicher S., Baly L., *Towards a footwear design tool: Influence of shoe midsole properties and ground stiffness on the impact force during running*, Journal of Biomechanics, vol. 43, nr. 2, 19, 2010, pg. 310-317, ISSN 0021-9290, http://www.sciencedirect.com

[4]. Sarghie Bogdan, Costea Mariana, Mihai Aura, *3D modelling of shoe lasts using templates based on anthropometrical measurements of the foot – case study*, Leather and Footwear Journal, vol. 13, nr. 3, 2013

[5]. Drişcu M., Costea, *Shoe last shape customization*, Leather and Footwear Journal, vol. 14, no.3, Certex Publishing House, 2014, ISSN 15834433, pg.181-190

[6]. Xiao M., Zhang Y., Luximon A., *A shoe–last selection system based on fit rating*, International Journal of Human Factors Modelling and Simulation, 2011,Vol. 2,Issue 4, pp. 327-340

[7]. Costea M., Vasilescu A. M, Hortal G, Mihai A., *Plantar footprints analysis - case study (part 2),* Leather and Footwear Journal, vol. 14, no.4, Certex Publishing House, 2014, ISSN 15834433, pg.243-250

[8]. Păştină M., Mihai A., Bilalis N., *Finite element analysis for insole-sole prototypes*, Proceedings of The 4th International Conference on Advanced Materials and Systems, (volum indexat SCOPUS), ISSN 2068-0783, ICAMS 2012, Bucureşti, 27-29 septembrie, pag. 359-364

[9]. Mihai A., Harnagea M-C, Păştină M., *Customized footwear inserts for high arched foot - one case study*, IITAS - „XIIth International Izmir Textile and Apparel Symposium, Oct 28–30, 2010", ISBN 978-975-483-872-5, pg. 490-493

[10]. Păştină (Costea) M., Mihai A, Mitu S., *Virtual and Physical Prototyping Technique for Footwear Bottom Components,* Proceedings of 14th Romanian Textiles and Leather Conference – CORTEP 2012, 2012, pg. 569-574, ISSN 978-973-730-962

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STUDY REGARDING THE STITCHING STRENGTH OF MATERIALS USED FOR FOOTWEAR UPPERS MANUFACTURING

HARNAGEA Florentina[1], IOVAN DRAGOMIR Alina[2], SECAN Cristina[3]

[1]Technical University of Iasi, Faculty of Textile, Leather and Industrial Management,"Gh.Asachi", Dimitrie Mangeron, No. 28, Iasi, 700050, România, E-Mail: harnagea@tex.tuiasi.ro

[3] University of Oradea, Faculty of Energy Engineering, Department of Textiles-Leather and Industrial Management, B.St.Delavrancea str., No. 4, 410087, Oradea, Romania, E-Mail: cris_secan@yahoo.com

Corresponding author: Harnagea Florentina, E-mail: harnagea@tex.tuiasi.ro

Abstract: *The shoes manufacturing implies the use of various types of leathers, leather substitutes and fabric. The sewing plays a very important role in shoe making, having an impact both in terms of functionality and outlook. One of the most important indicators of the sewed products quality is seam strength, which is influenced by a series of technological parameters such as: the shape of the needle's top, the needle's diameter, the seam thickness, the number of seams, the gauge of the thread, the type of seam and the material type. This paper studies the stitching strength of the full grain leather and full grain leather shiny surface used for footwear uppers, in order to improve productivity and seam quality.The experimental researches obtained for the stitching strength allow calculating the weakening coefficient of the material in the process of sewing (a= 0.33-0.48). The "a" coefficient is dependent on the stitch density, the shape of the needle's top and the joined materials. In terms of stitching strength, the results indicate that the full grain leather obtains higher values than the full grain leather shiny surface.*

Key words: *leather, stitch strength, needle, stitch density, open seam, lapped seam*

1. INTRODUCTION

The shoes manufacturing implies the use of various types of leathers: full grain leather, full grain leather shiny surface, sheep leather, pig leather etc

One of the process in typical footwear manufacturing facility is stitching. It consist of sequential processes, requires higher operator skills and relatively needs longer time compared to other shoes processing. Stitching line serve as assembly process to form upper-part of footwear [1].

The sewing of the footwear uppers provides a stitch strength that assures a corresponding choice of the thread and needle. The stitching of patterns uses synthetic threads that present a good breaking strength and elongation.

The stitching is dependent to the strength of materials and also seams strength [2, 3, 4, 5].

The materials' strength for a stitch of 1cm is given by the relation:

$$R_c = R_i (1 - a \cdot d \cdot n) \quad \textbf{(1)}$$

where: R_i-the materials' strength before stitching, daN/cm;

a- the weakening coefficient of the material during stitching;

d- the blade's diameter, cm;
n- the seam's thickness, stitches/cm [1].

The material's strength reduces through the stitching in connection to several parameters: the shape of the needle's point, the needle's diameter, the thickness of the seam and the number of seams.

The most used needle point shapes are illustrated in figure 1.

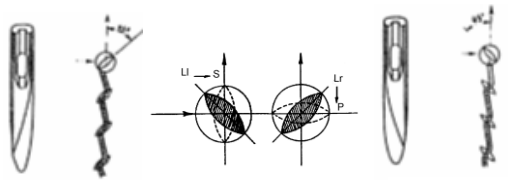


Fig.1: *Usual shapes of theneedle's point section [3]*

The shape of the needle's point section plays a significant part on the stitch density.

The thread strength depends on the initial characteristics of the thread and its weakening during stitching and also on the technological parameters of the stitch, as it follows:

$$R_a = 2\ n\ r\ s \qquad \textbf{(2)}$$

where: n- the seam's density, stitches/cm
r- the thread breaking strength, N;
s- the weakening coefficient of the material during stitching (s=0.6-0.8).

A higher quantity of thread is neccesary as the number of stitches/cm (the stitch density) is bigger, which determine a growth of the thread stength from the stitch.

Instead, as the stitch density grows the material has more holes which results in a decrease of its strength.

In order to obtain a maximum joint strength on tensile test there has to be achieved the next condition: the stitch strength (R_c) is equal to thread stitch (R_a).

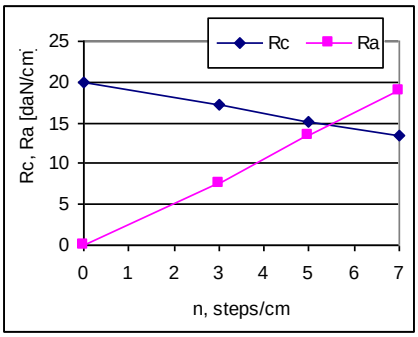


Fig. 2: *Materials and threads strength as function of the stitch*

For example, figure 2 shows the influence of the stitch density (steps / cm) on the thread and material strength, for a leather with PU film, needle NM 100, thread NM 65/3.

As illustrated in the graphic, an uniform increase of the thread strength for a length of 1cm, both with an uniform decrease of the material's strength material, according to stitch density. The two straight lines meet at a density of 5.5 steps/cm (Rc = Ra).

This paper presents the results of the research concerning the stitch strength of two types of leather used for uppers shoes manufacturing.

2. EXPERIMENTAL RESEARCHES

The experimental investigations were carried out using samples of 25 x 65 mm, assembled through simple stitches with 2 threads (type 301), with one or two rows of stitching.

The needles (LR) used are of 1,1mm (NM 110) diameter and the thread is PES (NM 30/3). The samples have been stitched at various densities such as 3, 4, 5 6 and 7stitch/cm. There have been done open seams (figure 3a) and lapped seams (figure 3b) using 2

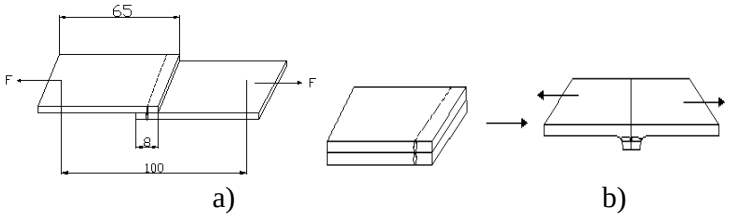


Fig. 3: *Lapped seam (a) and open seam (b)*

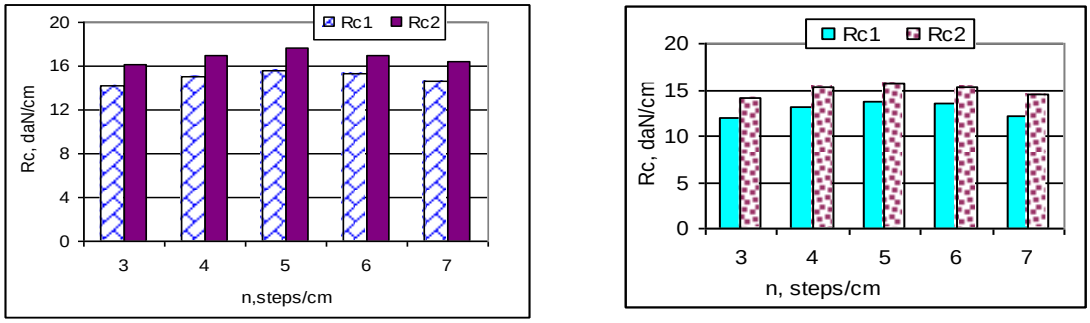
types of leather, full grain leather and full grain leather shiny surface (δ=1,1 mm).
The stitch strength (R_c) is determined experimentally with the relation:

$$R_C = \frac{F}{L} \quad \textbf{(3)}$$

where: F-the breaking force, N;
L-the seam's length, cm.

3. RESULTS AND DISCUSSIONS

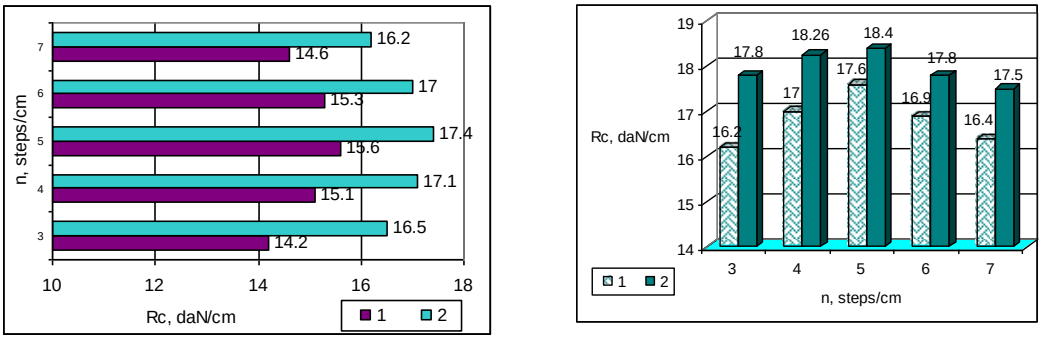
The variation of the strength as function of the stitch density is illustrated in figure 4a for the lapped seam and in figure 4b for the open seam. The stitches have been done with materials of the same type.



a) lapped seam *b) open seam*

Fig. 4*:The dependence of the stitch strength on the stitch density (n)*
Rc_1- the stitch strength of full grain leather; Rc_2- the stitch strength of full grain leather shiny surface

It results a maximum of strength for a stitch density of 5 steps/cm.The graphic shows that the lapped seam is more resistant than the open seam.
The stitch strength increases in the case of joining full grain leather using two rows of stitching, figure 5a. /The joints' strength through stitching grows in the case of full grain leather shiny surface, figure5b.



a) *b)*

Fig.5*: The variation of t he stitch strength (R_c) as function of the stitch density (n) --- lapped seam*
1- the stitch strength for one row of stitching; 2- the stitch strength for two rows of stitching

As the graphic shows, the maximum stitch strength is Rc=18,4daN/cm corresponding to 5 stitches/cm, two rows of stitching.

The experimental values of the stitch strength have allowed a calculation of the material's weakening coefficient through equalizing relation 1 with relation 3:

$$R_{exp} = R_i(1-a \cdot d \cdot n) \quad \textbf{(4)}$$

The weakening coefficient of the material during stitching is calculated as bellow:

$$a = \frac{R_i - R_{\exp}}{R_i \cdot d \cdot n} \quad \textbf{(5)}$$

In the case of the analysed materials: Ri =19.8daN/cm for full grain leather şi Ri=22.1daN/cm for full grain leather shiny surface. The experimental results show a weakening coefficient of 0.33-0.45 for full grain leather and 0.36-0.48 for full grain leather shiny surface.

4. CONCLUSIONS

The stitching strength is dependent on the layer's nature, the needle's diameter, the stitch density, the components layout and the number of seams. The stitching strength increases with the number of rows of stitching.The strength of the lapped seam has higher values than the strength of the open seam, therefore it is recommended to reinforce the open seam.

The experimental values for the stitching strength are highr than the minimum values specified in standard EN 9689/3-1984 leather: 8da6N/cm (one row of stitching) and 10 daN/cm (two rows of stitching). The experimental researches show that the stitching strength for the full grain leather is higher than the one of the full grain leather shiny surface.

The experimental researches obtained for the stitching strength allow calculating the weakening coefficient of the material in the process of sewing (a= 0.33-0.48).

REFERENCES

[1] JC. Chen, J.Chen, Yung-Sheng Su, Simulation Modeling and Analysis for Stitching Line of Footwear Industry, Proceedings of the 2014 International Conference on Industrial Engineering and Operations Management Bali, Indonesia, 2014, Available from http://ieomsociety.org/ieom2014/pdfs/249.pdf

[2] Harnagea F, Stabilirea influenţei unor parametri tehnologici asupra rezistenţei cusãturilor, Lucrãrile celei de a XI Conferinţe române de Textile pielãrie, vol.IV,Ed. Ankarom, Iaşi, 2012, Available from http://www.ius.edu.ba/sites/default/files/articles/16-53-1-PB.pdf

[3] Harnagea F, Stabilirea influenţei unor parametri tehnologici asupra rezistenţei cusãturilor, Lucrãrile celei de a XI Conferinţe române de Textile pielãrie, vol.IV,Ed. Ankarom, Iaşi,1997

[4]] Harnagea F., Cocea M., Aspecte cu privire la influenţa unor parametri tehnologici asupra rezistenţei cusãturilor utilizate la confecţionarea mãnuşilor, Analele Univ. din Oradea, fascicula Textile-pielãrie, vol.III, p 127-137, 2003

[5] Cociu V., Mãlureanu G., Bazele tehnologiei produselor din piele şi înlocuitori,Rotaprint, Iaşi 1993

[6] The Influence of Stitch Density and of the Type of Sewing Thread on Seam Strength, D. Barbulov – Popov, Nenad Cirkovic, Jovan Stepanović, TEM Journal – Volume 1 / Number 2 / 2012.104, Available from https://www.academia.edu/3323698/The_Influence_of_Stitch_Density_and_of_the_Type_of_Sewing_Thread_on_Seam_Strength?auto=download

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A NEW 3D DESIGN METHOD FOR FOOTWEAR SOLES USING DELCAM PowerSHAPE-e SYSTEM

IONESCU Cozmin[1], LUCA Cornelia[2], SÂRGHIE Bogdan[3]

[1] "Gheorghe Asachi" Technical University of Iasi, Doctoral School of Faculty Textile Leather and Management Industry, Bd. Dimitrie Mangeron 28 Postal code 70050, Iaşi, Romania, E-mail: ionescucozmin@yahoo.com

[2] "Gheorghe Asachi" Technical University of Iasi, Faculty Textile Leather and Management Industry, Bd. Dimitrie Mangeron 28 Postal code 70050, Iaşi, Romania, E-mail: cionescu@tex.tuiasi.ro

[3] "Gheorghe Asachi" Technical University of Iasi, Faculty Textile Leather and Management Industry, Bd. Dimitrie Mangeron 28 Postal code 70050, Iaşi, Romania, E-mail: bogdan.sarghie@ymail.com

Corresponding author: Luca Cornelia, E-mail: cionescu@tex.tuiasi.ro

Abstract: *Design methods of soles and soles injection moulds must be accurate, timely and at the same time, accessible to a wide category of soles and injection moulds designers and manufacturers. For designing soles and injection moulds for soles, various dedicated CAD/CAM systems have been developed, such as: Delcam Shoe Solution (3D), Delcam PowerSHAPE-e (2D and 3D), Padsy II (2D) and Padsy III (3D), Shoemaster System (2D and 3D), Lectra System (2D and 3D), Parmel System (2D) and ATOS II System (3D). These systems are equipped with colour displays, plotters, digitizers, terminals and other equipment dedicated for computer aided design activities. Designing 3D soles models using computer systems enables the prevention of ambiguities inherited from 2D drawings, thus reducing errors and remanufacturing. Depending on the design complexity of soles, the technical means available for copying shoe soles and the technologies at the disposal of the soles manufacturers, soles and injection moulds designers adopt various design methods. Not all CAD/CAM systems are accessible for all users, because often their purchasing costs are high. Design method developed and presented in this paper, uses Delcam PowerSHAPE software program, which has the advantage that it can be accessed free of charge from the manufacturer's website. At the same time, this software program provides the user with all the necessary tools and instruments needed to design the most complex injection moulds and footwear sole.*

Key words: *footwear, shoes soles, design shoes soles, mould's soles*

1. INTRODUCTION

Design methods for shoe soles and injection moulds for soles must be regularly updated in order to respond to the latest market demands and to new manufacturing methods and systems of moulds. CAM systems have largely replaced conventional machines from injection moulds manufacturing facilities and this imposed the adoption of CAD systems for the designing process of shoe soles and injection moulds [1]. Apart from the necessity to design shoe soles using CAD systems, the following advantages can be mentioned [2]: 3D visualization of designed soles, design corrections without the need to redesign from scratch, fast and easy grading for all shoe sizes, the

possibility to validate soles design using rapid prototyping [3], the possibility to reuse previous designs for new soles designs thus eliminating several steps, estimating the required volume of polymer mixture for manufacturing soles and estimating production costs. Conventional design methods find their applicability in CAD systems, from the simplest to the most complex soles designs, but CAD systems offer new design possibilities, particular for these systems [4]. This paper presents a new 3D design method, developed by the authors, for footwear soles, using Delcam PowerSHAPE-e software program.

2. DEVELOPED DESIGN METHOD FOR FOOTWEAR SOLES. CASE STUDY

Step 1. Importing the shoe last

To design a shoe sole, it is necessary to digitize or to 3D scan the shoe last into an electronic format recognized by PowerSHAPE-e, IGES is recommended. The shoe last in IGES format is imported in to the workplace. After import, the last is defined by a series of surfaces. For use in design, it is converted into solid. From *File* menu select the *Import / Export* option. Selecting this option opens the *Select file to import* window, that allows to select the file containing the shoe last. After importing the last, it can be visualized in the workplace [5], [6].

Step 2. Converting the shoe last into a solid

The last imported into PowerShape-e software is defined by a series of surfaces. To convert it from *surfaces* to *solid*, select all surfaces of the shape of the last and from *Solid* menu select *Create solid from selected surfaces* tool.

Step 3. Defining the solid from which the sole will be modelled

After positioning the shape of the last in the axis system, orientated correctly in relation to the bearing plane and with heel height set correctly, the primary solid is constructed, so that it encompasses the sole, as shown in Fig. 1. This is the only restriction to create the solid; to facilitate the modelling of the solid it is recommended that it's limits should not be much bigger than the limits of the sole. For modelling the sole, a cuboid will be activated as a solid, which will cover the lower area of the last in all three directions (length, width and height). The cuboid has to exceed the limits of the shoe last (lateral, posterior, anterior and inferior). To create the cuboid, *Create solid block* tool will be enabled, and associated tools will be used to positioning and resizing it.

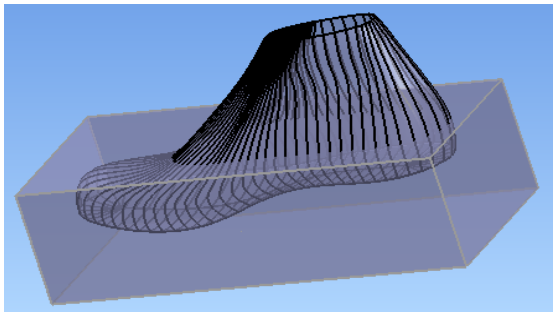
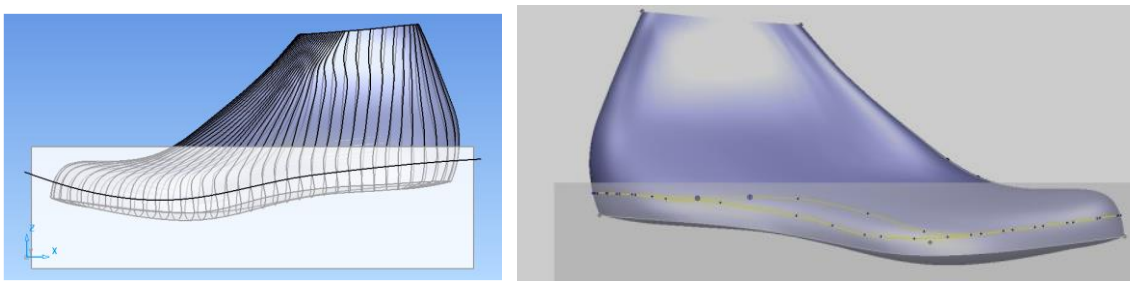


Fig. 1: *Defining the solid from which the sole will be modeled*

For the lateral contour of the sole and for the perimeter contour, slicing method with surfaces will be used [7], [8]. Slicing surfaces will be defined by a curved profile, linear, combined, opened or closed. In this case study, the upper lateral profile will be defined by an open type Bezier curve. Based on this curve, slicing surface will be created. The upper outline of the sole is defined by the adhesion limit between the sole and the footwear uppers, Fig. 2a. Depending of the destination of

the footwear product and the specific functions that must be ensured by the sole, the shape of the contour may be different from interior to exterior. Therefore, the interior upper contour limit can be higher to provide increased support for the arch of the foot, as shown in Fig. 2b. The difference between the lower contour of the last and the upper sole contour forms the lateral profile of the sole.



a. *b.*

Fig 2: *Defining the upper lateral profile of the sole*
a. upper outline of the sole; b. highlighting the difference between inner and outer contour

Step 4. Defining the surface for sectioning

After sectioning the solid and removing the excess from the top region, the sole profile in this area is obtained. The interface surface has to exceed the cuboid solid in all lateral direction. The tool used for slicing the contour by surface is *Split the active solid using the selected solid, surface or symbol.* Therefore, after deleting the upper section of the solid, the upper profile of the sole is visible. These steps are presented in Fig. 3.

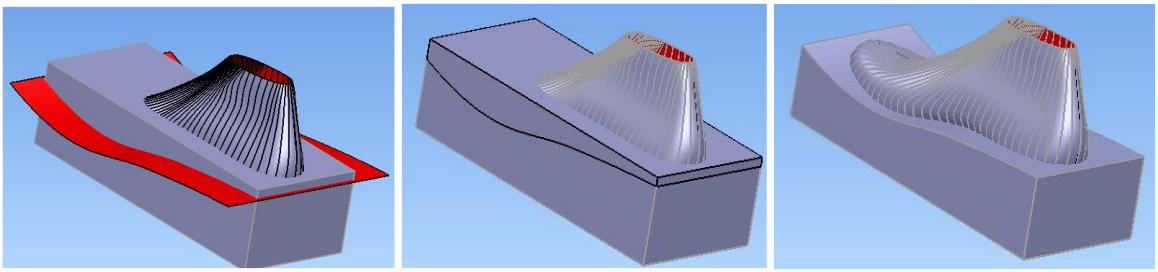
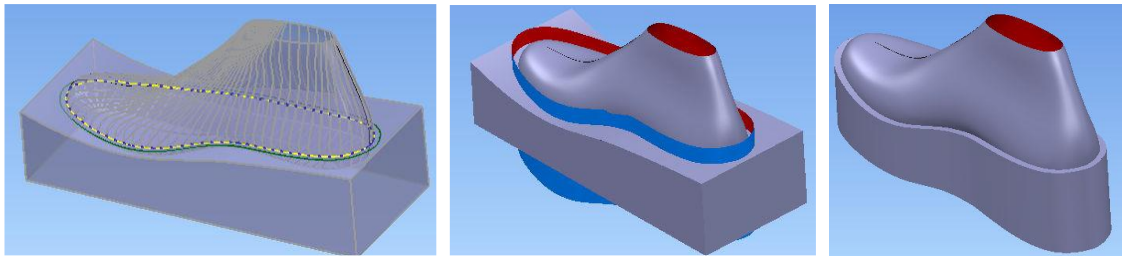


Fig. 3: *Defining the surface for sectioning*

Step 5. Defining the outer perimeter of the sole

The shape of the outer contour of the sole can be defined in several ways. The inner contour is defined by the intersection of the last with the solid. The resulting inner contour is represented by the curve of the yellow colour in Fig. 4. The outer contour is created by using *Offset object* tool, represented in the same Fig. 4a, by the green curve. To *offset* the contour to the exterior of the lasts, negative values were used. The outer contour (green colour) defines the sectioning surface profile. in this case, the outline is closed, and the area will be tubular.

If a contour that does not follow the shape of the last is desired, or which has a more complex shape, it can be traced by using line and/or curved segments. To define this contour, it is necessary to define an intermediary contour, resulted from the intersection between the last and the volume defining the sole, as shown in Fig. 4b. After that, the outer contour is traced by shifting the intermediary contour. the sectioning is carried out in the same way as in the case of the upper profile, equidistant from the inner contour. After sectioning the solid, the exterior is deleted, remaining the solid presented in Fig. 4c.



a. *b.* *c.*

Fig. 4: *Defining the outer perimeter of the sole*
a. defining the inner contour; b. defining the intermediary contour; c. sole exterior perimeter

Step 6. Defining the bottom lateral profile of the sole

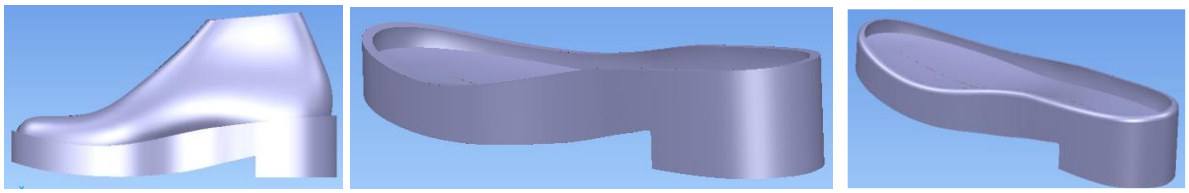
Designing the bottom profile of the sole is done as in the case of the upper profile. First, the profile of the sole is drawn, which can be composed of straight and/or curved sections. Based on the created profile, the sectioning surface is created. After the solid is sectioned, the bottom excess solid is removed and the bottom lateral profile of the sole is obtained, as shown in Fig. 5a.

Step 7. Defining the sole concavity on the upper surface

The sole concavity represents the area that will be in direct contact with footwear uppers. The actual volume of the sole, as shown in Fig. 5b, is defined by removing from the volume of the solid, defined in the previous phases, the part that intersects the volume of the last. Thi is done by using the logical operator.

Step 8. Adjustments to the shape of the sole

Depending on the design requirements, it make take a number of adjustments to the shape of the sole. For example, rounding the outer edge of the sole. This operation, presented in Fig. 5c, is obtained by connecting the upper surface to the lateral surface. In order to obtain different designs, the upper edge of the sole can be processed in several ways.



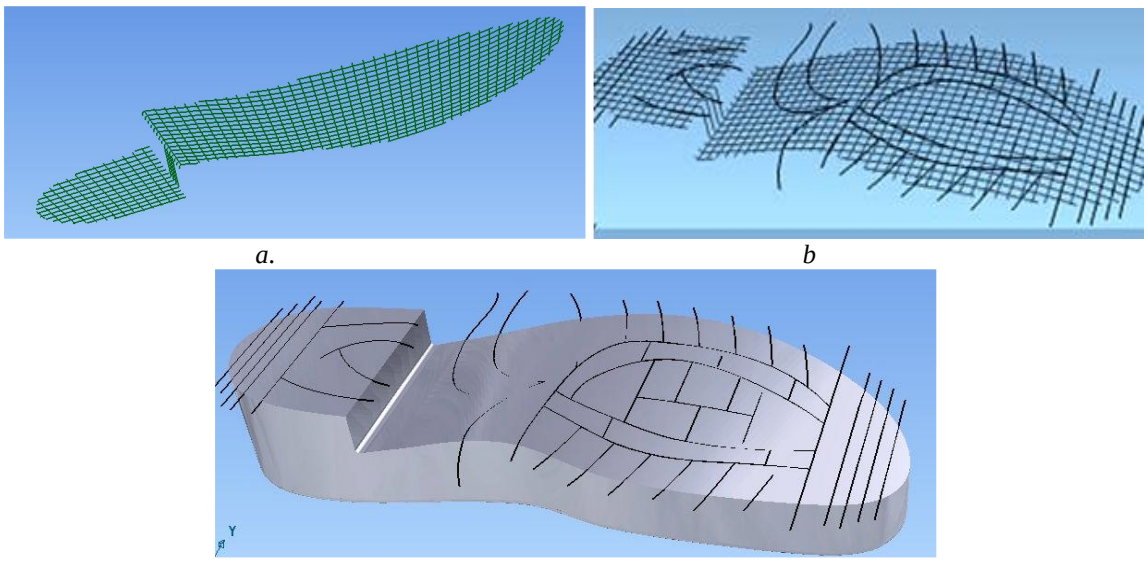
a. *b.* *c.*

Fig. 5: *Designing the 3D shape of the sole*
a. defining the bottom lateral profile; b. defining the sole concavity; c. finishing the 3D shape of the sole

Step 9. Designing the antiskid embossment design

In order to design various elements on the bottom surface of the sole, a network of construction lines is build, as shown in Fig. 6a. This network complies with the 3D shape of the plantar surface. The antiskid design is drawn on the defined network, using a series of segments composed of straight and/or curved lines. By projecting this network of lines on the plantar surface of the sole, a spatial network of lines is obtained. As long we comply with the spatial shape of the plantar surface, relief elements, defined as solids, can be defined by any available methods (primitive solid, generated or built). Based on this method, the whole assembly of components is designed in order to be catted, as shown in Fig. 6b. Depending on the designed model, the trajectories for generating various antiskid relief will have various shapes. By viewing the designed

solid and the trajectories, it can be verified the ownership of the trajectories on the surface of the sole. All curves are extended beyond the margins of the sole in order to ensure proper edge sectioning, as showed in Fig. 6c.

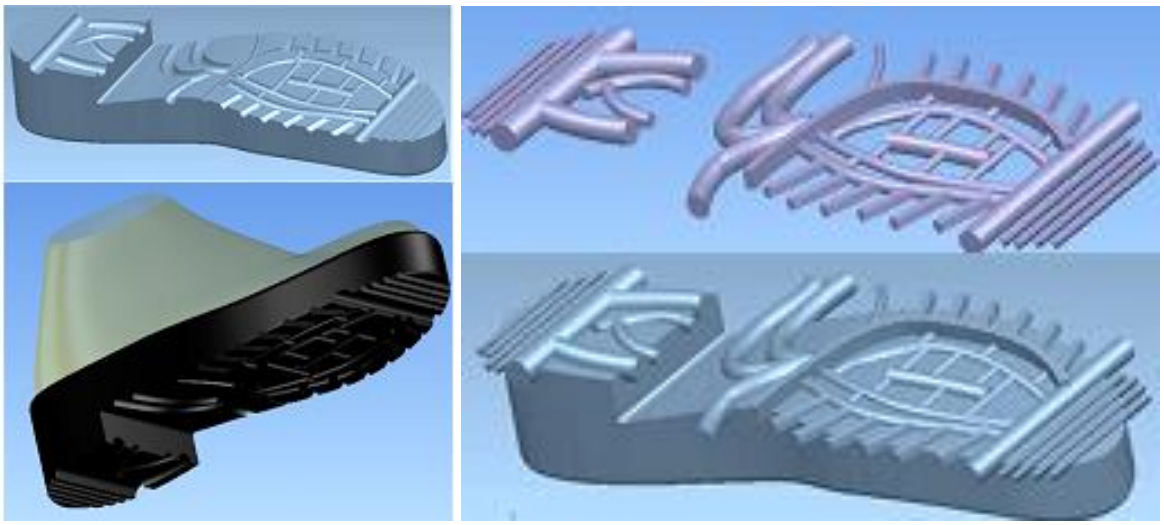


a. *b*

c.

Fig. 6: *Defining the antiskid design*
a. network of construction lines; b. drawing the antiskid lines; c. projecting the antiskid design lines on the bottom surface of the sole

For each trajectory individually, the base outline (section) is traced. Based on defined sections and associated trajectories, solids that define the antiskid relief are designed. Created solids are placed on the bottom surface of the sole, as shown in Fig. 7a. The final shape of the sole s smoothed using software specific tools, Fig. 7b. [5] , [9].



a. *b.*

Fig. 7: *Designing the antiskid relief*
a. defining solid shapes; b. defining smoothing the antiskid relief

5. CONCLUSIONS

Design methods of shoe soles and by default of soles injection moulds must be accurate, fast and accessible to a wide category of designers and manufacturers. Manufacturers adopt various design methods depending on the design complexity of soles, the technical means available for copying shoe soles and the available manufacturing technologies. In the field of footwear soles and injection moulds design, advanced CAD/CAM systems have been developed. Most of these systems are not accessible to all users because of their high price. Delcam PowerSHAPE-e software program used in the development of the design method presented in this paper, has the advantage that it can be accessed for free from the manufacturer website. On the other hand, PowerSHAPE allows a mixture of design instruments, combining solid shapes modelling with surfaces modelling and has the flexibility needed for designing complex shapes, such as footwear soles. The soles designed using PowerSHAPE can be easily modified to obtain various 3D soles designs with multiple layers and colours. Unlike other CAD environments, using PowerSHAPE, 3D solid shapes and surfaces can be designed with minimum effort. The developed design method can be approached in advanced design of footwear soles and injection moulds for sole.

REFERENCES

[1] M. Stein, E. Bowman, G. Pierce, ”Direct 3D. Professional Reference,” in New Riders Publishing, 2008, pp. 30-55.

[2] M. Costea, A. Mihai, ”The structure and design of footwear”, Publisher Performantica, 2015, ISBN 978-606-685-328-6, pp 125-142.

[3] M. Costea, “Footwear and rapid prototyping modeling components prophylactic”, Publisher Performantica, 2015, ISBN 978-606-685-328-6, pp. 80-97.

[4] M. Drişcu, “Modeling of Planar and Spatial Forms of Footwear”, in Romanian, Pim Press Iaşi, 2008, pp.109-134.

[5 C. Ionescu, R. Mocanu, C.Luca, “*Contributions to diversify soles moulds that forms directly on faces shoes”*, in Annals of the University of Oradea, Fascicle of Textiles-Leatherwork, Volume XVI, No. 1, 2015, pp.117-122.

[6] C. Luca, R.Mocanu, “*Geometrical Design Algorithms for Moulds Shoe Soles*” in Annals of the Oradea University, Fascicle Mechanical Engineering Department, 2011, pp.4.19-4.25.

[7] L. Mărcuş, “*Regarding the Lasting of Footwear Uppers Using Different Technological Variants*”, in Annals of the Oradea University, Fascicle of Textile Leatherwork, 2008, pg. 331-336.

[8] E. Chirilă, C. Luca, *“Solutions of the different models of cavities for soles obtaining”,* in Annals of the University of Oradea, fascicle of Textiles-Leatherwork, volume IX, 2008, p.236-240.

[9] C. Ionescu, R. Mocanu, I.Cioară *“Obtaining modular cavities in moulds used forming soles directly on the footwear”,* in Proceedings AUTEX 2015,15th World Textile Conference, Bucharest, Romania, ID 162.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

A REVIEW ON HEAVY METALS CONTENTS IN HIDE, SKIN AND PROCESSED LEATHERS

KOIZHAIGANOVA Meruyert [1,*]

[1] Denizli Vocational School of Technical Sciences, Pamukkale University, 20013 Denizli, TURKEY

*Corresponding author: Koizhaiganova Meruyert; E-mail: meruyertk@pau.edu.tr

Abstract: *Heavy metals are metals with high atomic weight which can be deposited in soil, water, plants and animals. It is generally known that mammal tissues are good bioindicators of trace elements, including heavy metals. Heavy metal analysis serves to identify and quantify the elements that are a potential hazard to the consumer after varying levels of contact. Usage area of leather is increasingly expanding in these days and it has also become a material requested and demanded by effect of fashion. Leather must protect its appearance and physical stability and also be problem-free in ecological terms and harmless to human health. There is a lack of data concerning the content of toxic elements in raw hide and skin of animals. Mainly information concerning metals content, including toxic ones, in processed leathers may be found in the literature. The aim of the present study was to review and compare the content of some heavy metals in raw hide, skin and the processed leathers in order to evaluate their accumulation and transition to the end-up product.*

Keywords: *Heavy metal, Hide, Bioindicator, Tanning, Leather*

1. INTRODUCTION

Heavy metals are metals with high atomic weight which can be deposited in soil, water, plants and animals. It is generally known that mammal tissues are good bioindicators of trace elements, including heavy metals. Hides and skins are generally one of the most valuable by-products from animals. The uses of animal skin and hide include food, cosmetics, medicine, pharmaceutical and photography industries. Gelatin extracted from animal skins and hides can be used for food. Approximately 6.5% of the total production of gelatin is used in the pharmaceutical industry. Collagen from hides and skins has a wide variety of applications, from food to medical. Collagen can be used as an emulsifier or filler in meat products or to make collagen sausage. It is used in cosmetic surgery and burn surgery [1]. The tanning industry enables the skin and hide to be recovered and made into special and fashionable material as leather. All kinds of leathers have to pass through three main stages viz. preparatory processes, tanning and finishing processes. Items harmful to environment and human health such as heavy metals may form within the leather due to chemicals added and methods used during leather processing steps to cause leather have desired characteristics [2]. Regulatory requirements are important for reasons of all product safety and quality.

Heavy metal analysis serves to identify and quantify the elements that are a potential hazard to the consumer after varying levels of contact. Interest in the heavy metal content of ecological textile has been increasing recently. It is likely that investigations concerning ecological textile will expand

in the future and will include leather goods as well [3]. It is important to have adequate information about the composition of trace elements in leather, because some of the elements could prove toxic to man at certain concentrations [4]. There is a lack of data concerning the content of toxic elements in raw hide and skin of animals. Mainly information concerning metals content, including toxic ones, in processed leathers may be found in the literature [3, 4, 5, 6]. But heavy metals may have been transferred to the leather through the metabolic activities of the animal while it was alive [5].

In this research, a review and comparison of the content of some heavy metals in raw hide, skin and the processed leathers in order to assess their accumulation and possible transition to the end-up products were performed.

2. HEAVY METAL CONTENS IN RAW SKIN AND HIDES

Environmental pollution highly influences the bioaccumulation of chemical elements in animals and plants [7]. Skin is an invasive matrix and its use in biomonitoring studies can be questioned because of ethical reasons [8]. There is lack of a data concerning the chemical composition, including the levels of toxic elements, in animal raw skin or hide and their possible relationship with the chemical composition of the processed leather.

Statistically significant differences for some heavy metals between wild and farm animals were detected in skins of foxes [8]. Farm and wild foxes differed significantly in terms of the content of Pb, Cr and Ni, and highly significantly with Zn and Cu content in skin (Table 1). The level of Pb was higher in wild animals, while that of Cu, Cr, Zn and Ni was higher in farm foxes. The latter group was probably fed with feed enriched with microelement supplements. Higher levels of Pb in wild animals can be justified with environmental exposure. Over a 2-fold higher content of Zn in skin of farm foxes as compared to wild ones is remarkable.

Table 1: *Heavy metal contents in fox skins (mg kg^{-1})*

Foxes	Cr	Cu	Ni	Pb	Zn	Ref
Wild	1.405	7.680	0.447	1.445	151.500	[8]
Farm	2.338	10.847	0.803	0.827	403.833	
Farm Silver (mean values)	0.422	10.846	0.970	0.826	403.833	[9]
Farm Arctic (mean values)	0.285	16.383	0.515	0.696	299.000	

In their latter study, authors have investigated the influence of two farms locations on the concentration of some heavy metals in skin of arctic and silver foxes [9]. Generally, considerably higher content of heavy metals was found in skins of these foxes, but Cr content was found lower than in the previous study even for the same silver farm fox (Table 1). Although there were differencies in the contents of heavy metals in skins of the arctic and silver foxes, the elements were placed in the sequence as Zn>Cu>Pb>Ni>Cr. Despite of the most prefered bioindicators as the tissues and organs of animals, the usefulness of skin of foxes in bioindication and ecotoxicological studies has been started by the mentioned studies [8, 9].

As it is known in African countries skins and hides of some animals like goat and cattle are used as food after dehairing or singeing with different methods. Researchers investigated the effect of singeing methods on heavy metals contents in goat skins [10]. The data regarding the contents of some metals in un-singed and un-cooked goat skins are given in Table 2. The heavy metal concentrations observed in the un-cooked samples were lower for some metals than results obtained for un-singed goat skins [11]. However, they confirmed the possible means of contamination of skin

samples with heavy metal prior to analysis by the metal content of the tyre scraps used [12]. Researchers reported that singeing is not the only means by which animals could pick up heavy metal residues, but also, the soil, feed and drinking water are potential avenues from which the heavy metal residues could be picked up by the animals [13]. This explained why there were heavy metal residues in the skins of the unsinged carcasses. The levels of Mn, Cu, Ni and Cd in fresh, un-singed goats hide were respectively 0.64 ± 0.12, 1.06 ± 0.12, 1.74 ± 0.24 and 1.89 ± 0.27 mg/kg (Table 2). The animals could potentially have picked heavy metals from the environment during grazing, drinking water from polluted drains and streams, scavenging in open waste dumps for fodder and exposure to atmospheric depositions particularly from automobile fumes [12].

Table 2: *Heavy metal contents in goat skins (mg kg^{-1})*

Process	Fe	Mn	Cu	Zn	Pb	Cd	Ni	Ref
Un-singed	NA	0.64±0.12	1.06±0.12	NA	NA	1.89±0.27	1.74±0.24	[10]
Un-singed	9.67	ND	10.24	19.01	0.04	ND	NA	[11]
Un-cooked	5.78±0.17	0.27±0.07	0.25±0.00	2.35±0.03	0.12±0.02	ND	0.016±0.01	[12]

ND - not detectable; NA - not available

The substantial levels of heavy metals revealed by analysis of the cattle hides are given in Table 3. Magnesium, Cu, Ni, Cd, Mg and Zn in un-singed cattle hide in Ghana were, respectively 1.43 ± 0.12, 2.47 ± 0.26, 2.63 ± 0.12, 1.12 ± 0.48, 41.30 ± 2.49 and 17.71 ± 3.48 mg/kg [10]. The hides of cattle slaughtered in Nigeria accumulated varying levels of heavy metals and the mean concentrations of Cd, Cu, Fe, Ni and Pb in un-singed hides were 1.93±0.39, 10.45±1.19, 9.88±1.11, 1.95±0.12 and 5.65±0.70 mg/kg, respectively [14]. The mean concentration of Cu and Cd were higher while Ni had lower value than those of the first study (Table 3).

The high concentration of heavy metals recorded in the unsinged hides may be attributed to the presence of heavy metals in the local environment which the animal could easily have come in contact with through scavenging in open waste or refuse dumps, free range grazing, drinking water from polluted streams and drains and exposure to atmospheric depositions especially from automobile fumes and open burning of solid waste [10]. These metals could also have come from various sources like vehicle emissions, tyre and engine wears, and agricultural chemicals, urban and industrial wastes [15]. Authors reported high levels of lead and cadmium in polluted soils could serve as a source of heavy metals in animals grazing in such area [16].

Table 3: *Heavy metal contents in raw cattle hides (mg kg^{-1})*

Process	Cu	Zn	Cd	Pb	Fe	Cr	Ni	Ref
Un-singed	2.47±0.26	17.71±3.48	1.12±0.48	NA	NA	NA	2.63±0.12	[10]
Un-singed	10.45±1.19	NA	1.93±0.39	5.65±0.70	9.88±1.11	NA	1.95±0.12	[14]

NA - not available

3. HEAVY METAL CONTENS IN THE PROCESSED LEATHERS

Although the heavy metals may have been transferred to the leather through the metabolic activities of the animal while it was alive, large quantity of some of them in the natural leathers may originate from the metal based chemicals used in the many steps of leather manufacture, heavy metals in the water used in processing, or contamination from mechanical processes [6].

European Commission completely prohibited Pb, Cd, Cr (VI), As, Hg content and their compounds in textile and leather products. Limit values were imposed for other heavy metals as well [17]. Therefore, a more awareness and controlled manufacturing process has become mandatory for leather industries.

Table 4 shows the analysis results for As, Br, Co, Fe, Rb, Sb and Zn in leather samples from Kano, Nigeria. When 12 samples were analysed, As was determined in 2 of them, while Sb was determined in 1 of the samples. It was stated that arsenic was used to protect cattle from parasites and it is possible that this could be a source of arsenic in hides [4]. The presence of antimony may be due to the metal salts in the dyes and fixing agents for dyes used in leather production [3].

Table 4: *Trace metal contents in leathers from tanneries of Kano, Nigeria (mg kg^{-1})*

	Places taken	As	Br	Co	Fe	Rb	Sb	Zn
Processed leather	Craft market	-	4.4	0.33	242	-	-	10.9
	Local tannery	1.16	0.7	0.93	4000	-	0.2	41.7
	Collected	-	3.7	0.6	5333	8.9	-	39.6

Most of studies concerning heavy metal contents, including toxic ones, in the processed leathers were performed in Turkey (Table 5). Aslan (2009) observed eleven chemical elements in tanned leathers with the amounts dependent on tanning technique. Chromium, aluminium and zirconium showed the highest levels, while Hg, As, Sb, Cd and Ni the lowest. It was observed that tanned animal hides contain from 0 to 36,000 ppm of Cr depending on tanning technique [2]. Basaran et al. (2006) obtained the highest amount of Cr, and a considerably lower level of Zn and Cu [5]. The heavy metal detected in natural upholstery leathers in the greatest quantity was chrome. Small amounts of aluminum, cobalt, copper, nickel and zinc were also determined [6]. An amounts of heavy metals revealed by exposure of the furniture leathers to sweat during use have been identified and compared to limit values presented for leather products [18].

Table 5: *Heavy metal contents in different types of the processed leathers (ppm)*

Metals	Gloving leather	Bootee leather	Garment leather	Upper leather	Insole leather	Upholstery leather	Furniture leather	Leather solid waste
Cd	0.29	1.28	0.39	0.55	0.34	-	0.52	0.41
Co	1.13	-*	1.40	1.65	7.99	2.94	31.74	-
Cr	22 105	29 614	19201	17.728	-	168.42	16 549	36 000
Cu	83.46	-	9.46	35.37	51.60	6.57	53.74	18.11
Zn	33.45	-	28.06	31.66	27.35	11.93	-	27.70
Pb	11.42	1.21	14.42	4.19	11.16	-	2.13	5.15
Ni	3.97	-	3.27	2.26	2.25	0.11	1.89	2.59
Sb	-	1.45	-	-	-	-	-	2.71
As	-	0.63	-	-	-	-	-	0.13
Ba	-	0.91	-	-	-	-	-	-
Se	-	1.63	-	-	-	-	-	-
Hg	-	0.51	-	-	-	-	-	0.01
Al	-	-	-	-	-	602.33	-	581.99
Zr	-	-	-	-	-	-	-	180.37

*- not available

Authors reported that the high concentration of heavy metals in the processed leathers may be attributed to the industrial chemicals used during the leather manufacture. For example, the presence of cobalt in some of the leather samples may be attributed to dyes that are used for leather finishing, since leather dyes may contain cobalt metal complex [4]. Presence of cobalt may also be originated from bioaccumulation while animal was alive or from the machines used during the processing of the leathers [6]. The amounts of cadmium determined can varied according to the color of leathers, and be resulted from pigments used in the leather production process [5]. The high amount of chrome is the result of the fact that tanning is mostly done with chrome sulfate salts. Manufactured goods tanned with chrome contain at least 2.5% Cr_2O_3 [19]. Calculated by the atomic weights of chrome and oxygen, this amounts to approximately 17 100 ppm chrome. The high chrome content may be a result of colorants and contamination during mechanical processes as well [20, 21]. The copper detected in processed leathers may be caused by contamination during the production of leathers and metal complex dyes used in dyeing [5, 20]. The presence of Zn and Al may have been caused by contamination, inorganic pigments, or the water used in leather manufacture [6]. Besides Zn may have originated from the metabolic activities of the animal while it was alive as it was seen in the above studies [8-12, 14], and aluminum is used during the tanning and retanning of the natural leathers [2]. Lead and mercury determined in natural leather samples may derive from the environment of the animal or the slaughterhouse [22]. Ni detected in leathers might be caused by dyestuffs used in leather production process or stainless steel based machines and tools [6].

4. CONCLUSIONS

Toxic metals are accumulated in plants, and animals fed with these plants will tend to accumulate toxic metals themselves. The effects of their accumulation must be taken into account when considering the increased expectation of life quality. Although contamination of animal feed by toxic metals cannot be entirely avoided given the prevalence of these pollutants in the environment, there is a clear need for such contamination to be minimized, with the aim of reducing both direct effects on animal health and indirect effects on human health. In addition, the heavy metal restrictions in consumer products have had a significant impact on industrial developments. It is extremely important that all the by products from hides and skins contain only a low quantity of harmful substances or, if possible none at all.

REFERENCES

[1] K. Jayathilakan & Khudsia Sultana & K. Radhakrishna, A. S. Bawa, *"Utilization of byproducts and waste materials from meat, poultry and fish processing industries: a eview"*, J Food Sci Technol 49(3):278–293, 2012.

[2] A. Aslan, "*Determination of heavy metal toxicity of finished leather solid waste*". B Environ Contam Tox**.** 82: 633-638, 2009.

[3] H. A. Karavana, B. Başaran, A. Aslan, B. O. Bitlisli, G. Gülümser, "*Heavy metal contents of bootee leathers tanned with different process recipes*", Tekstil ve Konfeksiyon 3/2011, 305-310, 2011.

[4] S. Okoh, D.J. Adeyemo, R.A. Onoja, S.A. Arabi, "*Determination of Some Trace Elements in Leather*". International Journal of Applied Science and Technology 3(1), 101-105, 2013.

[5] B. Basaran, M. Iscan, B.O. Bitlisli, A. Aslan, "*A study on heavy metal contents in different types of finished leathers*", J. Soc. Leath Tech. Chem. 90, 229, 2006.

[6] A. Aslan, N. O. Üzüm (Işik), "*Determining the heavy metal contents of natural and artificial upholstery leathers*", Tekstil ve Konfeksiyon, 25(1), 33-37, 2015.

[7] V. R. Angelova, R. V. Ivanova, J. M. Todorov, K. I. Ivanov, "*Lead, Cadmium, Zinc, and Copper Bioavailability in the Soil-Plant-Animal System in a Polluted Area"*, TheScientificWorld Journal 10, 273–285, 2010.

[8] A. Filistowicz, Z. Dobrzański, P. Przysiecki, S. Nowicki, A. Filistowicz, "*Concentration of heavy metals in hair and skin of silver and red foxes (Vulpes vulpes)*", Environ. Monit. Assess. 182, 477–484, 2011.

[9] A. Filistowicz, P. Przysiecki, S. Nowicki, A. Filistowicz, M. Durkalec, *"Contents of Copper, Chromium, Nickel, Lead,and Zinc in Hair and Skin of Farm Foxes"*, Pol. J. Environ. Stud. 21(4), 865-869, 2012.

[10] K. Obiri-Danso, J. N. Hogarh, P. Antwi-Agyei, "*Assessment of contamination of singed hides from cattle and goats by heavy metals in Ghana*". African Journal of Environmental Science and Technology, 2(8), 217-221, 2008.

[11] I. Adam, D. Okyere, M. Teye, "*Assessment of Heavy Metal Residues in Hides of Goats Singed with Tyres, and the Effect of Boiling on the Heavy Metal Concentrations in the Hides*", J. Vet. Adv. 3(5), 165-169, 2013.

[12] N.C. Igwemmar, J. I. Tankwo, U. E. Okoh, N. L. Umedum, *"Assessment of Heavy Metal Contaminantsi Goat Hides Singed Using Tyre Scraps and The Effect of Cooking on The Metal Concentrations in The Hides"*, Academic Journal of Science, 04(01), 115–123, 2015.

[13] C.A.I. Qiu, M. Long, J. Liu, M. Zhu, Q-Z. Zhou, Y-D. Deng, Y. Li, Y.J. Tain, *"Correlation between heavy metals concentration in cattle tissues and rearing environment"*, Chinese J. of Ecol. 27(2), 202-207, 2008.

[14] K. Ekenma, N. J. Anelon, A. A. Ottah, "*Determination of the presence and concentration of heavy metal in cattle hides singed in Nsukka abattoir"*, J. Vet. Med. Anim. Health, 7(1), 9-17, 2015.

[15] C.O.B. Okoye, J.N. Ugwu, "*Impact of environmental cadmium, lead, copper and zinc on quality of goat meat in Nigeria*". Chem. Soc. Ethiop. 24(1):134. (2010).

[16] C.O.B. Okoye, C.N. Ibeto, Book of Proceedings of the 31st Annual International Conference of the Chemical Society of Nigeria, Chemical Society of Nigeria: Warri. pp 767-771. (2008).

[17] European Commission, 2004. "Official Journal of the European Communities", http://europa.eu.int/comm/environment/ecolabel/pdf/furniture/draft_criteria_furniture _june2002.pdf (20 March 2016).

[18] N. O. Işık, A. Aslan, G. Gözaçan, A. Ersen, H. A. Karavana, "*Determination of Heavy Metal Content in Processed Furniture Leather"*, II International Leather Engineering Congress "Innovative Aspects For Leather Industry" May 12 – 13, 2011, Izmir/Turkey.

[19] BASF, 2010, "*Pocket Book for the Leather Technologist*", http://visdombasfcrm.com/lp/Blue%20book.pdf (04 April 2016).

[20] G. John, "*Finishing*", Possible Defects In Leather Production. Druck Partner Rübelman GmbH, Germany, 158-209. 1997.

[21] D.Graf, "*Formation of Cr (VI) Traces in Chrome Tanned Leather: Causes, Prevention and Latest Findings*", JALCA, 96, 169-179, 2001.

[22] J.H. Sharphause, "*Leather technician's handbook"*, Leather Producers Association, Northampton, 1989.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CONTRIBUTIONS TO CLASSIFICATION ZIPPERS USED IN INDUSTRY FOOTWEAR AND LEATHER GOODS

MALCOCI Marina[1], PASCARI Ioana[1]

[1] University Technical of Moldova, Faculty of Light Industry, Postal address MD 2045, S. Rădăuțan str., 4, degree block number 11, Chisinau, Republic of Moldova, E-Mail: mmalcoci2005@yahoo.com

Corresponding author: Malcoci, Marina, E-mail: mmalcoci2005@yahoo.com

Abstract: *Now customary accessory companies of all leather garments, zipper began to enjoy popularity only after 80 years of its invention. The first is considered the inventor of the zipper Elias Howe. Essentially involves fashion, change, innovation, originality, creativity and is defined as a succession of trends or fads, short. Create fashionable leather confections from home means accepting a contract with the producer and / or consumer, showing a profit motivating all at the right time. Continuous which require the exercise involves creative skills of fashion design, leading to a wide range of products. Current zipper is composed of: slider, teeth, strips shooter stops. Currently there is possibility to customize shooters to customer requirements, and even to form their own zippers. The present work presents the classification criteria zippers. They are after construction fastener after destination zippers, after the role they fulfill zippers, after the presentation at the procurement zippers, after finishing module of the metallic elements, as visibility zipper in the product, by type of teeth, by nature material strip zipper, after the type of materials they are made pullers, after the nature of the materials they are made of sliders and stops after the oxidation of metal components after finishing module teeth after shaped zipper, after slider type, by mode of ornamentation zippers. Knowing appearance zippers, elements of which it is composed, and their classification criteria allow us to correlate the shape of the product and destination.*

Key words: *classification, zipper, elements, history, criteria*.

1. HISTORY ZIPPER

Now customary accessory companies of all leather garments, zipper began to enjoy popularity only after 80 years of its invention. The first is considered the inventor of the zipper Elias Howe, who also invented, and the sewing machine. In 1851 he invented an "automatic closing mechanism for clothes". Forty-four years later, Whitcomb Judson brought to market a "closure" very similar to Howe invented the zipper. Being first to market, Withcomb remained known as the "inventor of the zipper", but in 1893, when it was officially launched on the market was not yet used the term "zipper". Imboltul for this invention was from his wife, who always complained of sore toes on sewing a button [1]. Whitcomb within a few years invented and patented the first zipper of which is used for the first time in footwear (fig. 1) [2]. Initially, the product has not enjoyed great success.

In 1913 Swedish engineer Gideon Sundback zipper modernized model, giving life to a new and zipper that we use in our everyday life [3].

A romanian inventor, Lucian Balan, considered that the zipper has many undiscovered qualities and invented the "zipper multifunctional", which incidentally invention and patented it.

"The zipper multifunctional" has provided a kind of contact, which produce noise or light when the zipper is open. This zipper bag is made specifically for cases in which the dark looking for something in your bag or in cases where someone tries to steal purse [1].

Fig. 1: *First appearance zipper used in the footwear industry*

2. ELEMENTS ZIPPER

The zipper is a device for the conclusion of clothing, shoes, handbags, briefcases, etc., consisting of two rows of blades (attached to a strand of cloth, leather, etc.) facing each other, which intermesh each other using a small parts made to slide between them [4].

The zipper is made (fig. 2) [5]:

- slider - device slid along the zipper to unite or separating zipper teeth;
- teeth - the elements that make possible closure and zipper opening;
- strips - that part of the zipper teeth are fixed;
- shooter - fixed element cursor to easily raise and lower it;
- stops - do not allow elements which strips out the zipper slider, the zipper stop at the beginning and end.

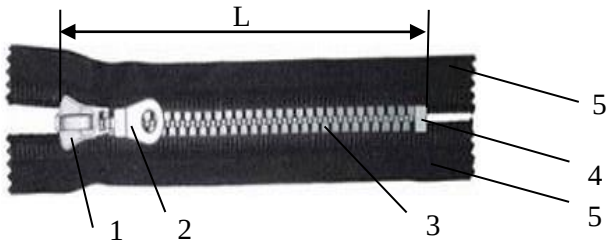


Fig. 2: *The components of the zipper: 1 - slider; 2 - shooter; 3 - zipper teeth; 4 - stop at the beginning of the zipper; 5 - fastener strip; L - length zipper.*

The most commonly used lengths of zippers designed for footwear and leather goods are presented in table 1 [6].

Table 1: *Parameters zipper*

Name of material for teeth	**Length zipper, L, mm / Range, mm**			
Metal	70-160/10	160-300/20	300-500/25	500-1000/100
Plastic	-	100-300/20	300-1000/50	>1000/100

3. CONTRIBUTIONS TO CLASSIFICATION ZIPPERS

With the modernization and development of the company have developed many different types of zippers, they were classified as follows:

- After making the fastener [7]: undetachably; removable; 2 removable sliders; 2 sliders type a non-detachable; non-detachable type X; removable loop and detachable quick opening.
- After zippers known destination for footwear, leather goods and clothing.
- After fulfilling the role zippers [8-9]: functional products used to open and close; decorative and functional - decorative.
- After the presentation at the procurement zippers: zippers, zippers film and precast (finite).
- After finishing module of metal elements [8-9]: covered with a protective layer; covered with a protective layer.
- After the zipper visibility in the product [7]: visible and invisible.
- By type of teeth, distinguish [7]: teeth spiral; metal; injected. Injected zips teeth and tooth spiral is characterized by attractive design, high quality and versatile, being lighter than metal.
- After fastener strip material nature [7]: polyester; polyamide; cotton.
- By nature of the materials they are made pullers: metal; plastics; natural skin; artificial leather etc.
- By nature of the materials they are made of sliders and stoppers: metal; plastic.
- After the oxidation of metallic elements [10]: easily oxidized; oxidised environment; hard oxidized.
- After finishing module teeth [7]: standard finish (colored belts); metallic finish; transparent or transparent-color finish.
- After the zipper form: straight; curve.
- After slider type [7]: non-lock slider; double pull; automatic slider; semi-automatic slider; pin lock slider; integrated slider; reversible slider; plastic slider.
- By way of ornamentation zippers [7; 11]: zipper decoration applied (eg., rock crystal); without ornaments.

Classification criteria identified can be grouped as follows: feature zippers, destination zipper, zipper role, technological character (fig. 3) [12].

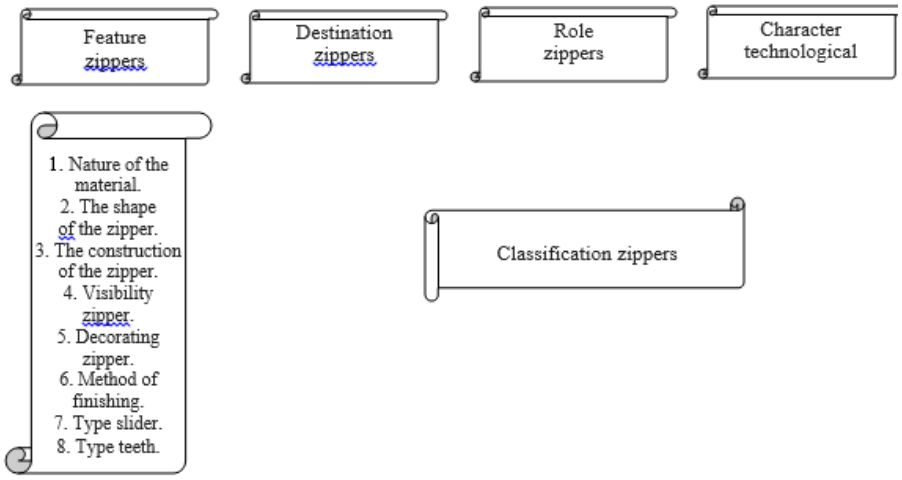


Fig. 3: *Classification zippers*

4. CONCLUSION

Essentially involves fashion, change, innovation, originality, creativity and is defined as a succession of trends or fads, short. Create fashionable leather confections from home means accepting a contract with the producer and / or consumer, showing a profit motivating all at the right time. Continuous which require the exercise involves creative skills of fashion design, leading to a wide range of products. But provided that the general criteria have been fulfilled: functional, aesthetic, socio-economic and technological [12].

Currently there is possibility to customize shooters to customer requirements, and even to form their own zippers. Manufacturers of zippers presents numerous variations and combinations possible: elastic band, narrow, transparent, abrasion resistant, recycled materials, Satin, antistatic various combinations of colors and textures, etc. All this helps to ornamental leather products. Often ornaments are those that give charm and beautify the product.

The bibliographic study and certified worldwide developments have allowed the identification of 15 criteria for the classification of zippers.

Knowing appearance zippers, elements of which it is composed, and their classification criteria allow us to correlate the shape of the product and destination. Because of a misunderstanding of the role they have zippers on products they will adversely affect their appearance. So as required, balance, sensitivity, talent and creative imagination in their use.

REFERENCES

[1] http://www.blackoutlet.ro/istoria-fermoarului/.

[2] https://en.wikipedia.org/wiki/Whitcomb_L._Judson.

[3] https://ro.wikipedia.org/wiki/Gideon_Sundback.

[4] https://dexonline.ro/definitie/fermoar.

[5] F. Harnagea, *Proiectarea şi tehnologia articolelor de marochinărie*. Ed. Cermi, Iaşi, 2000.

[6] Л.Н, Резванова и др. *Технология кожгалантерейных и шорно-седельных изделий*. Изд. Феникс, Ростов-на-Дону, 2008.

[7] http://zipsolution.ro/cataloage/YKK%20Functii%20Fermoare%20si%20Cursori.pdf

[8] Ж. Б. Николаева, и др. *Кожгалантерейная промышленность. Справочник*. Изд. Легкая промышленность и бытовое обслуживание, Москва, 1985.

[9] Л. П. Морозова и др. *Справочник обувщика. Проектирование обуви, материалы.* Изд. Легпромбытиздат, Москва, 1988.

[10] http://www.gemarindustries.ro/content/fermoare.html.

[11] http://www.mercerie-az.ro/fermoare.html

[12] V. Bulgaru, M. Malcoci, I. Pascari, A. Ischimji, *Bazele tehnologiei confecțiilor – încălțăminte.*Indicații metodice privind efectuarea lucrărilor de laborator. Partea II (lucrările 5-8). Ed. Tehnica – UTM, Chișinău, 2013.

[13] A. Mihai, A. Curteza, *Design. Designul produselor din piele.* Ed. Performantica, Iaşi, 2005.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

CONSIDERATIONS REGARDING THE DESIGN OF FOOTWEAR WHICH ASSURES THE HEALTH OF THE FOOT

MĂRCUŞ Liviu

Technical University "Gh. Asachi" Iaşi, Faculty Textile Leather and Management Industry, bd. Dimitrie Mangeron nr.28, postal code 70050, Iasi, România, E-mail: liviumarcus@yahoo.com

Abstract: *The high demands for cheap footwear can only be satisfied by mass fabrication. Costumed footwear would represent a regress, despite the advantages that it brings. This paper regards mainly the demands that mass footwear requires, in order to maintain the health of the foot. The desire to maintain the foot shape and functionality requires certain last forms and fabrication algorithms. We analyze certain aspects referring to: the correct design of the inner sole, insuring the flexibility of the lower part of the footwear by choosing the right type of materials and confection systems, choosing the right height of the heel, setting the adequate shape by increasing the number of different shoe sizes. In order to give a loose space to the adults' toes, where they are not pressed, but have a complete range of motion, the orthopedists and the last specialists have set several requirements for building the contour of the inner sole. The technique of building a bond between the footwear forepart and the inferior ensemble is dependent to the purpose and partially to the fashion demands of the shoe. The sole shape is influenced by the buyers, as seen by the development of the ex-flex footwear. There must be noted that in this case, the work of the model designer coincides with the exigencies of the specialist in footwear health. With the help of certain functional considerations and of several mechanical calculations, it can be proven that a heel with a height of 3 cm does not necessarily have a negative impact on the foot health. This is why even the orthopedics consider this limit as acceptable. Higher heels must be avoided if we want to maintain a normal function and development of the foot.*

Key words: *footwear, functionality, foot health, fabrication, orthopedic.*

1. INTRODUCTION

The increased demands for cheaper footwear can only be satisfied by mass production. This means that the obvious advantages of custom made footwear are definitely not compatible with low prices, and emphasizing this type of manufacture would be a regress.

Therefore we must first reveal the demands required for mass production footwear, which also takes into account the foot health. The desire to maintain the foot shape and functionality requires certain last forms and fabrication algorithms.

Our paper analyses several aspects regarding the way in which the so-called "healthy footwear" should be made.

We analyze certain aspects referring to: the correct design of the inner sole, insuring the flexibility of the lower part of the footwear by choosing the right type of materials and confection systems, choosing the right height of the heel, setting the adequate shape by increasing the number of different shoe sizes.

2. THE CONTOUR OF THE INNER SOLE

The shape of the footwear, and more importantly its tip is determined by the contour of the inner sole. The last specialist often starts from a correct contour of the sole, which is modified depending on the shape that we want to give to the tip of the shoe. This aspect is conditioned by the supplementary add at the tip. It is sufficient to look at different types of tips that are used today (for example square shape, plateau, national or dutch) in order to recognize the influence that it has on the shape of the inner sole.

The main requirement that we claim when it comes to functionally correct footwear is this: the shoe must give the foot a fitting that does not bring any inconvenience to its radial shape. This happens when the radial shape of the footwear is not pushed towards the center by the margin of the shoe. Although loose footwear does not put so much pressure on the toes, it does not fill all the requirements for a fan setting. By pressuring the fingers at the tip, they are not only taken out of their normal position, but also, as comparative x-rays show, this also happens with the metatarsal bones.[1]

Moreover, as the toe musculature also contributes to the sole arch, weakening them can dangerously lead to a foot insufficiency and with it, to a skeletal deformation. Also, by pressing the toe, the blood circulation is affected, this limiting the blood flow to the toe tissues. As a consequence, the toes are pressed by lateral forces which increase as the foot is being pushed further from the sole. The result of wearing sharp tip shoes is the pressure on the big toe, that increases gradually. The deforming action increases as the individual is used to walk keeping his feet oriented towards the exterior.

The pathological consequences of placing the foot in a sharp tip shoe is already known. As the toes must handle high pressures, incompatible with normal function, in points that are inadequate to receiving such pressures, durions, callosities and wefts are formed. Besides that, the normal relationship in the basal joint is disrupted, by deforming the hallux (hallux valgus) and the metatarsal-phalangeal joint is being pushed outward. This causes osseous formations (exostoses).

In order to avoid this, it has often been tried to give the anterior side of the footwear a shape that is functionally adapted. All these tries have failed so far, mainly because the variable shape of the shoe tip is dictated by the fashion tendencies. Next to the heel height, the shoe tip is an important aspect that must adapt to the fashion demands. Only for children footwear the radial shape of the foot has yet been preserved. Comparing the radial footwear for children with the fashion driven footwear for adults, the negative influence of fashion becomes very obvious.

A normal, radial foot of a child will further develop in a radial shape if the toes will not be pushed in an abnormal position by the footwear. So, there is no justification to force the foot of an adult in a layer that blocks the normal development, only to adapt to accidental fashion prescriptions. Women's feet develop "hallux valgus" deformation, while men's feet will only be affected at the big toe. [2]

In order to give a loose space to the adults' toes, where they are not pressed, but have a complete range of motion, the orthopedists and the last specialists have set several requirements for building the contour of the inner sole.

3. THE INFERIOR ENSEMBLE OF FOOTWEAR

The technique of building a bond between the footwear forepart and the inferior ensemble is dependent to the purpose and partially to the fashion demands of the shoe. The sole shape is influenced by the buyers, as seen by the development of the ex-flex footwear. There must be noted

that in this case, the work of the model designer coincides with the exigencies of the specialist in footwear health.[3]

The flexibility of the inner side of the footwear in the toe region is necessary so that the active and passive movement in the basal joints of the toes can be used completely. In flexible footwear the foot is able to push the sole strongly during walking. This allows the toe musculature to develop and become stronger and its capacity to connect to the skeleton increases.

Contrarily, in the lower side of the rigid footwear, the foot dangles in the toe region and the toes cannot function correctly. As known, an increased shaping of the tip compensates the lack of toe movement inside the footwear.

Although the sole flexibility must be looked at as another exigency for maintaining the range of motion of the foot, this necessity cannot always be met. The special footwear for mountain climbers, the protection footwear must have an especially resistant sole, protecting the foot from mechanical and thermal actions, as well as against damp. The wooden soles for street workers and the mountain climbers' boots have two or three sewed soled, which are not flexible. In order to maintain the toe muscle activity, the footwear that needs to protect the foot from special actions can be made with a rigid lower part. The street footwear must allow the toes to extend and slowly flex.

The frame-sewed shoe corresponds mostly to this demand, when the height of the inner sole is as low as possible. The manually frame sewed shoe is superior to the mass frame sewed shoe. For the footwear that imitates the CR system, a fixed frame is often applied in the lower side of the frame, which is fixed with metallic clams, which make the sole more rigid. An increased flexibility of the sole is characteristic by the CB system, where the faces are sewed without perforating the inner sole. [4]

The footwear with a glue sole is also quite flexible if we use an adhesive which keeps it's elastic properties.

4. THE HEEL HEIGHT

The theoretical research show that the heal is actually a useless part of the shoe, a high heel being in fact quite harmful for the foot health. Pro-heel researches have two more frequent arguments: on one side, the heel would ease rolling the foot, which is necessary especially on rough surfaces as for instance the street pavement, and on the other side, they claim that a large number of women declare themselves uncomfortable walking with a small-heel footwear.[5]

However, from the physiological and functional point of view, the heel is in no way conditioned by the normal foot.

The heel increases the tension in the tendons and ligaments of the dorsal side of the foot, this causing unpleasant sensations, which are often compensated by flexing the knee while walking, causing a slightly elastic walk.

The other objection, claiming the some women simply cannot walk on low heels is justified. When the foot is placed in a shoe with a small heel, the tension in the calf and foot musculature is moved (shortening the Achilles' tendon, contracting the capsule and the ligaments), this causing unpleasant sensations, thus justifying the above mentioned complaint.

The data that we have gathered so far pleads without a doubt against using high heels. By tilting the entire sole, the forces push the foot to the front of the shoe, which overtakes the pressure. The toe area receives a supplementary pressure, which can be reduced by widening the tip of the shoe. Besides this aspect, the footwear specialist knows very well that a high heel shoe with a wide tip does not have a pleasant aspect when placed on the foot, this observation being typical for the escarpen shoe last. We believe that the moment when it will be proven without a doubt that even a

pressure of 95 g/cm^2 causes a significant compression on the vascular system of the skin, the serious disadvantage of pressing the toes in a high-heel shoe will be recognized. This disadvantage causes a partial interruption/decrease of the blood flow to the toes. By such a decrease in the blood flow, the capacity of action can be decreased in the tissues, ignoring the inactivity hypertrophy of the long and short muscles of the toes, which is directly conditioned by the pressure that is exercised on the toes.

As a general conclusion, we must affirm that the normal foot does certainly not need a high-heel footwear, this being only conditioned by the fashion tendencies. With the help of certain functional considerations and of several mechanical calculations, it can be proven that a heel with a height of 3 cm does not necessarily have a negative impact on the foot health. This is why even the orthopedists consider this limit as acceptable. Higher heels must be avoided if we want to maintain a normal function and development of the foot.[6]

Given the fact that the usage of the heel is often mentioned when appreciating the position of the foot, we ought to also research these relations. If a normal foot moves correctly from the functional point of view, we can observe an uniform usage of the heel at it's posterior margin, symmetrically to the medial line if the repartition of the wood in the heel area and in the anterior part of the last is correct. This premises means that the heel will be used at its interior part when the foot is placed in a valgus position. However, if the heel area is not stable, then the heel can also be pressed outward, by pushing the heel in the valgus position; this is observed when the heel is mostly used at the exterior side.

Appreciating the foot position by the heel usage is a process that must take into consideration all possible situations in order to avoid incorrect conclusions. The practical results cannot be totally satisfactory, because on one side each person develops a different type of walking, and on the other side, the usage is relatively higher because even when the heel is completely intact, it lacks material that can be found in wide heels.

Finally, the usage of the heel material is directly dependent to the shoe model. An accurate footwear specialist knows that the same foot can determine different types of pressure on different heels with different shapes and therefore, he uses them in different manners.

5. CONCLUSIONS

The appearances analyzed in the writing refers, in particular, on footwear series. Within each chapter are presented aspects regarding the design of parts , the way which you need to chose the materials and the role for some patters have to ensure footwear fuctions.

REFERENCES

[1] Mălureanu G, Harnagea F, „*Unele deficienţe constructive ale încălţămintei şi implicaţiile lor asupra funcţionării piciorului"*, Simpozion 1989 Iaşi

[2] Miller RG, "*Manual of Shoemaking*", Ed. Clark Ltd, UK, 1989

[3] Schroter H, "*Grundlagen der industriellen Schuherstellung*", VEB Fachbuchverlag Leipzig, 1989

[4] Witana C.P. Goonetilleke R.S., Feng J.,"*Dimensional difference for evaluating the quality of footwear fit. Ergonomics*", 1301-1317, (2004)

[5] Costea M., Mihai A. "*The structure and design of footwear",80-97, Publisher Performantica, 2015*

[6] Mărcuş L., "*Regarding the Lasting of Footwear Uppers Using Different Technological Variants"*, Annals of the Oradea University, Fascicle of Textile Leatherwork, ISSN 1582-5590, p. 331-336, 2008.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

DETERMINING LIGHTFASTNESS PROPERTIES OF VEGETABLE TANNINS AND CHEMICAL PROPERTIES OF THE LEATHERS TANNED WITH MODIFIED MIMOSA AND QUEBRACHO

OMURSukru[1], MUTLU Mehmet Mete[2]

[1]Adnan Menderes University, Aydın Vocational High School, Aydin, Turkiye, sukruomur@gmail.com

[2]Ege University, Engineering Faculty, Department of Leather Engineering, Bornova, izmir, Turkiye, mete.mutlu@ege.edu.tr

Corresponding author: Mutlu, Mehmet Mete E-mail: metemutlu@gmail.com

Abstract: *The vegetable tannins are the oldest tanning agents used in leather industry. They give their natural character and colour to the leathers which they are applied to, but they have the disadvantage of colour change when they are exposed to light for prolonged times. In this study light fastness properties of leathers tanned with mimosa, quebracho, valonea and chestnut tannins were measured. Lightfastness properties of mimosa and quebracho tannins were found lower. Then these tannins were modified with sulphitation, novalac synthesis and sulphomethylation processes. Lightfastness and determination of volatile matter, determination of matter soluble in dichloromethane, determination of sulphated total ash and sulphated water-insoluble ash, determination of water soluble matter, water soluble inorganic matter and water soluble organic matter, determination of nitrogen content and hide substance, calculation of degree of tannage determination of formaldehyde content analyses were performed to the leathers tanned with modified mimosa and quebracho tannins. From comparison of results, it was understood that sulpmethylation process can be used for production of leathers with higher lightfastness and without major change on chemical properties. When chemical properties of leathers tanned with modified quebracho and mimosa are considered: volatile matter, sulphated total ash and sulphated water- insoluble ash, water soluble matter, water soluble inorganic matter and water soluble organic matter, hide substance and formaldehyde contents were found compatible with standard mimosa and quebracho. However degree of tannage and matter soluble in dichloromethane values were found lower, which means some enhancements in modification or fatliquoring process should be considered.*

Key words: *Leather, Lightfastness, Vegetable Tannins*

1. INTRODUCTION

The leather-tanning industry is one of the most ancient in operation. Although the technology of leather manufacture has evolved over centuries, the basic principles for the production of leather have remained the same. Hide proteins, mainly collagen, are rendered insoluble and dimensionally more stable by treatment with chemical products able to fix on them and render them both more resistant to mechanical wear and less susceptible to biological and other types of attack. Forestry-derived, natural polyphenolic tannins and polyflavonoid extracts, used mainly for the manufacture of heavy, rigid, and hard leathers for shoe soles, saddles, belts, and other implements subject to high wear, are one of the main products still used today for leather tanning. Natural

polyphenolic tannins have a strong astringent effect and give considerable hardness, and toughness to the leather produced with them. They present, however, among others, the considerable disadvantage to have marked darkening problems when exposed to light. [1].

The vegetable tannins are obtained from wood, bark, fruit, seed and leaves of some trees. Mimosa and quebracho tannins are obtained from wood part of trees and chemically they belong to the condensed group of tannins. Chestnut and valonea tannins are obtained from wood and fruit part of the trees and belong to the hydrolysable group of vegetable tannins. The tannins behave like dyestuffs and the hides also get the colour of the tannin itself. Especially the hides tanned with mimosa and quebracho becomes brownish colours. The valonea and chestnut tannins give leather pale colours of yellow.

While the condensed tannins have a flavonoid structure and contains benzene rings they are sensitive to light, especially to the UV light which have highest energy level in sunlight. Sunlight is reaching to earth as electromagnetic radiation the spectral form and intensity of light exposed on a dyed material have great effect on fading degree. [2].

The variation of leather colour as a function of aging time on prolonged irradiation with UV light of the leather produced based on different vegetable tannins was found to be composed of two main effects: The first one of these is the darkening reaction of the leather. This is due to the formation of quinones on the phenolic structure of the vegetable tannin. The second one is the leather-lightening reaction due to the photo degradation of the system [1]. Light fastness of dyed textiles is related to the chemical structure and physical characteristics of the fibre itself [3].

In this research firstly, the colour changing of mimosa, quebracho, chestnut and valonea tanned leathers which were exposed to light according to lightfastness test conditions, had been measured. After definition of which tannin group had the most colour change, some modification processes, like sulphomethylation, sulphitation and novalac synthesis were applied. Then, all the hides were tanned with these modified tannins, and colour measurement tests and chemical analyses were performed to these leathers. The aim of the study was to test and enhance lightfastness properties of vegetable tannins without major quality change in final leathers.

2. EXPERIMENTAL

2.1. Material

10 pickled domestic hides each weighting approximately 10 kg and at pH 2.5 were used as the raw material for vegetable tanning. The thicknesses of pickled hides were adjusted to 1.4 mm.

Commercial mimosa, quebracho, chestnut and valonea tannins were used for tanning. Modified quebracho and mimosa were obtained by sulphomethylation, novalac synthesis and sulphitation processes [4].

2.2. Method

2.1.1. Tanning Process

Before the main vegetable tannage, a depickle process was applied and pH of pickled leathers were adjusted to pH 5.5 Then, the leathers were tanned by using the vegetable tanning process illustrated in Table 1. Then the leathers were dried in a dark place and mechanical processes like milling and toggling were carried out.

2.1.2. Lightfastness tests and Colour Measurement

For the evaluation of stability of vegetable tanned leathers to the light, the light fastness test was carried out according to ISO 105-B02 [5], after that determination of colour change in leather surfaces were detected by the colour change tests according to ISO 105-A05 [6].

Table 1: *Vegetable Tanning Recipe*

Material	Pickled Hide	Temperature	Time
Weighting	Pickle weight + 20%		
Vegetable Tanning	200% Water	30°C	
	2% Lightfast Syntan		30min
	10% Tannin		
	1% Lightfast synthetic fatliquor		20min
	20% Tannin		60min
	60% Water	55°C	10 min
	6% Lightfast synthetic fatliquor		300min
Fixation	1.5% Formic Acid (1/10 Diluted)		240 min
Draining			pH=3.8
Fixation	300% Water	50°C	
	0.3% Formic Acid (1/10 Diluted)		30min
Draining	150% Water	50°C	15min
Rinsing	300% Water	25°C	20 min

2.1.3. Chemical analysis of tanned leathers

The analyses were carried out using TSE ISO standards. The tests were performed on samples of leather collected and treated as reported in methodology [7], [8]. Determination of volatile matter [9], matter soluble in dichloromethane [10], sulphated total ash and sulphated water-insoluble ash [11], water soluble matter, water soluble inorganic and organic matter [12], nitrogen content and hide substance [13] and calculation of degree of tannage [14] were performed. Chemical determination of formaldehyde content was performed according to the standard [15].

3. RESULTS AND DISCUSSION

Colour measurements of leathers tanned with mimosa, quebracho, valonea and chestnut before and after the light fastness tests are given in Table 2. “0” indicates not exposed to test light and “1” indicates exposed to test light. dE figure shows the colour difference which means the lower value it is, the less colour change occurs.

Table 2: *Colour Measurements of Leathers before and after Lightfastness Tests*

Tannin Type	**L**	**a**	**b**	**dE**
Mimosa 0	44.87	14.57	17.46	
Mimosa 1	29.29	20.01	16.12	16.55
Quebracho 0	52.39	18.24	25.40	
Quebracho 1	31.51	21.64	17.92	22.44
Valonea 0	44.55	7.26	19.36	
Valonea 1	40.29	9.91	21.38	5.40
Chestnut 0	53.50	8.15	21.66	
Chestnut 1	46.54	10.14	25.54	8.21

From Table 2, it is seen that colour changes of leathers tanned with condensed tannin tanned were found higher than the hydrolysable ones. So it can be understood that, the condensed tannins are more sensitive to exposure to light and so their colour can change more. Ozgunay (2008) has stated that condensed tannins change their color more and more rapidly than hydrolysable tannins due to their polyflanoid structures. [16].

Due to the reason that light fastness properties of quebracho and mimosa tanned leathers were lower than the others, these tannins were chosen for modification processes. Non-modified quebracho, sulphomethylated quebracho, novalac synthesis quebracho and sulphited quebracho were coded as KS, K1, K2 and K3 respectively. Non-modified mimosa, sulphomethylated mimosa, novalac synthesis mimosa and sulphited mimosa were coded as MS, M1, M2 and M3 respectively.

Colour measurements of the leathers tanned with non-modified and modified mimosa and quebracho are shown in Table 3.

Table 3: *Lightfastness test results of modified quebracho and mimosa tannins*

Sample Code	L	a	b	dE
KS	51.61	18.63	28.99	18.73
K1	43.1	20.7	27.93	11.16
K2	30.06	16.97	12.75	17.54
K3	51.84	19.27	29.76	15.89
MS	55.85	17.18	29.51	23.72
M1	42.47	17.94	25.28	9.72
M2	46.59	20.46	29.90	21.91
M3	53.43	13.19	28.45	14.38

As it can be seen in Table 3, the dE value which is the criteria of colour change of leather was obtained the lowest from the sulphomethylation modification of quebracho and mimosa tannins.

Since the modification of tannins differs the lightfastness properties, it can also affect the chemical properties of leathers. So the chemical properties of non-modified and modified quebracho and mimosa tanned leathers were measured and the results are shown in Table 4.

Table 4: *Chemical Analysis on Leather Tanned with Modified Quebracho and Mimosa Tannins*

Leather Sample	**Volatile matter**	**Matter soluble in dichloromethane**	**Sulphated total ash**	**Water soluble matter**	**Hide Substance**	**Degree of Tannage**	**Formaldehy de Content**
KS	7.09	4.00	0.31	0.72	56.91	54.37	0.95
K1	7.62	2.93	0.76	0.71	61.82	42.30	2.28
K2	7.87	2.70	0.47	0.52	69.19	28.54	1.46
K3	7.12	4.11	0.32	0.71	61.82	41.48	1.09
MS	6.95	3.39	0.17	0.67	59.35	49.67	0.87
M1	8.37	1.06	0.68	0.60	69.30	29.05	1.45
M2	7.93	2.63	0.19	0.37	61.86	43.65	1.23
M3	7.11	3.28	0.58	0.75	69.30	24.43	1.66

Determination of volatile matter in leather is affected from climatic conditions, tanning type, fatliquoring and unfixed organic and mineral materials. The dryness of leather causes crinkle grain and loss in leather surface. Higher rates can result looseness in leather structure [17]. Ozgunay (2000) found volatile matter 7.05 % for non-modified valonea tannin and 6.2 % for thiosulphate modified one [18]. As seen from Table 4, values for volatile matter of leathers are similar.

In leather production procedure some fatliquoring agents have been used for providing softness and flexibility of leather fibres. UNIDO (1994) suggests that matter soluble in

dichloromethane value should be in a range of 3-12 % [19]. In this research these values were found lower from the values suggested in the literature for the leather samples of K1, K2, M1 and M2; although same production recipe and same amount of fatliquor were used. However this can be adjusted by using different or more fatliquoring .

In beamhouse operations some organic and inorganic chemicals are used for transformation of raw hide to the leather. It is required to keep the inorganic matter amount as low as possible. If the sulphated total ash value is higher, it shows that there are much inorganic matters left or used. So this affects the leather quality too [18]. In literature [17], this value advised no to be not higher than 2.5 % for vegetable tanned leathers. The values for this research seem suitable for advised limits.

It is mentioned that water soluble matter value should not be higher than 6% for vegetable tanned leathers[20]. As seen in Table 6, the these values are lower and compatible with the literature.

Ozgunay (2000) found that, modification of valonea with sodium meta bisulphide gives the hide substance content of 45.90% for vegetable tanned leathers [18]. As shown in Table 4 the hide substance content of leathers tanned with modified and non-modified tannins are higher than 45 %.

Degree of tanning indicates the amount of vegetable tannin fixed to 100g of skin substance. It should be at least 50 for vegetable tanned leather; values below 50 indicate that penetration of tannin might be inadequate [17]. From the Table 4, it is clear that the degree of tannage values for non-modified mimosa and quebracho tannins are exactly 50 or upper degree. But the value for the leathers tanned with modified tannins is below from the value of 50. So it may be because of the higher molecular structure of modified tanning agents causing inadequate penetration to the hides.

Ecological and toxicological demands are playing increasingly important role in the marketing of leather. Formaldehyde initially came under scrutiny from automobile manufacturers, and shoe and garment manufacturers have followed in their footsteps [21]. In literature [22], it has been suggested the limits of formaldehyde for leathers in direct contact with skin, leathers with no direct contact with skin, decoration material as 75ppm, 300ppm and 300ppm respectively. From the Table 4 it appears that the obtained results from the study are found below the limits.

4. CONCLUSIONS

In leather technology, vegetable tannins are widely used tanning agents which can give their own colour to the leather while tanning process. However these colours are not stable to light most of the time and this can cause quality problems in consumer leather goods. The lightfastness is a very important property for all type of leather goods. The sun light or mainly strong light may affect the colour of the leather surface. Most of coloured organic surfaces, e.g. leather, textile, and wood have the disadvantage of discolouring, namely fading or reddening.

In this research it has been found that the condensed tannins; mimosa and quebracho, are more sensitive to exposure to the light. They quickly turn the leather surface to reddish colour, called reddening. So some modification processes were applied to them to enhance their lightfastness properties. Accordingly sulphomethylation, novalac synthesis and sulphitation trials were applied and modified tannins were obtained. The lightfastness properties of the leathers tanned with sulphomethylated mimosa and quebracho were found better than non-modified ones and then the other modifications. So this modification was found successful in terms of lightfastness. Afterwards chemical tests have been applied to the leather samples to determine if these modifications had any effect on chemical properties of leathers. When chemical properties of leathers tanned with modified quebracho and mimosa are considered: volatile matter, sulphated total ash and sulphated water-insoluble ash, water soluble matter, water soluble inorganic matter and water soluble organic matter, hide substance and formaldehyde contents were found compatible with standard mimosa and quebracho. However degree of tannage and matter soluble in dichloromethane values were found

lower, which means some enhancements in modification or fatliquoring process should be considered.

REFERENCES

[1] Roddy, W.T.; Jacobs, J.; Jansing, J. J. Am. Leather Chem. Assoc., 44 , 308, 1949

[2] Pizzi, A. Simon, C., George, B., Perrin, D., Triboulot, M. C., "*Tannin Antioxidant Characteristics in Leather versus Leather Light Stability"*, Journal of Applied Polymer Science, Vol. 91, 1030 –1040, 2004

[3] Öktem, T., Demir, A. ve Seventekin, N., 2008, "*Reaktif Boyalı Pamuklu Materyallerin Işık Haslığına UV Absorplayıcıların Etkisi*", Tekstil ve Konfeksiyon, vol. 2, 2008

[4] Cumming, J.W., Giles, C.H., McEachran, A.E., *"A study of the photochemistry of dyes on proteins and other substrates"*, Journal of the Soc. of Dyers and Colourists, 72, pp. 373–380, 1956

[5] TS EN ISO 105-B02, Tekstil- Renk haslığı deneyleri- Bölüm B02: Yapay ışığa karşı renk haslığının tayini- Ksenon ark soldurma lambası deneyi, Türk Standartları, Ankara, 2014

[6] TS 423-5 EN ISO 105-A05, Tekstil renk haslığı deneyleri- Bölüm A05: Gri skala haslık değerinin tayini için renkteki değişimin cihazla değerlendirilmesi, TSE, Ankara, 2001

[7] Ömür, Ş., Mutlu M.M., *"Modification Of Mimosa And Quebracho Tannins and The Lightfastness Properties of The Proccessed Leathers"*, Tekstil ve Konfeksiyon, 2016

[8] TS EN ISO 2418, Mamul Deriler Kimyasal, Fiziksel, Mekanik Renk Haslığı Deneyi Numune Alma Bölgesi, TSE, Ankara, 2006

[9] TS EN ISO 4044, Kimyasal Deneyler, Kimyasal Deney Numunelerinin Hazırlanması, TSE, Ankara, 2009

[10] TS EN ISO 4684, Uçucu Madde İçeriğinin Tayini, TSE, Ankara, 2009

[11] TS EN ISO 4048, Deri, Kimyasal Deneyler, Diklorometanda Çözünen Madde Ve Serbest Yağ Asidi Muhtevasının Tayini, TSE, Ankara, 2013

[12] TS 4125 EN ISO 4047, Deri- Toplam Sülfat Külü Ve Suda Çözünmeyen Sülfat Külü Tayini, TSE, Ankara, 2000

[13] TS EN ISO 4098, Deri , Kimyasal Deneyler , Suda Çözünen Madde, Suda Çözünen İnorganik Madde Ve Suda Çözünen Organik Madde Tayini, TSE, Ankara, 2009

[14] TS 4134, Mamul deriler- Azot ve Deri Maddesi Tayini, TSE, Ankara, 2009

[15] TS 4128, Mamul deriler- Tabaklama Sayısının Hesaplanması, TSE, Ankara, 1985

[16] TS EN ISO 17226-1, Deri - Fomaldehit İçeriğinin Kimyasal Tayini-Bölüm 1: Yüksek Performans Sıvı Kromotografik Yöntem, TSE, Ankara, 2009

[17] Ozgunay, H., "*Lightfastness Properties of Leathers Tanned with Various Vegetable Tannins*", Journal of American Leather Chemists Association, 103, 345-351, 2008

[18] John, G., Possible Defects in Leather Production, Druck Partner Rübelman GmbH, Hemsbach, 379 p, 1997

[19] Özgünay H., Meşe Palamutu Ekstarktı Valeksin Deri Sanayiinde Kullanılabilirliğinin Artırılması Üzerine Araştırmalar, Ege Üniversitesi Fen Bilimleri Enstitüsü, İzmir, 181 s. 2000.

[20]UNIDO, Acceptable Quality Levels in Leathers, United Nations Publications, Sales Nr. E.76 II.B.G., New York, 1994

[21]BASF, Pocket Book for The Leather Technologist. Aktiengesellschaft 67056 Ludwigshafen, Germany, 1996

[22]Wolf, G., and S. Huffer. "*Formaldehyde in leather - a survey*", Journal of the American Leather Chemists' Association 97.11, 456, 2002.

[23]OEKO-TEX, Limit Values, Available: https://www.oekotex.com/en/manufacturers/test_criteria/ limit_values/limit_values.html, 2015

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

STRETCH FABRICS IN LEATHER MANUFACTURING: PERFORMANCE PROPERTIES OF STRECH LEATHERS

ORK Nilay[1], ADIGÜZEL ZENGİN Arife Candas[1], ZENGIN Gökhan[1]

[1] Ege University, Engineering Faculty, Leather Engineering Department, Bornova, 35100 Izmir, Turkiye,
nilay.ork@ege.edu.tr; candas.adiguzel@ege.edu.tr

Corresponding author: Zengin, Gokhan, gokhan.zengin@ege.edu.tr

Abstract: *Product variability of manufactured leather goods such as garment leathers could be closely related to the wear comfort because each material forming the garments are affected the comfort properties of the products. Considering the significant demand to elastic woven stretch fabrics and the advantages provided to leather goods like allowing easy body movements, well-fitting and keeping the shape make the use of stretch fabrics focus in interest. In this study, the performance properties of stretch leathers, leathers and spandex fabrics were presented and the differences between the characteristic properties of the leathers were described. For this purpose, physical characteristics of leathers were investigated in terms of thickness, weight, drape ability, stiffness, bending stiffness, air and water vapor permeability. The drape ability, stiffness and bending stiffness properties were significantly affected by the stretch fabrics laminated on the suede side of the leathers. The drape ability, stiffness and bending values were increased due to the implementation of stretch fabrics. There was no significant difference between the air permeability values of the leathers prior and after the implementation of stretch fabrics in contrast to water vapor permeability. The results of this study showed that the aesthetic behavior of clothing materials such as drape and stiffness properties as well as water vapor permeability was mainly affected from the implementation of the stretch fabrics.*

Key words: *stretch, leather, physical characteristics, drape ability, bending behavior*

1. INTRODUCTION

In recent years, consumers are more conscious and selective about clothing materials. Their expectations are increasing in time due to the fast development of technology, continuous change in fashion and also the product variability of manufactured goods [1]. Especially challenging working conditions, long working hours, business travels and also social activities drive consumer demands for comfortable clothing materials. Bahadir et al., 2015 was defined the comfort of the clothing material as the satisfaction and feeling the balance of a person inside the wear material and environmental conditions [2].

Nowadays, the interest for woven fabrics including elastane is quite high due to the advantages provided to the clothing materials. The wear materials including elastane or in other words stretch or spandex fabrics allow easy body movements; they fit well to body, maintain their shape during the usage and provide considerable comfort in wear [3].

Elastic yarns and fabrics have played an important role in the world textile industry and a great effect on comfort and functionality of the clothing materials [4]. Elastic yarns can be used with all natural and synthetic fibers. In order to provide the desired comfort in clothing materials, 2-5% of

spandex is sufficient to use in the mixture of the fibers. The stretch fabrics seem similar in appearance, touch and performance to the non-stretch ones. These fabrics have characteristic properties such as comfort, elasticity and resilience. A clothing material consisting of spandex can be stretched in ratio of 25-35% and right after the removal of the cloth, it can return to its original shape [3].

The elastic or spandex fibers can be also used with the leather goods by implementing the stretch fabrics on the suede side of the leathers. The application of the stretch fabrics to garment leathers is mostly focus in interest nowadays especially for the outwear materials.

Leather goods provide many unique properties to consumers like heat insulation, comfort, softness, water vapour and air permeability etc. In addition, the aesthetic behavior of the leather clothing materials like drape ability becomes focus in interest [5, 6]. Lojen and Jevsnik 2007 explained that a drape of a fabric is related to the mechanical properties of fabric such as bending, shear, formability, weight and thickness [7]. Also Frydrych et al., 2000 revealed that drape is also related to rigidity [8]. In addition, it should be considered that mechanical properties will be the indicator to determine the behavior of the fabrics [9].

In contrast to textile material, leather is not homogeneous substance due to its production from individual skins [5, 10]. Besides, characteristic properties of the leathers are differed depending on the region of the leather like neck, shoulder, croupon and belly. Also, different leather types have different physical and chemical properties and they have different surface appearances. Lastly, the eating habits of the animals, environment, age, sex, and the tanning procedures are the other reasons of the leather inhomogeneity [11].

In this study, the performance properties of stretch leathers, leathers and stretch fabrics were presented and the differences between the characteristic properties of the leathers were described. In the literature survey, few studies were found on the subject of mechanical, aesthetic and the biaxial stretching properties of the leather material [5, 10, 11]. Up to date, no study was found about the description of the aesthetic and performance properties of stretch and non-stretch leathers. For this purpose, physical and aesthetic characteristics of leathers and fabric were investigated in terms of thickness, weight, drape ability, stiffness, bending stiffness, air and water vapor permeability.

2. MATERIAL METHOD

2.1 Material

Eight domestic sheep garment leathers were used in the study. The tanning process of the leathers was performed by chromium. Half of the leathers were laminated with spandex fabric while the other half was the control group.

2.2 Method

Sampling of the leathers for all tests was performed according to TS EN ISO 2418 standard. The test samples were conditioned in accordance with TS EN ISO 2419, at 23 ± 2°C temperature and 50% ± 5 relative humidity [12,13].

The thicknesses of test samples were measured according to TS 4117 EN ISO 2589 standard by using Satra-Thickness gauge [14].

Drape coefficient was determined using drape tester according to TS 9693 [15]. The drape coefficient was expressed as a percentage. A circular leather specimen of 30cm diameter was sandwiched between two horizontal discs of smaller diameter (18cm), and the unsupported annulus of leather and fabric were allowed to hang down. The draped specimens were taken the picture by a cam. The pixels of pictures of draped materials were count. The drape coefficient was calculated with the formula (1):

Drape coefficient (DC %) = [(M - S) / (L - S)] x 100 **(1)**

M: Material Pixels Count
S: Small Diameter Pixels Count
L: Large Diameter Pixels Count

Flexural or bending rigidity was determined according to ASTM D1388 by Shirley Fabric Stiffness Tester [16]. A rectangular strip of fabric was supported on a horizontal platform of the stiffness tester and extended in the direction of its length, so that an increasing part was over hanged and bended under its own mass. When the tip of the specimen was reached a plane passing through the edge of the platform and inclined at an angle of 41.5° below the horizontal, the bending length was read off the scale. Bending rigidity in the horizontal and vertical directions is calculated using the formula given below (2):

$G = 0.1 \times W(gr) \times C^3$ **(2)**

where:
G = bending rigidity, mg.cm,
W = material mass per unit area, g/m^2,
c = bending length, cm.

Material bending rigidity was calculated by the mean values of horizontal and vertical bending rigidities (3).

$G_{material} = (G_{vertical} \times G_{horizontal})^{1/2}$ **(3)**

SDL Atlas Digital Pneumatic Stiffness Tester was used for the softness of the materials according to ASTM D4032 [17]. A plunger of 25.4 mm diameter pushed the fabric through a 38 mm diameter orifice for a distance of 57 mm (2.25 in) in 1.7 seconds and the maximum forces were recorded.

The air permeability test was performed according to the TS 391 EN ISO 9237 using Textest FX 3300 Air Permeability Tester [18]. The test was repeated 10 times in all areas of the leathers under 400Pa pressure with 20cm^2 diameter ring.

The water vapor permeability values of the leathers were determined in accordance to TS EN ISO 14268 [19].

3. RESULTS AND DISCUSSION

The thickness, weight, drape coefficient, bending rigidity, stiffness, air and water vapor permeability properties of stretch garment leathers, non-stretch garment leathers and spandex fabric were determined and the results were shown in Table 1.

Garment leathers combined with spandex fabric were found thicker and heavier than the non-stretch leathers and spandex fabric (Table 1) due to the two-fold application of spandex fabric on the suede side of the leathers.

The values of average drape coefficient were determined as 28.9 to 62.52% for non-stretch and stretch leathers respectively. The stretch leathers had the highest values while the lowest drape coefficient was found from the non-stretch ones. When the opposite correlation was considered between the drape coefficient and drape ability, it was normal to found out that non-stretch leathers had the most drape ability than the stretch leathers and spandex fabric.

The mean values of bending rigidity for non-stretch and stretch leathers were found as 5.09 and 95.95 mg/cm, respectively. The spandex fabric applied to the suede side of the leather was directly

affected the aesthetic properties of the leathers such as drape ability and bending rigidity. After the impregnation of the spandex fabric, bending rigidity was increased. Von Hoven et al. (1999) explained that higher values of bending rigidity indicate greater resistance to flexing whilst lower values indicate easier flexing and hence better drape ability. Krishnaraj et al., 2009 also found out that the correlation between the average bending rigidity and drape coefficient was excellent and the drape coefficient values were inversely related to the softness values.

The softness of leathers was assessed traditionally by hand evaluation and subsequently by compression methods. In the softness tester [21], the softness values are measured by the distention of leather when a constant load is applied perpendicular to the surface of the leather [5]. In order to determine the softness values of the leathers, stiffness test was performed to the leather samples in this study and determined that the stiffness values were ranged from 0.92 to 13.32 N. Stretch leathers had the highest stiffness that was an indication of the firmness property.

Table 1: *The performance and aesthetic properties of the spandex fabric, stretch and non-stretch leathers.*
*L: chromium tanned leathers, L+S: chromium tanned leathers combined with spandex fabric, S: spandex fabric, (M): Mean

*	Thickness (mm)	Weight (g/m^2)	Drape coefficient (DC %)	Bending rigidity (mg.cm)	Stiffness (N)	Air permeability ($m^3/m^2/min$)	Water vapor permeability ($mg/cm^2.h$)
L-1	0.49	189.43	24.30	5.27	1.32	0.33	0.027
L-2	0.46	197.39	31.66	6.09	1.67	0.16	0.029
L-3	0.53	195.67	28.87	6.40	1.62	0.24	0.025
L-4	0.58	186.38	30.75	8.72	1.45	0.26	0.026
L (M)	**0.52**	**192.22**	**28.90**	**6.62**	**1.52**	**0.25**	**0.027**
L + S -1	1.00	395.97	61.15	78.32	10.62	0.22	0.005
L + S -2	0.84	424.97	56.38	81.84	10.72	0.25	0.03
L + S -3	1.03	424.26	61.46	98.35	12.50	0.21	0.001
L + S -4	1.13	458.48	71.07	125.30	19.42	0.30	0.0004
L + S (M)	**1.00**	**425.92**	**62.52**	**95.95**	**13.32**	**0.24**	**0.01**
S (M)	**0.30**	**114.22**	**41.17**	**5.09**	**0.92**	**242.40**	**-**

The air permeability results of the spandex fabric were found significantly higher than the stretch and non-stretch leathers. When the air permeability values of stretch and non-stretch leathers were compared, it can be seen that similar test results were obtained on which we could reveal that the spandex fabric had no significant effect on the air permeability properties of the leathers.

In contrast to air permeability results, spandex fabric had a negative impact on water vapor permeability results of the leathers. The water vapor permeability results of the stretch leathers were found nearly half of the non-stretch leathers.

Table 2 showed that the values of thickness, weight, drape coefficient, bending rigidity and stiffness properties of non-stretch leathers, stretch leathers and spandex fabric had a significant correlation and a consistent relation.

The air permeability gave different correlation values than the other properties (Table 2). The correlation value between air permeability and thickness was found -0.7420 which demonstrated the lower thickness values led higher air permeability results.

Table 2: *The correlation between the performance and aesthetic properties.*

Properties		**Correlation Values**
Drape coefficient (DC %)	Thickness (mm)	**0.7768**
Drape coefficient (DC %)	Weight (g/m2)	**0.8187**
Drape coefficient (DC %)	Bending rigidity (mg.cm)	**0.9273**
Drape coefficient (DC %)	Stiffness (N)	**0.9163**
Bending rigidity (mg.cm)	Thickness (mm)	**0.9560**
Bending rigidity (mg.cm)	Weight (g/m2)	**0.9741**
Bending rigidity (mg.cm)	Stiffness (N)	**0.9996**
Stiffness (N)	Thickness (mm)	**0.9639**
Stiffness (N)	Weight (g/m2)	**0.9800**
Air permeability	Thickness (mm)	**-0.7420**
Air permeability	Water vapor permeability	**0.0015**
Water vapor permeability	Thickness (mm)	**0.6693**

In addition, the correlation between the bending rigidity/drape coefficient, and bending rigidity/stiffness was significant and determined as 0.9273 and 0.9996 respectively.

5. CONCLUSIONS

In this study, characteristic properties of spandex fabric, stretch and non-stretch leathers fabric were investigated in terms of thickness, weight, drape ability, stiffness, bending stiffness, air and water vapor permeability and following conclusions have been drawn;

1. The drape ability, stiffness and bending stiffness properties were significantly affected by the stretch fabrics laminated on the suede side of the leathers.
2. The drape ability, stiffness and bending values were increased due to the implementation of stretch fabrics.
3. There was no significant difference between the air permeability values of the leathers prior and after the implementation of stretch fabrics in contrast to water vapor permeability.
4. The results of this study showed that the aesthetic behavior of clothing materials such as drape and stiffness properties as well as water vapor permeability as a performance characteristic was mainly affected from the implementation of the stretch fabrics.

REFERENCES

[1] H. Işıktaş, "*Geri Kazanılan Yünlerden Elde Edilen Kumaşların Islak Haldeki Konfor Özellikleri Üzerine Bir Araştırma*", Ege Üniversitesi, Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi, 2009.

[2] Z. Bahadir Ünal, E. Acar and Funda Yildirim, "*Evaluating performance characteristics of lining fabrics used for children dresses*", Tekstil ve Konfeksiyon, vol. 25(4), pp. 323-328, 2015.

[3] A. Gürarda, "*Konfeksiyon sanayinde lcyra'lı kumasların dikiş problemlerinin incelenmesi*", Uludag Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, pp. 1-259, 2005 .

[4] J. Rupp and A. Böhringer, "*Yarns and Fabrics Containing Elastane*", International Textile Bulletin, vol. 15(1), pp. 10-30, 1999.

[5] K. Krishnaraj, P. Thanikaivelan and B. Chandrasekaran, "*Relation between drape and mechanical properties of goat suede garment leathers*", Journal of the Society of Leather Technologists and Chemists, vol. 93, pp. 1-7, 2009.

[6] N., Kenkare, and T., May-Plumlee, , Int. J. Clothing Sci. Technol, vol. 17(2), pp. 109, 2005.

[7] D. Z., Lojen, and S., Jevsnik, Fibres and Textiles in Eastern Europe, vol. 15 (4), pp. 63, 2007.

[8] Frydrych, I., Dziworska, G. and Cieslinska, A., Int. J. Clothing Sci. Technol., vol. 12 (3), pp. 171, 2000.

[9] K. Ancutienė, E. Strazdienė and A. Nesterova, "*The Relationship between Fabrics Bending Rigidity Parameters Defined by KES-F and FAST Equipment*", Materials Science (Medžiagotyra), vol. 16(4), pp. 346-352, 2010.

[10] E. J. Sturrock, C. Boote, G. E. Attenburrow and K. M. Meek, "*The effects of the biaxial stretching of leather on fibre orientation and tensile modulus*", Journal of Materials Science, vol. 39, pp. 2481 – 2486, 2004.

[11] V. Urbanija and J. Gersak, "*Impact of the mechanical properties of nappa clothing leather on the characteristics of its use*", Journal of the Society of Leather Technologists and Chemists, vol. 88, pp. 181, 2004.

[12] TSE, TS EN ISO 2418 Leather - Chemical, physical and mechanical and fastness tests - Sampling location.

[13] TSE, TS EN ISO 2419 Leather - Physical and mechanical tests - Sample preparation and conditioning.

[14] TSE, TS 4117 EN ISO 2589 Leather - Physical and mechanical tests - Determination of thickness.

[15] TSE, TS 9693, Textiles the Assessment of Drape of Fabrics.

[16] ASTM D1388 Standard Test Method for Stiffness of Fabrics.

[17] ASTM D4032 Standard Test Method for Stiffness of Fabric by the Circular Bend Procedure.

[18] TSE, TS 391 EN ISO 9237 Textiles-Determination of permeability of fabrics to air.

[19] TSE, TS EN ISO 14268 Leather - Physical and mechanical tests - Determination of water vapour permeability.

[20] T. M., Von Hoven, B. D., Belleau, T. A., Summers, I. I., Negulescu, *"Determination of Testing Techniques to Define Textile Properties of Emu Skins"*, J. Amer. Leather Chem. Ass., vol. 94, pp. 368, 1999.

[21] K. T. W., Alexander and R. G., J., Stosic, *"A new nondestructive leather softness test"*, Soc. Leather Technol. Chem., vol. 77, pp. 139, 1993.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

NEW ECO-EFFICIENT PRODUCTS USED IN LEATHER INDUSTRY

**ROSU Dan[1], CRUDU Marian[2], ROSU Liliana[1],
CRUDU Irina-Alexandra[1], VARGANICI Cristian-Dragos[1]**

[1]Advanced Research Centre for Bionanoconjugates and Biopolymers
"Petru Poni" Institute of Macromolecular Chemistry Gr. Ghica Voda Alley 41A, 700487, Iasi, România,
drosu@icmpp.ro; lrosu@icmpp.ro; varganici.cristian@icmpp.ro

[2]National Research & Development Institute for Textiles and Leather Division:
Leather and Footwear Research Institute, Bucharest, Romania, mariancrudu@yahoo.com

Corresponding author: Rosu, Dan, E-mail: drosu@icmpp.ro

Abstract: *In today's move to "sustainable production" the leather industry, as well as many other industries is recognized as a polluting one. Traditional chemical operations are polluting because of the levels of inorganic chemical waste. Process chemicals which are not consumed within the reactions necessary to convert collagen to leather are currently discharged to waste. These are usually applied during bulk production, such as inorganic agents from beam house and tanning processes, e.g. lime, sulphide, ammonium salts, sulphuric acid and sodium chloride, mineral tanning agents – mainly Cr(III) and the less common Al(III), Zr(III), Ti(III), Fe(III) salts -, whereas depending on the tanning process and the leather article produced organic chemical waste discharged comprises aldehydic and polyphenolic tanning products, bating enzymes, organic carboxylic acids and excess electrolyte stable synthetic fat liquors. It is rare for chemicals and water to be recovered for re-use from several of these process steps. Moreover, tanners worldwide are required to operate within strict legislative boundaries. Serious drawbacks continuously arise concerning the chrome–tanning process in leather industry and the environmental hazardous consequences of chromium containing effluents. In order to overcome this impediment, a great deal of research has been focused on developing chrome–free tanning methods in the past years, such as titanium tanning. In the present study, Ti–Al tanned bovine leather was characterized by means of SEM microscopy, EDAX elemental analysis, ATR–FTIR spectroscopy, thermogravimetry TGA, and differential scanning calorimetry DSC techniques.*

Key words: *bovine skin, tanning process, titanium, leather, ATR-FTIR, SEM/EDAX*

1. INTRODUCTION

It is a well known fact that the leather industry always has been one of the most polluting ones. This is due to the resulting of inorganic chemical waste levels during different chemical operations. Such waste results usually during bulk production, and usually consists of inorganic agents resulted during beam house and tanning processes (ammonium salts, lime, sodium chloride, sulphide, sulphuric acid and mineral tanning agents – mainly Cr(III) and the less common Zr(III), Ti(III), Fe(III), Al(III) salts. Other discharged chemical waste depends on the tanning process and the nature of the produced leather article [1-3]. The hazardous environmental consequences which usually arise in the leather industry from the chrome–tanning process are due to chromium based

effluents. It is therefore that a great deal of research has been conducted in overcomeing this issue, and which is focused on developing chrome–free tanning methods, such as titanium tanning [4-6].

2. EXPERIMENTAL

2.1. MATERIALS

Wet salted bovine hides weighing 20-25 kg (Constanta, Romania), limed and delimed bovine hide waste, bovine hide waste pretreatment with titanium based product, tanning product based on titanium recovered from scrap metal, technical grade auxiliary materials used in leather processing - succinic anhydride.

2.2. EQUIPMENT

Differential scanning calorimetry (DSC)

The glass transition temperature domain (*T*g) was determined by using the DSC technique. The thermograms were recorded on a DSC 200F3 Maia (Netzsch, Germany) calibrated with five metals (In, Sn, Bi, Hg, Co) according to standard procedures. Samples were heated in aluminium crucibles with pierced and pressed lids for removal of any volatiles released during heating. Sapphire is used for absolute heat capacity values determination. The used DSC device covers a temperature range of –150 ^{0}C ÷ 500 ^{0}C and cooling is made with liquid nitrogen. The experiments were conducted in nitrogen, as inert atmosphere, with a heating/cooling rate of 10 ^{0}C/ –10 ^{0}C and in the temperature range –50 ^{0}C ÷ 300 ^{0}C.

Fourier transform infrared spectroscopy (FTIR)

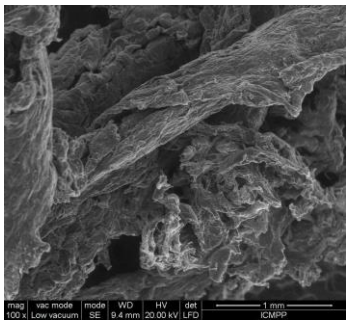
Through FTIR method one can obtain qualitative and quantitative detailed spectral analyses. The FTIR spectra were recorded with a Bruker Vertex 70 apparatus equipped with a MIRacle accessory designed for single or multi-reflection attenuated total reflectance (ATR). The ATR crystal plate was from diamond 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.

Scanning electron microscopy (ESEM)

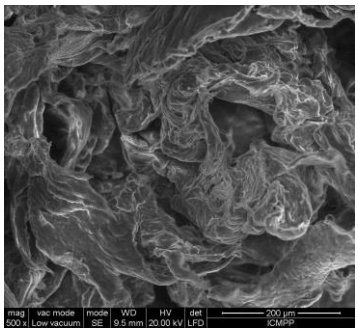
Samples materials surfaces were examined with a Quanta 200-FEI environmental scanning electron microscopy (ESEM). The investigations were performed in Low Vacuum mode using a secondary electron detector ETD at accelerating voltage of 20 kV. The Quanta 200 scanning electron microscope is equipped with an EDX system for allowing quantitative and qualitative compositional analysis. Double-sided carbon tape was used to mount the samples on aluminum stubs. The samples were covered in gold. The following chemical elements were identified through EDAX analysis: C, N, O, Na, Mg, Al, Si, S, Cl, Ti, V, Fe.

3. RESULTS AND DISCUSSIONS

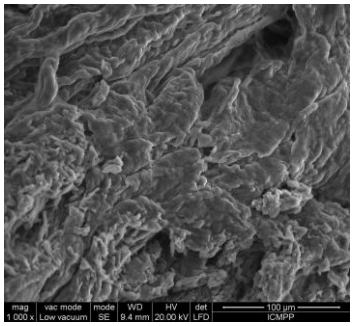
Relevant information regarding surface topology and sample structure was obtained with scanning electron microscopy SEM technique. ***Figs. 1a-d*** shows the SEM/EDAX micrographs of the studied sample in different sections and at different resolution values.



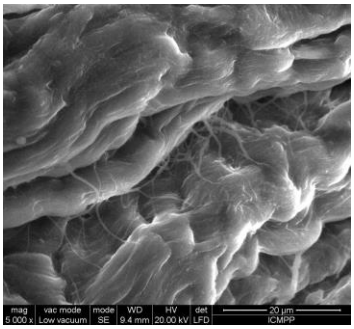
a



b



c



d

Fig .1a: *Micrograph of sample (1) at 100x*
Fig. 1b: *Micrograph of sample (1) at 500x*
Fig. 1c: *Micrograph of sample (1) at 1000x*
Fig. 1d: *Micrograph of sample (1) at 5000x*

The micrographs in ***Figs. 1a-d*** evidence a fibrillar and relatively compact surface. At higher resolution (5000x) there may be observed thin cross-linking bridges (**Fig. 1d**).

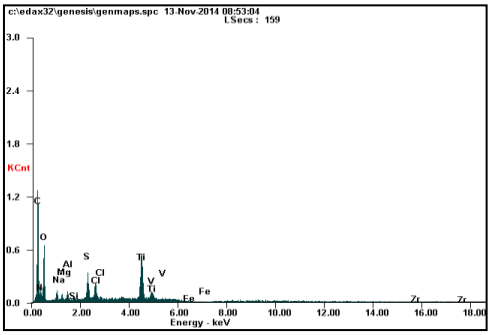


Fig. 2: *EDAX analysis of bovine skin tanned with Ti-Al salts*

By analyzing the ATR-FTIR spectrum in ***Fig. 3*** one may observe the presence of absorption bands specific to collagen structure. Bands at 1651 cm^{-1} and 1541 cm^{-1} are characteristic to polypeptides, which describe deformation vibrations of C=O structure (amide I band), and C–NH bonds vibration (amide II band). The vibration bands at 3427 cm^{-1} and 1030 cm^{-1} are proof of C–N bonds presence from primary amine groups existing in different types of collagen. The absorption band at 3427 cm^{-1} is a sign of humidity traces present in the tanned skin samples.

The DTG curve in ***Fig. 4*** indicates at least three consecutive stages of thermal degradation for the tanned bovine skin with maximum thermal decomposition rates recorded at 89 ^0C, 319 ^0C and 386 ^0C, respectively, corresponding to DTG curve peaks.

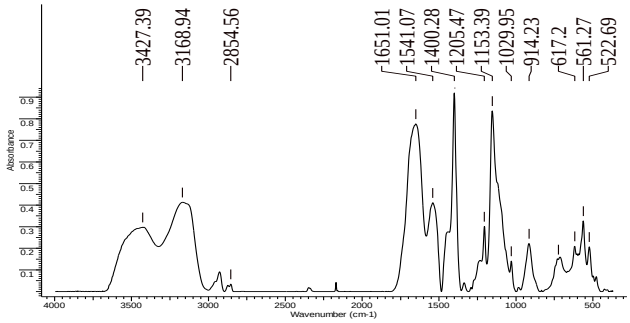


Fig. 3: *ATR-FTIR spectrum of bovine skin tanned with Ti-Al salts*

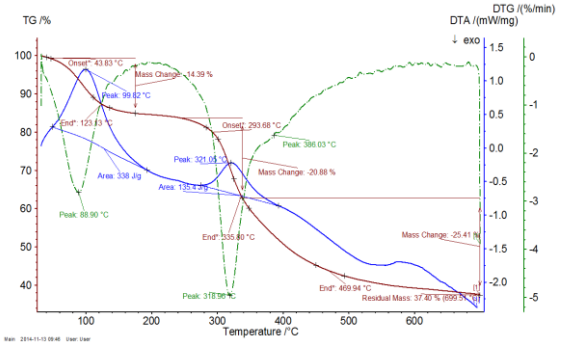


Fig. 4: *TGA curve of bovine skin tanned with Ti-Al salts recorded in the temperature range 30–700 ^{0}C in nitrogen and at a heating rate of 10 ^{0}C min^{-1}*

The DTA curve peaks indicated that all three thermal decomposition processes were endothermic. The first thermal decomposition stage ranges between 44 ^{0}C and 200 ^{0}C with a total mass loss of 14.4%. The second thermal decomposition stage ranges between 294 ^{0}C and 335 ^{0}C with a total mass loss of almost 21%. The third thermal decomposition stage ranges between 335 ^{0}C and 700 ^{0}C with a total mass loss of over 25%. The residue remained at the end of the thermal decomposition process of the studied material represented 37.4% of the initial sample mass.

REFERENCES

[1] M. Seggiani, M. Puccini, S. Vitolo, C. Chiappe, C. S. Pomelli, D. Castiello, "*Eco-friendly titanium tanning for the manufacture of bovine upper leathers: pilot-scale studies",* Clean. Techn. Environ. Policy, vol. 16, pp. 1795–1803, 2014.

[2] M. Crudu, V. Deselnicu, I. Ioannidis, L. Albu, A. Crudu, *"New wet white tanning agents and technology",* ICAMS – 4th International Conference on Advanced Materials and Systems, Bucuresti, Romania, 2012.

[3] A.D. Covington, "*Tanning Chemistry: The Science of Leather",* RSC Publishing, Cambridge; RSC Publishing: Cambridge, UK, 2011.

[4] M. Crudu, V. Deselnicu, D.C. Deselnicu, L. Albu, "*Valorization of titanium metal wastes as tanning agent used in leather industry"*, Waste Manag., vol. 34, pp. 1806-1814, 2014.

[5] E. Zuriaga-Agustí, M.V. Galiana-Aleixandre, A. Bes-Pia, J.A. Mendoza-Roca, V. Risueno-Puchades, V. Segarra, "*Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes"*, J. Clean. Product., vol. 87, pp. 874-881, 2015.

[6] W. Kangjian, X. Shiwei, L. Meng, "*Chrome-free tanning: a nonpickle process using a Zr–Al–Ti complex tanning agent",* J. Soc. Leather. Technol. Chem., vol. 96, pp. 141–147, 2012.

ACKNOWLEDGEMENTS

Authors acknowledge the financial support of a grant of the Romanian National Authority for Scientific Research, CNCS−UEFISCDI project number PN-II-PT-PCCA-2013-4-0436.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ANALYZING CORPORATE SOCIAL RESPONSIBILITY REPORTING IN THE EUROPEAN UNION

ANDREESCU Nicoleta Alina[1]

[1] University of Oradea, Faculty of Energy Engineering and Industrial Management, Department Textiles-Leather and Industrial Management, Str. B.Șt. Delavrancea nr.4, 410085, Oradea, Romania,
E-Mail: nandreescu@uoradea.ro

Corresponding author: Nicoleta Alina, Andreescu, E-mail: nandreescu@uoradea.ro

Abstract: *In the context of national and international developments, Corporate Social Responsibility is becoming an increasingly important element on national and transnational policy agendas. An ever more diverse range of businesses are adopting CSR strategies as a core part of their business model. Socially responsible business can contribute to restoring trust in the market in the post-crisis context. In last years European Commission encouraging international business development and in same time, CSR instruments development in all types of organizations for encourage responsible business conduct. In this paper our purpose was to analyse the current stage of CSR in the EU. For this, we divided our research in two parts: in first part we analyze the current stage of CSR reporting of the EU members and in the second part, we study the organizational sectors of company wich fulfill their report of sustenability. Our results prove us that are a few factors that influence the current stage of reporting and in last years number of company that report their CSR activity is increasing in all sectors and in all contries. Given the fact that CSR activities are becoming more and more important in any successful business, and taking into account the legislative changes that took place in European Laws, we consider CSR reporting to be even more intense in the years to follow, in EU member states.*

Key words: *Corporate Social Responsibility, reports, European Union, organizational sectors.*

1. INTRODUCTION

An ever-increasing number of organizations want to make their operations sustainable. Profitability should go hand-in-hand with social justice and protecting the environment. These expectations are only set to increase and intensify as the need to move to a truly sustainable economy is understood by companies' and organizations' financiers, customers and other stakeholders. [1], [2], [3]

CSR reporting helps organizations to set goals, measure performance, and manage change in order to make their operations more sustainable. A sustainability report conveys disclosures on an organization's impacts on the environment, society and the economy. Sustainability reporting makes abstract issues tangible and concrete, thereby assisting in understanding and managing the effects of sustainability developments on the organization's activities and strategy. [1], [4]

2. CURRENT STATE OF CSR REPORTING IN THE EU

In recent years, a series of guides, principles and directing lines have been created for companies that want to formally report their CSR activities. To analyze the situation of EU reporting company, we have studied the Global Reporting Initiative (GRI) database – a non governmental organization that promotes sustainability for companies by combining long term profitability with an ethical behavior towards the environment. [5] GRI provides all companies and organizations reporting framework that is widely used around the world. Through a responsible and transparent reporting, companies can increase their confidence that stakeholders have in them. We mention that more companies update their actions according to GRI standards. [5]

Table 1: *CSR reports*

Crt. No	**Country**	**No of reports**	Crt.No	**Country**	**No of reports**
1.	Austria	513	15.	Lithuania	9
2.	Belgium	367	16.	Luxembourg	60
3.	Bulgary	17	17.	Malta	-
4.	Cyprus	2	18.	Poland	169
5.	Croatia	71	19.	Portugal	401
6.	Denmark	326	20.	Czech Republic	90
7.	Estonia	9	21.	Romania	48
8.	Finland	711	22.	Slovak Republic	49
9.	France	696	23.	Slovenia	26
10.	Germany	1083	24.	Spain	1809
11.	Greece	335	25.	Sweden	947
12	Ireland	68	26.	Netherlands	939
13.	Italy	736	27.	Hungary	263
14.	Latvia	20	28.	United Kingdom	1189
	Total no of reports				**12.562**

Source: *made by the author according to the GRI database*

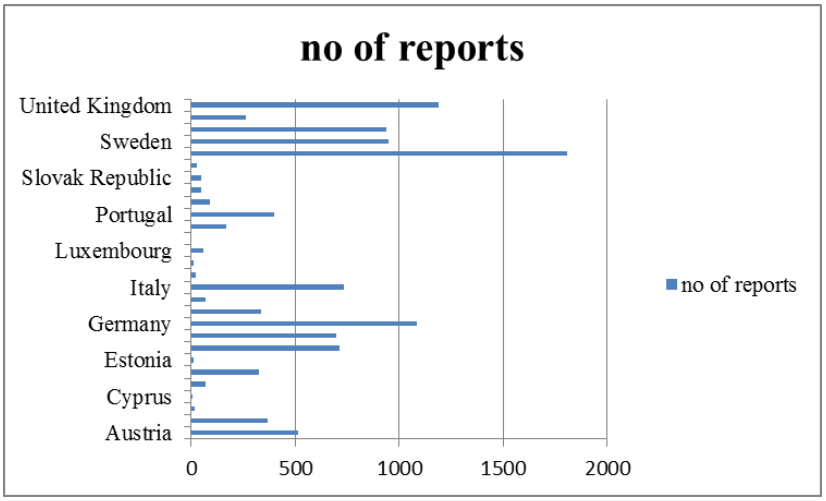


Fig. 1: *CSR reports*

Source: *made by the author according to the GRI database*

According to the GRI database, in april 2016, a number of 33.072 CSR reports belonging to 9.047 organizations from accross the world were filed. European Union countries have filed 12.562 reports, and their structure is presented in Table 1 and Chart 1. We can see that the bigger number of reports are Spain, UK si Germany and whit the lowest number of reports are Malta, Cyprus and Lithuania. Romania is in the second half of the order, with 48 sustainability reports. This is based on the fact that some countries joined the EU later (S-E European countries), and this fact had a direct impact on CSR reporting. If in country like UK and Germany, reporting was ussualy since 1999, in Romania, CSR reporting started in 2007. [6]

Table 2: *No of reports in organization sectors*

Crt.no	**Organization Sectors**	**No of.reports**	Crt.no	**Organization Sectors**	**No of.reports**
1.	Agriculture	72	20.	Logistics	282
2.	Automotive	279	21.	Media	235
3.	Aviation	244	22.	Metals Products	278
4.	Chemicals	298	23.	Mining	197
5.	Commercial Services	358	24.	Non-Profit /Services	428
6.	Computers	50	25.	Public Agency	225
7.	Conglomerates	298	26.	Railroad	121
8.	Constructions	448	27.	Real Estate	344
9.	Constructions Materials	319	28.	Retailers	387
10.	Consumer Durables	94	29.	Technology Hardware	154
11.	Energy	817	30.	Telecommunications	477
12.	Energy Utilities	577	31.	Textiles and Apparel	153
13.	Equipment	218	32.	Tabacco	33
14.	Financial Services	1736	33.	Tourism/ Leisere	265
15.	Food and Beverage	845	34.	Toys	8
16.	Forest and Paper	248	35.	Universities	93
17.	Healt Care Products	305	36.	Waste Management	220
18.	Healt Care Services	112	37.	Water Utilities	165
19.	House Hold and Personel	147	38.	Others	1041

Source: made by the author according to the GRI database

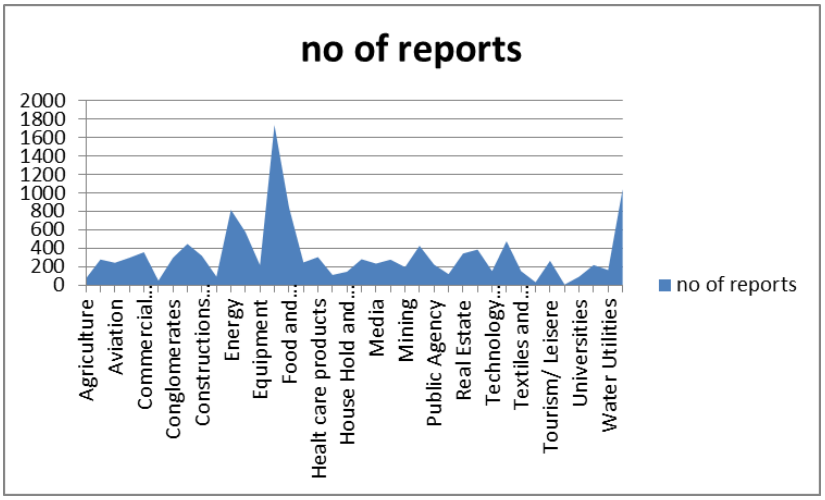


Fig. 2: *No of reports in organization sectors*
Source: made by the author according to the GRI database

In graph no. 2 is presented the structure of the number of reports, based on the activity sectors, by companies belonging to all 37 activity sectors, which represents 38% of the total reports filed with the GRI. The reporting period is 1999-2016. [6]

By analyzing the situation of the activity sectors of the companies that file CSR reports, we can see that most of them belong to companies from the financial service, food and beverage service and energy sectors. The number of reports filed by the Textile and Apparel companies is in the second half of the order, with 153 sustainability reports.

3. CONCLUSIONS

In this paper we analyse the situation of EU regarding CSR reporting and our results prove us that in last years CSR reporting is growing regardless organizational sectors. The countries that are UE oldest members have the biggest number of organisation that submitt CSR reports. The legislation is an important factor too, and from 2017 the number of companies which reports their activity will increase, because Directive 2014/95/UE [7] regarding the obligation of large companies to report anually a series of nonfinacial aspects and information regarding diversity it will enter into force.

The contries wich became in last ten years member of EU start to submit reports too, and their number is increasing every year. New members of EU have two reasons for increasing their CSR reporting, first, they understand the importance of and the impact of CSR in community, and in same time they have to obey the rules of EU Community.

REFERENCES

[1] *** *GRI G4-Reporting Principles and Standard Disclosures;*

[2] *** *Corporate Social Responsibility - National Public Policies in the European Union*, European Commission, April 2011;

[3] *** European Commission, *A Renewed EU Strategy 2011-2014 for Corporate Social Responsibility*, 2011, [Online]. Available: http://ec.europa.eu/enterprise/newsroom/cf/_getdocument.cfm?doc_id=7010;

[4] *** *Corporate Social Responsibility National Public Policies in the European Union Compendium*, 2014;

[5] M. Berinde, N.A. Andreescu, 2015, *„Reporting corporate social responsibility according to GRI standards*", [Online]. Available: http://anale.steconomiceuoradea.ro/volume/2015/AUOES-1-2015.pdf;

[6] http://database.globalreporting.org/search;

[7] *** *Directiva 2014/95/UE*, 2014, [Online]. Available: http://eur-lex.europa.eu/legal-content/RO/TXT/?uri=CELEX:32014L0095.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE MODERATING EFFECT OF GENDER ON ENTREPRENEURIAL INTENTION AMONG COLLEGE STUDENTS

PEREZ Lucía[1], MILLET José[2], MIRÓ Pau[1], DÍAZ-GARCIA, Pablo[1], WILLOUGBY Michael[2], BOU-BEDA, Eva[1]

[1] Universitat Politècnica de Valencia, 03803 Plaza Ferraniz y Carbonell s/n, Spain. lupebla@ideas.upv.es

[2] Universitat Politècnica de Valencia, 46022 Camino de Vera s/n, Spain. mwilloughby@ideas.upv.es

Corresponding author: Díaz, Pablo pdiazga@txp.upv.es

Abstract: *The main objective of this research is to determine whether the gender of college students influences entrepreneurial intention, with the purpose of providing the institutions with information on whether this socioeconomic variable can influence university entrepreneurship. Such information can be useful for institutions to take effective measures to promote gender equality policies in the field of education.*
The first part of the article describes the research methodology and definition of the variables measured therein and the hypotheses. The second section contains the descriptive analysis of the results and the independence tests for the measurement variables. The final sections include the contrast of hypotheses and the conclusions obtained.
The study uses descriptive statistics that allows for the analysis of convenient data and identifies patterns of behavior of the variables analyzed. Data were analyzed using frequency analysis, contingency tables and independence tests. The data collection instrument was by a questionnaire conducted with first and fourth year students, obtaining a total of 630 surveys. The variables used in this survey were structured according to gender and the intention to create a company, having first extensively analyzed the references on the relationship between these variables.
Finally, after statistical analysis and hypothesis testing, it can be concluded that the gender variable does not influence the entrepreneurial intention of college students, so there is no need to implement extra policies on gender equality to foster university entrepreneurship.

Key words: *entrepreneurship, entrepreneurial profile, university, gender equality, business creation, entrepreneurial intention*

1. INTRODUCTION

This article examines entrepreneurial intention among university students according to gender and is organized into three parts.

2. EMPIRICAL STUDY

2.1 Methodology

The main objective of this research is to determine whether the gender of college students influences their entrepreneurial intention, with the purpose of providing institutions with information

on whether this socioeconomic variable can influence university entrepreneurship. This information can be used by educational institutions to take effective measures and aid decision-making in the allocation of resources for gender equality policies in the field of education.

For this purpose, we propose the following global hypothesis: the gender of university students is closely related to entrepreneurial intention, i.e., there are significant differences between men and women students in their propensity to start a business.

In order to contrast this hypothesis, we carried out an extensive literature review in order to construct the measuring instrument. We then proceeded to formulate the questionnaire and to consult experts on its adequacy and applicability. Following various alterations after feedback we went on to conduct the questionnaire, as described below.

We identified the target population, conducted the questionnaire and collected data based on a sample of 630 students from 6 different undergraduate degrees at the Alcoi Campus of the Polytechnic University of Valencia.

The statistical data analysis was performed using the IBM® SPSS® Statistics 20 program. Therefore, the data were analyzed using frequency analysis, contingency tables and independence tests.

2.2 Measurement variables

Gender: In previous studies that examine the age of entrepreneurs, people who make the decision to become an entrepreneur are usually between 25 and 40 years of age [1], while, in terms of gender, data indicate that 44.4% of men have the initiative to create a company as opposed to 30.9% of women [2]. Recent research framed within the analysis of entrepreneurial profile and the motivations that lead people to start a new business conclude that there is no dependent relation either between gender and the intention to create a company, or with the motivations for starting a business [3, 4]. Other studies focus on the university level, examining the attitude of students by gender toward entrepreneurship and the intention to create a business. Studies conducted in Spanish and Latin American universities conclude that there is no significant difference between these variables [5, 6].

Intention to create a business: this classifying item is based on two factors; the first is a dichotomous variable establishing whether or not an individual is an entrepreneur, while the second reflects the intention to create a new firm.

Table 1: *Measurement variables*

Items	Relevant questionnaire	Measurement scale
EDUCATION AND GENDER	B3P1.- Name of degree course	Categorical variable: 6 Subcategories of 6 degree courses include din the study
	B3P2.- Gender	Dichotomous variable. Male/ Female
INTENTION TO START A BUSINESS VENTURE	B2P1. - Do you consider yourself an entrepreneur?	Dichotomous variable. Yes/ No
	B3P19. - Have you seriously considered creating your own business?	Likert scale 1 to 5, 1 no, never to 5 yes, I firmly intend to create my own business.

3. RESULTS

3.1. Results analysis

We undertook a process to identify the subjects taken by the largest number of students by degree course and year (first and fourth year), coinciding with core or compulsory subjects. The survey was conducted in person after authorization from the relevant professor, with a total of 630 students, representing 72.83% of the total enrolment in these subjects (865 students enrolled).

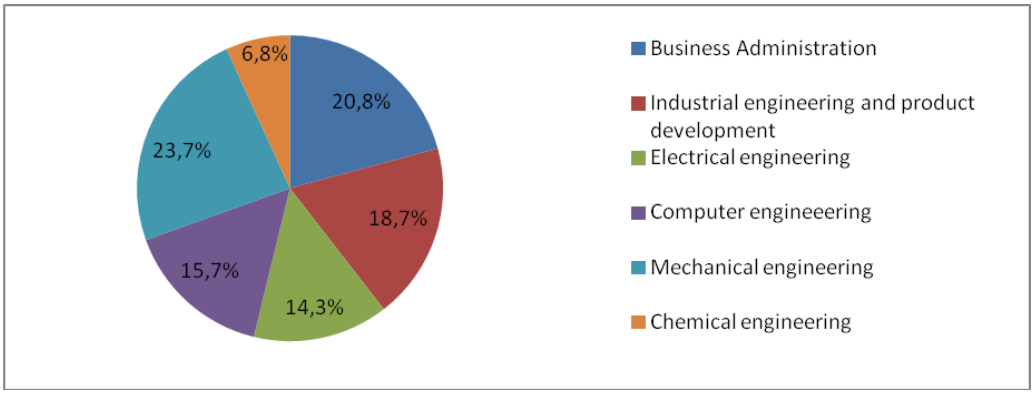


***Fig. 1**: Percentage of students by degree course*

The final sample obtained indicates that, in terms of the overall characteristics of the population, 73.2% are male. With regard to the intention to create a business, 69.2% considered themselves entrepreneurs and 80.5% had a firm intention to create their own business.

From the global hypothesis H, and by using contingency tables, we generate two possible scenarios that match each variable related to the intention to create a business venture with the gender variable. Scenario HA analyzes the relationship between those that consider themselves to be entrepreneurial (B2P1) and gender, and the second scenario HB examines the relation between those that wish to create their own business and gender.

The study also addresses the question of gender among university students who answer both items affirmatively (B2P1 vs B3P19), obtaining 384 affirmative responses for both items, which represents 61.0% of the conducted surveys.

As a partial conclusion drawn from the data obtained from this analysis of the contingency tables, we can again establish characteristics according to the gender variable, obtaining percentages that are similar to those obtained from the frequency study (73.8% are male), and therefore, no statistically significant differences can be observed between the two sexes.

3.2. Independence tests of the variables

The data shown in Table 2 were obtained following the Chi-Square analysis questions B2P1 and B3P19 referring to gender.

***Table 2:** Dependency of the items included in the hypotheses*

SUB-HYPOTHESES	Chi-squared value	Type of dependency
1A. vs Gender	0.684	Independent
1B. vs Gender	0.327	Independent
1A&B. vs Gender	0.443	Independent

4. CONCLUSIONS

With regard to the comparison of sample data against the reference questions related to entrepreneurial nature and future intention to start a business among students, we can state that this section of the university population is male-dominated according to the study frequency.

In order to confirm this statement, we proceeded to analyze the hypothesis by observing the dependency test between variables. These results coincide with data from the GEM study [7], which indicates in its analysis of entrepreneurial profiles that 54.6% of entrepreneurs are male. The GEM study also indicates that 35.9% of these cases possess higher education qualifications.

As a final conclusion, we can infer that there is no need for institutions to implement further policies on gender equality in terms of fostering university entrepreneurship.

REFERENCES

[1] J.M. Veciana, M. Aponte, D. Urbano, *University students' attitudes towards entrepreneurship: A two countries comparison. The International Entrepreneurship and Management Journal*, 1(2), 2005, pp.165-182.

[2] I. Arribas, J.Vila, *La actitud emprendedora del universitario valenciano. El emprendedor innovador y la creación de empresas de I+ D+ I*. Valencia: PUV, 2004. p. 201-212.

[3] F.J.F García, S.M.S Cañizares, *Análisis del perfil emprendedor: una perspectiva de género. Estudios de economía aplicada*, 28(3), 2010, p. 696.

[4] M. López-Fernández, P.M. Romero-Fernández, R. Díaz Carrión, *Motivaciones para emprender: un análisis de diferencias entre hombres y mujeres*, 2012, p. 82.

[5] S.M.S Cañizares, F.F.García, *Mujer y emprendimiento: Un análisis en el contexto universitario español*. Revista de Ciencias Sociales, 19(1), 2013, p. 146.

[6] M. Noguera, C Alvarez, D. Urbano. *Socio-cultural factors and female entrepreneurship. International Entrepreneurship and Management Journal*. 2013 Jun 1;9 (2):183-97.

[7] Red Española de Equipos Regionales, GEM. Informe GEM España 2013. 2014. [Online]. Available: http://www.gemconsortium.org/country-profile/109. P. 60-62.

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

THE EVOLUTION OF THE INTERNATIONAL TRADE AND ITS IMPACT ON THE ROMANIAN EXPORTS

TRIPA Simona[1], CUC Sunhilde[2]

[1, 2] University of Oradea, Faculty of Energy Engineering and Industrial Management, Department of Textile Leather and Industrial Management, Str. B. Şt. Delavrancea, no. 4, 410058, Oradea, Romania, E-Mail:tripasimona@yahoo.com

Corresponding author: TRIPA, Simona, E-mail: tripasimona@yahoo.com

Abstract: *This paper analyzes the impact of the financial and economic crisis on the evolution of international trade and implicitly on Romanian exports during 2000-2014. Methods of the research that have been employed in the paper are analysis and summarizing of scientific literature, mathematic calculations and comparative analysis of statistic dates. This paper presents in the first part the quantitative evolution of world exports and highlights the role of international trade in both the financial and economic crisis propagation, and in process of economic recovery in the world in the coming years. It continues with the manner in which international trade evolution and structural changes that have occurred in the world economy in the last two decades or reflected in trade of Romania not only from a quantitative but also structurally. Quantitatively was noted that Romanian exports have followed the trend recorded worldwide and from the structural viewpoint were identified the dominant characteristics of the evolution of trade in Romanian, the past two decades, namely the dynamic growth of trade flows of processed products (in particular Machinery and transport equipment) as well as their share in total trade and increased exports on the markets outside the EU in proportions higher than the growth in intra EU market.*

Key words: *economic crisis, trade, market, exports, Romanian*

1. INTRODUCTION

The evolution of international trade cannot be dissociated from the structural changes which have occurred in the world economy in the last two decades. This evolution was influenced by a number of factors of which the most important are: progress in information technology and communications; reducing trade barriers as a consequence of liberalization of international trade; liberalization of capital flows and technology and increase the supply of labor in the global market and its liberalization. Global financial and economic crisis which broke out in 2008 and the recession deep and comprehensive from the global economy that followed have determined a strong contraction in world trade (eg. international trade contraction in 2009 was -12.2%). [1]

Several explanations have been proposed for the collapse of trade. The first is that trade may be collapsing because of the transmission of shocks through vertical production linkages. [2] Chor and Manova (2009) demonstrate that credit conditions in exporting countries affected international trade during the current crisis. [3] Another group of explanations points to transmission channels in the real economy. [4] Bénassy-Quéré, Agnès consider the new patterns of the international division of labour may also have played a big role in the collapse of trade. [5]

According to the World Bank, the fall of the international trade had a big contribution the recession in manufacturing, especially on durable goods and equipment. Tightening of the lending conditions by commercial banks caused the decline in sales from this product category, with a big share in the international trade and affected the level of international trade. [6]

Whatever the causes of this financial and economic crisis, the extent of the negative impact on cross-border transactions revealed commercial and financial links, increasing close of the world's economies and the high degree of interconnectivity that currently exist between the financial markets and commodity markets (goods and services) which was a factor of propagation of the negative effects of the crisis on all world regions. The global crisis and prelaunch unequal the international trade, has further accentuated shifting in the global economy - moving the economic and trade weight center from developed countries towards developing /emerging countries and have contributed to the expansion of the system of global production managed by the transnational corporations and increasing the foreign direct investment flow oriented towards developing economies. Moreover, supported by the export successes and by the increase their income, developing countries / emerging have become increasingly important players in the international financial system. [7]

This is why we considered opportune carrying out an analysis on the effective evolution of international trade in the 2000-2014 period and determine how it was reflected in the evolution of Romanian exports both from the point of view of quantity and structurally.

The main aim of this paper is determining the impact of the international trade evolution on exports Romanian, both from the point of view of quantity and structurally, in the 2000-2014 period.

Methods of the scientific research that have been employed in the paper are scientific analysis and summarizing of literature, mathematic calculations and comparative analysis of statistic dates. The paper is organized in three parts: the first part shows the quantitative evolution of world exports in the 2000-2014 period and the main factors which led to this development. The second part shows the quantitative evolution of Romanian exports and the third part presents the structural changes recorded in Romania's exports in this period .

2. THE QUANTITATIVE EVOLUTION OF WORLD EXPORTS IN THE 2000-2014 PERIOD

The volume value of international trade in goods amounted to 19.002 billion dollars in 2014, equivalent to an increase of 2.94 times compared to 2000 when it was $ 6.458 billion. (See Fig. 1).

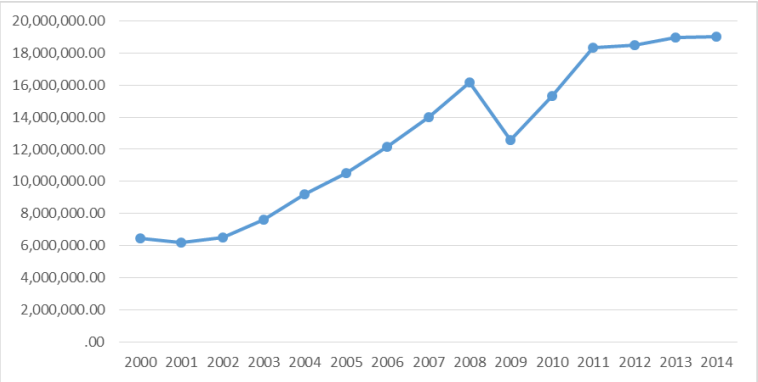


***Fig. 1**: The evolution of world exports, 2000-2014*
Source: Made by the authors based on the data from Eurostat

Except the decline from the year 2009 (while the value of world trade declined by 23.31%) as against that of 2008 can observe as its evolution over the analyzed period is one ascending. From the multiple factors that have influenced the flows of international trade, in 2009, could be considered: weaker global demand and, implicitly decreased the basic commodity prices, decreased activity of the global networks production and the negative multiplier effect on the regional and international trade, limited access to credit, etc. [8]

In 2010, international trade has recovering from the losses incurred in previous year and reached 94.68% of the 2008. As the unprecedented decline of trade in 2009 WAS one of the major channels through Which financial and economic crisis spreads, trade has been a major factor Also supporting the process of economic recovery in the world.[9] The recovery of trade in 2010 was constrained by a number of factors among which stands out: the reduction of tax incentives in many countries; High and persistent unemployment in developed countries - with its influence on domestic consumption of these countries and the high price of crude oil which caused increases in energy for households and businesses. [10] The World Bank assumes that the delay recovery of trade was generated mainly by lack of financing imports and the decrease in investment but also because declining of demand worldwide. [6] In addition, the European level has made a transfer of powers of the Member States to a Commission subject of a weak democratic control, so that the European Central Bank which sets monetary policy at European level has conserved a dominion over its monetary policy in outside democratic control, with influences on the evolution of trade of these countries. [11]

3. THE QUANTITATIVE EVOLUTION OF ROMANIAN EXPORTS IN THE 2000-2014 PERIOD

The evolution of Romanian exports in the analyzed period broadly follows the evolution recorded worldwide, just that it decrease of the Romanian exports was not so great in 2009 compared to 2008, the reduction being only by 18.11% compared to 23.31% as it was worldwide. (See Fig. 2)

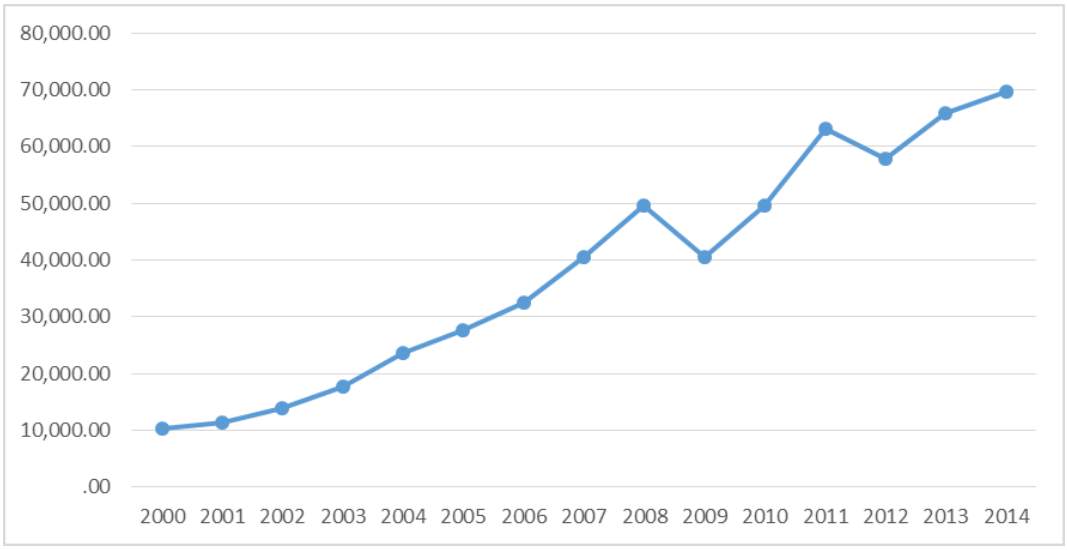


Fig. 2: *The evolution of Romanian exports, 2000-2014*
Source: Made by the authors based on the data from Eurostat

The 2009 crisis has made its mark on the Romanian exports, both extra EU markets - these decreased in 2009 with 24.53% over the previous year and on the intra EU market - these decreased with 9.15%. Given the fact that Romania's exports are predominantly oriented to the EU market, even if in percentage share the decrease was lower than that recorded on markets outside the EU, in absolute value the decrease was approximately equal on the two markets, respective in the EU market the decrease was 2,184,165,835 Euro and extra EU market the decrease was 2,410,243,610 Euro. (See Fig. 3)

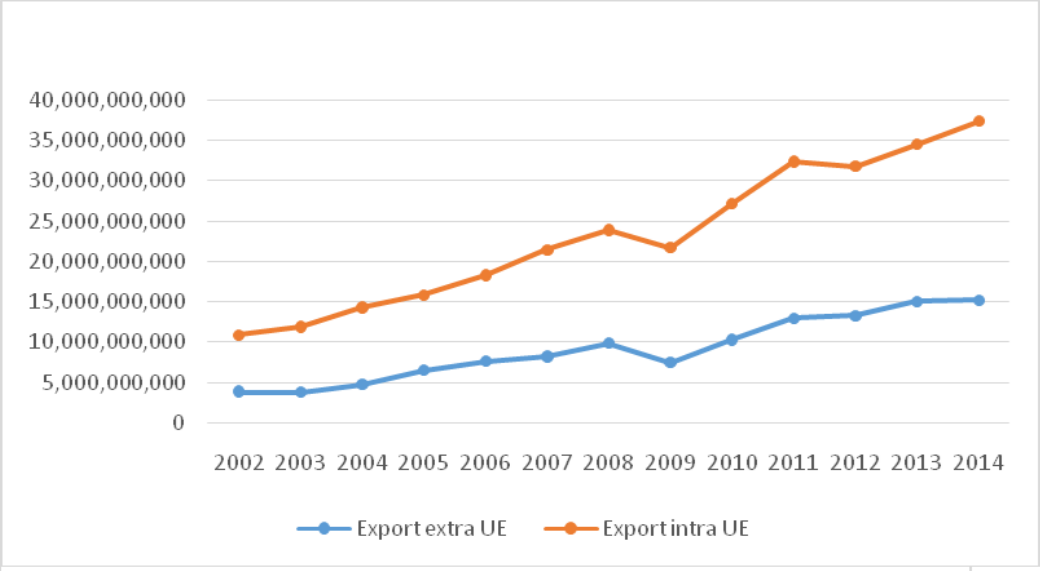


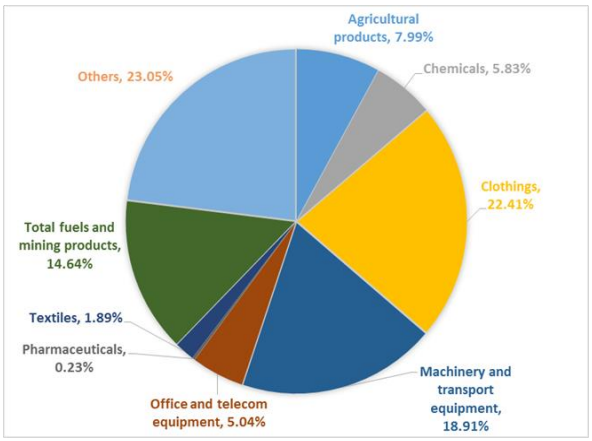
***Fig. 3**: Evolution of Romanian exports during 2000-2014 , intra and extra EU markets*
Source: Made by the authors based on the data from Eurostat

The years following the crisis from 2009 are characterized by annual increases of world exports - in different rhythms, namely: in the first two years the annual increases are significant - of 21.87% and 19.84%, succeeding thus at the end of 2011 the world exports to be above the one registered before the crisis. After this year, the annual growth is continuous, but in the rhythms much lower: 0.86%, 2.47%, 0.25%.

The evolution of Romanian exports after 2009 is increasing in the next two years; they increased with 22.21% in 2010 and with 27.14% in 20111. In 2012 total Romanian exports decreases with 8.24% and then increases with 13.82% in 2013 and with 5.92% in 2014.

4. THE STRUCTURAL CHANGES RECORDED IN ROMANIA'S EXPORTS IN THE 2000-2014 PERIOD

The evolution of the international trade and the structural changes that have occurred in the world economy in the last two decades was reflected in the Romanian trade, not only quantitatively but also structurally. (See figures 4 and 5)



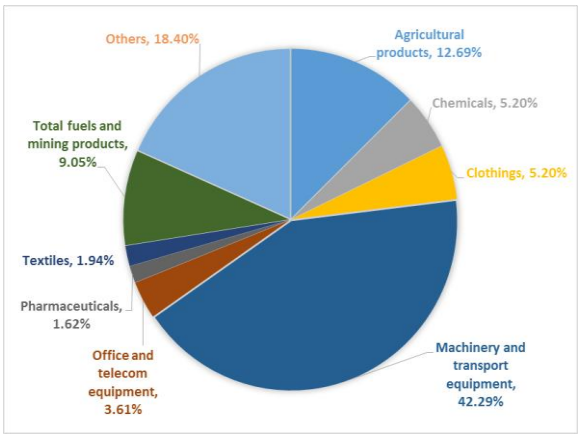


***Fig. 4**: Structure of Romanian exports in 2000* ***Fig. 5**: Structure of Romanian exports in 2014*
Source: Made by the authors based on the data from National Institute of Statistics

Thereby can be notice the increasing of the share of the agricultural exports, the share of exports of machinery and transport equipment and the share of exports of pharmaceutical products in total exports. In contrast to them, the share of the garments exports and of fuels and mining products in the total exports was reduced. For all other product categories were not recorded significant changes in shares held in total exports.

Machinery and transport equipment ranks first in Romanian exports in 2014, with $ 29.492 million. Share of exports of Machinery and transport equipment increased in the period under review from 18.91% to 42.01%, thus reaching in the 2014 to be $ 29.492 million to and holders of the largest share of total exports of Romania. This evolution is mainly due to applied technologies, the high technological level, the high productivity, the high degree of specialization and not least the high level of products quality.

Agricultural product export is ranked at second in the top of Romanian exports in 2014 and it was of $ 8847.39 million. The export of these products has steadily increased especially after partial liberalization of the trade between Romania and EU with agricultural products - by concluding conventions reciprocal to a range of agricultural products: exemptions and reduction of duties, tariff quotas and eliminating of export subsidies at some products up to full liberalization that took place when Romania joined the EU (2007).

The export of pharmaceutical products has registered significant growth in the recent years and reached in 2014 at $1.127 million. Increase the share of pharmaceutical products exported in total exports was from 0.23% in 2000 to 1.87% in 2014.

The highest decrease during the analyzed period was recorded on garment exports, falling from the first place in 2000 (when they was 22.41% of total exports) at the sixth place in 2014 (when they represent only 5, 20% of total exports). Dynamics of exports of this subsector from year to year, was influenced by a series of factors such as: liberalization of trade in 2005, reduction the production type CMT, changing the consumer demand etc. These factors determined essential structural changes in the sector and have led to a reorientation of Romanian producers on the domestic market and to the development some domestic brands internationally recognized.

Total fuels and mining products have one reducing significantly; reaching out to a share of 9.05% of total exports in 2014 compared to 14.64% how it accounted in 2000.

The exports of textile and the chemicals retains it's the share in Romanian exports (in 2014 are like in 2000).

5. CONCLUSIONS

Growth in global trade volumes has slowed in recent years, thanks to a tepid economic recovery from the financial crisis and the changing structure of the Chinese economy. Also stands out a new generation of trade agreements (Trans-Pacific Partnership and Transatlantic Trade and Investment Partnership) characterized by less tariff barriers on dismantling tariff barriers and more on tackling tough issues such as intellectual property, labour and environmental standards.

The evolution of the international trade and the structural changes that have occurred in the world economy in the last two decades was reflected in the Romanian trade, not only quantitatively but also structurally. From a quantitative Romanian exports have followed the trend recorded worldwide and from the structural point of view the dominant feature of the evolution of Romanian trade, in the last two decades, has been the dynamic growth of trade flows of processed products (especially Machinery and transport equipment) and growth their share in total trade (the export growth on the extra EU markets was in proportions higher than the growth in intra EU market).

REFERENCES

[1] Florina POPA, "*Impactul crizei mondiale asupra comerţului internaţional*" Management Intercultural, Volumul XV, Nr. 3 (29), pp.280-288, 2013.

[2] Levchenko, Andrei A., Logan T. Lewis, and Linda L. Tesar. "*The collapse of international trade during the 2008–09 crisis: in search of the smoking gun*", IMF Economic review 58.2 (2010): 214-253.

[3] Chor, Davin, and Kalina Manova, 2009, "*Off the Cliff and Back? Credit Conditions and International Trade during the Global Financial Crisis*", Mimeo, Singapore Management University and Stanford University (October)

[4] O'rourke, Kevin H., and Barry Eichengreen. "*A tale of two depressions*." Chartered Accountants Journal 88.4 (2009): 70-71.

[5] Bénassy-Quéré, Agnès, et al. "*Economic crisis and global supply chains*", (2009).

[6] World Bank – Financial Crisis enterprise surveys (decembrie 2010)

[7] Ghibuțiu, Agnes. "*Structural Changes Reshaping the World Economy and International Trade*", Journal of Global Economics 4.3 (2012).

[8] Oehler-Şincai, Iulia Monica. "*Evoluţii, mutaţii şi tendinţe în comerţul mondial cu bunuri. Determinanţi structurali şi conjuncturali*" [Online]. Available: http://mail.iem.ro/fisiere/Sinteze-comunic%C4%83ri/M-oehler-SINTEZA%20comert%20cu%20bunuri.pdf

[9] Albu, C. coord., "*Perspective şi provocări ale exporturilor româneşti în perioada 2010-2014, prin prisma relaţiilor comerciale bilaterale şi regionale ale Uniunii Europene*", Institutul European din România, Bucuresti, 2013

[10] Ghibuțiu, Agnes, "*Evoluția comerţului internaţional în 2010 şi perspectivele pentru 2011*" in "*Conjunctura economiei mondiale 2011*", Institutul de economie mondiala, Bucuresti, 2011

[11] Timofte Claudia Simona, Timofte A.I, *"Some Critical Aspects Concerning the Institutional System of European Union"*, Analele Universitatii din Oradea., Revista de Stiinte Economice, 2013, pag 381

ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ANALYSIS OF THE WORKING CONDITIONS WITH CONSIDERATION-HAZARD POTENTIAL HEALTH AND SAFETY OF EMPLOYEES IN TEXTILE INDUSTRY

UROŠEVIĆ Snežana[1], STEFANOVIĆ Violeta[2], ĐORĐEVIĆ Dragan[3]

[1,] University of Belgrade, Technical Faculty in Bor, Bor, Serbia, surosevic@tf.bor.ac.rs

[2] City Administration for Inspection Affairs of the City of Leskovac, Leskovac, Serbia, bobiviki@gmail.com

[3] University of Niš, Faculty of Techology, Leskovac, Serbia, drdrag64@yahoo.com

Corresponding author: Urošević Snežana, surosevic@tf.bor.ac.rs

Abstract: *Safety and health measures have a very important role in any kind of industry, especially in the textile, which emit a wide range of pollutants at all stages of processing fibers into textile materials. Most processes have a negative impact on the living and working environment. However, their health and their safety at work are exposed almost daily dangers, depending on the nature of work and the conditions under which the work takes place. Therefore, the modern organization requires to create a safe and harmless working conditions, in order to adequate protection of their health and their safety. This paper will analyze the work environment in three textile factories involved in the production and processing with consideration of end jobs where there are potential threats to the health and safety of employees. An effective and powerful system of managing the health and safety of employees at work can help to translate the uncontrolled hazards controlled risk and thus better protect the welfare of employees and companies.*

Key words: *textile industry, working conditions, safety, health, employees*

1. INTRODUCTION

From contemporary organizations required to create a safe and harmless working conditions, in order to adequate protection of their health and their safety. Among other things, for them to undertake the imperative legal norms inherent in every modern country. Such norms are contained in the applicable legislation of the Republic of Serbia. Frequent injuries and accidents at work, an increasing number of disabled workers and occupational diseases and other reasons contributed to the observance of laws and other regulations on safety and health at work and regulations on so-called special protection. vulnerable categories of employees.

The system of health and safety at work involves the interplay of different factors such as legislation, inspection, insurance, technical knowledge and solutions, occupational health services, health, information, education, research and others. All factors that occur in the work process in the workplace and in the working environment, which may cause or lead to an occupational injury or damage to health or illness of the employee are dangers in terms of regulations on safety and health at work. Poor working conditions, and the irresponsible attitude of the management towards achieving the general welfare of employees has resulted in the emergence of a high level of

absenteeism. Due to injuries and occupational diseases today are losing huge financial resources for treatment, rehabilitation, compensation for absence from work in case of disability insurance, and other, which results in a reduction of the profit organization and change its competitive position.

The consequences of inadequate exposure values microclimate, lighting, noise and vibration, biological and chemical factors do not pose a direct threat to the life of an employee, or excessive and prolonged exposure to unsuitable values of these parameters leads to damage in the body and affects the health of workers.

Employees are fully aware of the importance of health, safety and well-being, because it is their life and future [1]. All measures are aimed at primary goal - an employee who is satisfied with giving higher productivity at work. Adequate working environment ensures the well-being of employees who will always allow you to carry out their roles with all the fervor that can provide higher productivity [2]. It can also be concluded that the work environment affects job satisfaction and achievement of the objectives of the organization [3]. Daud [4] in their study shows that the quality of working life of employees is an important factor for employers who are interested in improving employee satisfaction with work and their dedication.

Identifying hazards, assessing risks of injury and identifying measures to eliminate or reduce risk in the workplace is an extremely complex and highly responsible job persons responsible for the safety and preservation of health. It is therefore necessary to define guidelines that can assist organizations in formulating krtierijuma to take risks for professional environments [5].

Analysis of the working environment and working conditions was performed in textile organizations engaged in the production and processing of yarn. On the basis of data obtained from several textile organization, analyzed the conditions of the working environment, obtained by measuring microclimate parameters: tempterature, relativine humidity, air speed and comfort zone in winter, as well as the presence of chemical origin identification, noise, vibration and the presence of light levels on workplace which are also set out in the winter.

2. ANALYSIS OF WORK ENVIRONMENT AND WORKING CONDITIONS IN TEXTILE ORGANISATIONS

The analysis was conducted based on the data of the measured values of the parameters of the working environment, for the winter period, as determined by an authorized organization, the workplace when applicable safety and health at work. In the analysis were considered Param: air temperature and comfort zones in winter (microclimate), the presence of chemical origin identification and hazards that occur using work equipment, noise, vibration and the presence of light levels in the workplace. In analyzing the parameters of a comparison of values obtained by measuring sixteen jobs and making comparisons with the maximum allowable values.

Based on these data, by the person in charge of safety at work, established the division of the impact of these factors on the safety of employees in the manufacturing process, where the parameters of quality were awarded to: Increased risk allowable level, moderate, and negligible level where no there are harmful effects. The same data were used in the next phase of research.

Testing of the working environment shall be conducted in these organizations in accordance with legal regulations, periodically during the summer when the temperature is above 15° C and in winter when the temperature is below 5°C. The law establishes the duty of every employer to carry out these periodic tests at every workplace in the working environment within three years from the date of the previous tests.

The temperature, velocity and relative humidity are the parameters of the microclimate, whose trial is conducted in workplaces in the working environment in which takes place the process of work, or in places where employees move or retain more than two hours during working hours.

Lighting is very important for the conduct of business and significantly affects the quality of work of workers [6]. Required illumination in the workplace is determined by the standard: daylight and electrical lighting rooms in buildings SRPS U. C9. 100/62 and in accordance with the same in these organizations control measurements were carried out in all workplaces, and the results thereof are shown in Table 1.

Testing of physical harmfulness of noise and vibration is performed in the workplace where the work process of the same occur. Test noise [7] and vibration [8] is achieved by measuring, analyzing and comparing them with the standard values. Increase the value of certain significant influence on the health of workers [9]. The noise level was found in the work of machines in the production process for each position in the drive, the organizations in which the survey was conducted. The allowed noise level is defined with respect to the type of activity and the exposure of workers to noise than 8 hours and determined the ordinance on measures and norms of protection at work against noise in work areas (Official Gazete of RS, No.101/05). The level of vibrations is determined as the impact of vibration on the whole body, a limit of daily exposure in the workplace in accordance with the time of exposure is 1.15m/s².

Determining the origin of chemical identification is carried out by taking at least one sample to the nearest source of workplace štetnosti.Vrednosti maximum allowable concentration exposure limits (WEL) are determined standards: SRPS Z.B0.001/91, or by measuring the maximum permissible concentrations of harmful gases, vapors and aerosols in atmosphere of working premises (JUS Z.BO 001 of 1991) and the Regulations on preventive measures for safe and healthy work when exposed to chemical substances (Official Gazette of RS, No. 106/09).

After examining the expert findings made by authorized organizations - institutes, we found that the organizations of the textile industry, in which the survey was conducted, there are jobs in which the parameter values due to increased working environment, in excess of the health and safety of workers at risk. Based on research in Table 1 and Figure 1 shows the values of the six parameters of the working environment, determined to sixteen different production sites in textile factories (measured at the time of controls), which are used in the further study of the working conditions. Measurements were carried out during the work and values are shown in black, and the maximum permissible value expressed in red.

Table 1: *The values of parameters of the textile organizations dealing with production and processing of Yarns*

No	Workplace	Microclimate T (C^0)	Physical hazards		Chemical harmfulness mg/m^3	The lighting Lx	Dangers that occur using work equipment
			Noise dB	Vibration m/s^2			
a1	**knitter in a knitting unit (smooth and rough knitting unit)**	25,1 *(28)*	71 *(85)*	0 *(1,15)*	a) 1,4 *(2)* b) 2,04 *(5)*	145 *(80-150)*	5 *(10)*
a2	**rough socks production**	25,1 *(28)*	80 *(85)*	0,6 *(1,15)*	a) 0,4 *(2)* b) 4,07 *(5)*	104 *(80-150)*	10 *(10)*
a3	**fine tighs production (tighs sewing machine)**	23,9 *(28)*	87 *(85)*	0,51 *(1,15)*	a) 0,4 *(2)* b) 4,03 *(5)*	105 *(80-150)*	10 *(10)*

a4	**tighs shaping (hand-fixing of tighs)**	25,5 *(28)*	79 *(85)*	0,51 *(1,15)*	a) 0,3 *(2)* b) 4,05 *(5)*	104 *(80-150)*	5 *(10)*
a5	**dyer (textile dyeing tub - open machine**	25,5 *(28)*	83 *(85)*	0,51 *(1,15)*	a) 1,7 *(2)* b) 4,01 *(5)*	102 *(80-150)*	5 *(10)*
a6	**fibre – production**	23,9 *(28)*	77 *(85)*	0 *(1,15)*	a) 1,0 *(2)* b) 4,05 *(5)*	105 *(80-150)*	5 *(10)*
a7	**finishing and packaging**	24,2 *(28)*	75 *(85)*	0 *(1,15)*	a) 0,3 *(2)* b) 4,01 *(5)*	103 *(80-150)*	5 *(10)*
a8	**tighs fixing-ironig**	25,0 *(28)*	93 *(85)*	0,6 *(1,15)*	a) 0,5 *(2)* b) 4,01 *(5)*	104 *(80-150)*	5 *(10)*
a9	**bowe machine operator (dyeing textile machine)**	25,5 *(28)*	70 *(85)*	0 *(1,15)*	a) 2,1 *(2)* b)1,4 *(5)*	147 *(80-150)*	7 *(10)*
a10	**thread net making**	25,0 *(28)*	77 *(85)*	0 *(1,15)*	a) 0,7 *(2)* b) 4,01 *(5)*	104 *(80-150)*	5 *(10)*
a11	**nitiworker winding rubber thread**	25,0 *(28)*	98 *(85)*	0 *(1,15)*	a) 0,9 *(2)* b) 4,02 *(5)*	103 *(80-150)*	5 *(10)*
a12	**dyeing-rewinding**	25,5 *(28)*	81 *(85)*	0 *(1,15)*	a) 1,7 *(2)* b) 4,03 *(5)*	103 *(80-150)*	5 *(10)*
a13	**the head of dyeing unit**	25,3 *(28)*	83 *(85)*	0 *(1,15)*	a) 2,03 *(2)* b) 1,4 *(5)*	146 *(80-150)*	7 *(10)*
a14	**laboratory worker**	25,5 *(28)*	77 *(85)*	0 *(1,15)*	a) 2,52 *(2)* b) 0,3 *(5)*	145 *(80-150)*	1 *(10)*
a15	**worker at dyeing and mercerising**	25,5 *(28)*	76 *(85)*	0 *(1,15)*	a) 2,03 *(2)* b) 4,1 *(5)*	13 *(80-150)*	1 *(10)*
a16	**laboratory technician**	25,5 *(28)*	70 *(85)*	0 *(1,15)*	a) 2,33 *(2)* b) 0,4 *(5)*	147 *(80-150)*	10 *(10)*

Based on the value of the microclimate and insight into professional findings we found that the temperature in all production plants, or in the workplace, in the winter in a comfort zone. The figure can be determined that the level of noise in the workplace fixing-board socks and wrap the rubber worker threads, the sign of the measured values at the time of control, exceeding the legally prescribed value, and the same can adversely affect the health of employees. It can be seen that the measured mechanical vibration, expressed as the impact of vibration on the whole body, as a potential threat to the health of employees do not exceed the standards established values, and emerge as a result of the work machine.

From enclosed can see that they are employed in the laboratory exposed to the harmful effects of substances used during the processing of the fabric and that the employees at the site operator Bowe machine (machine for dyeing fabrics - closed machines), in that part of the drive is exposed to higher concentrations chemical substances, due to the fumes, which can significantly affect their health by prolonged exposure of workers to harmful effects of this.

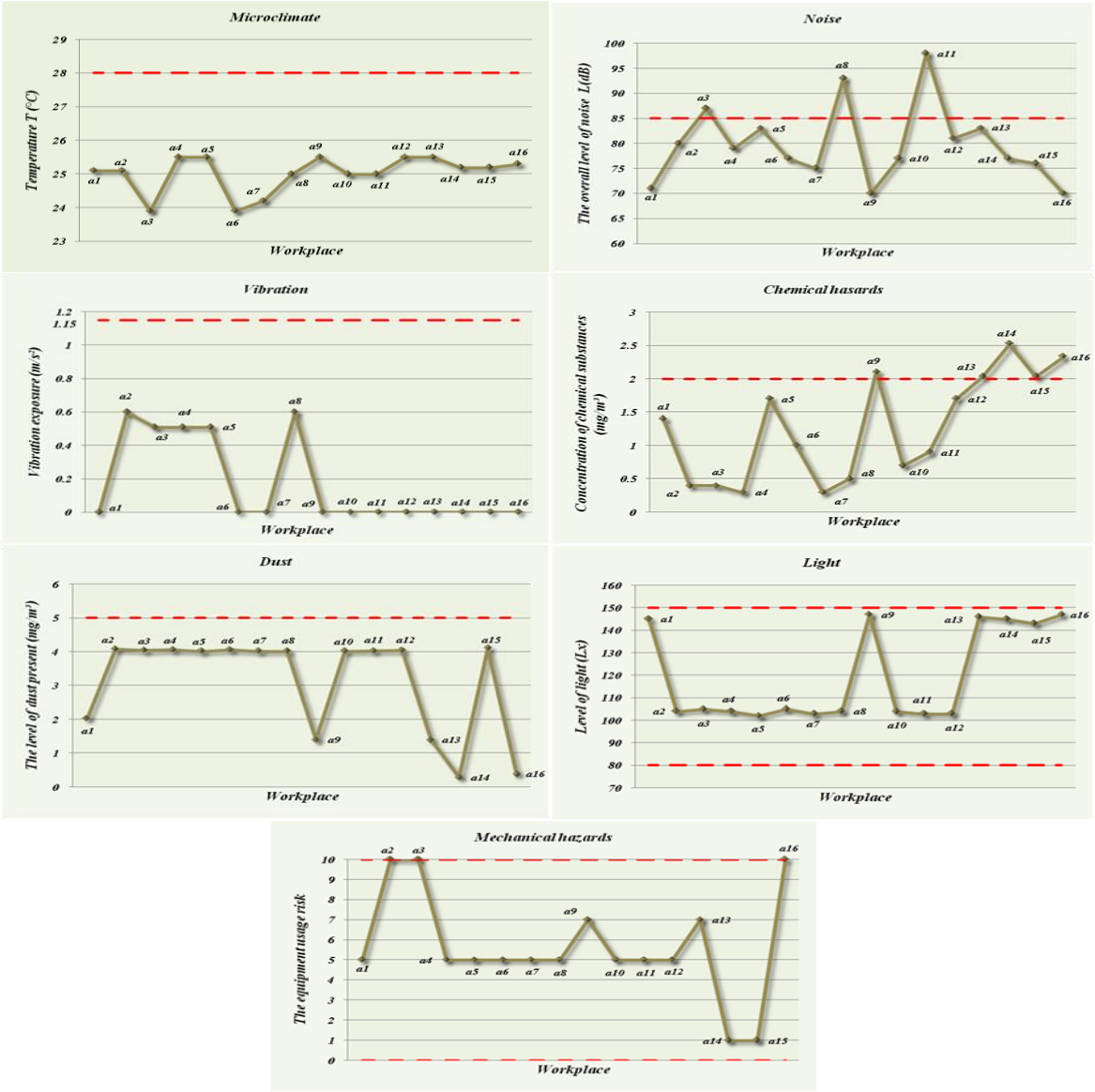


Fig. 1:*The values of the parameters of the working environment for the observed workplaces*

Values Measured light levels are shown in figure 1, the average value expressed in the unit Lx, and compared with the average values per standard requirements Repbulike Serbia. It can be seen that all the measured values are in the range 80-150 Lx. Based on practical research and explanations given by the persons responsible for safety and health at work, we have found that this is an important parameter of a healthy and normal functioning of the labor employed, and the removal of the measured values of the border is not favorable to the health of employees. In the manufacturing process of the textile industry due to the use of work equipment, complex production process and inappropriate or maladaptive methods can identify the mechanical hazards that occur in conjunction job characteristics [10]. The level of mechanical hazard is defined in the range of 0 to 10, and the table is displayed in red the maximum risk and severity of consequences for the employee. From enclosed can be determined that due to the lack of security due to the presence of

rotating or moving parts on the machine knitting confection fine and rough socks because "first flight" parts as well as free movement of parts or materials can be injured employee, and it can cause very serious consequences per employee. The level of serious consequences for the employee expressed an on-site technical laboratory to the realization of activities, performs the transfer of colors and products, but also to use complicated technical means, so that when the work may be falling objects.

3. CONCLUSIONS

In the manufacturing process of the textile industry due to the use of work equipment, complex production process and inappropriate or maladaptive methods can identify the mechanical hazards that occur in conjunction job characteristics. After examining the expert findings made by authorized organization - the Institute, it was found that the organizations of the textile industry in which the survey was conducted, there are jobs in which they are due to increased values of parameters of the working environment, in excess of the health and safety of workers at risk. From all the above it can be established that the individual workplaces values of parameters of the working environment exceed the maximum permitted legally prescribed value, and increased the value of the parameters can have negative consequences on the health and safety of employees in textile organizations. The data obtained will serve to further research to capture the jobs in textile factories in which there are potential threats to the health and safety of employees. The significance of these analyzes is a big primarily aimed at improving the working conditions, the preservation of the health of workers, increasing employee satisfaction and achieving better performance.

REFERENCES

[1] D. Torrington, L., Hall and S. Taylor, "*Menadžment ljudskih resursa"*, Data Status, Beograd. 2004.

[2] S.T. Akinyele, "*A critical assessment of environmental impact on workers productivity in Nigeria"*, Research Journal on Business Management. 1(1) 2007, 50-61.

[3] Y. Noah and M. Steve, *"Work environment and job attitude among employees in a Nigerian work organization"*, Journal of Sustainable Society, 1 (2), 2012, 36-43.

[4] N. Daud, *"Investigating the Relationship Between Quality of Work Life and Organizational Commitment Amongst Employees in Malaysian Firms",* International Journal of Business and Management, Vol: 5, No. 10. 2010.

[5] M. Rodrigues, P. Arezes and P.C. Leão, *"Risk criteria in occupational environments: critical overview and discussion".* Procedia-Social and Behavioral Sciences, 109, 2014, 257-262.

[6] A. Steidle and L. Werth, *"In the spotlight: Brightness increases self-awareness and reflective self regulation"*, Journal of Enviromental Psychology, 39, 2014, 40-50.

[7] M.T. Thompson, "*Intuitive Analog Circuit Design"*, Intuitive Analog Circuit Design, Newnes, USA, 2013, 617-643.

[8] R. Wolfgang and R. Burgess-Limerick, *"Using consumer electronic devices to estimate whole-body vibration exposure",* Journal of Occupational and Environmental Hygiene. 11(6) 2014, 77-81.

[9] F. Faramarzi, M.A.E. Farsangi and H. Mansouri, "*Simultaneous investigation of blast induced ground vibration and airblast effects on safety level of structures and human in surface blasting"*, International Journal of Mining Science and Technology, 24(5) 2014, 663-669.

[10] S. Urošević, V. Stefanović and D. Đorđević, "*Menadžment sistem zdravlja i bezbednosti na radu u tekstilnoj industriji"*, Tekstilna industrija, 62(4**)** 2015, 39-46.

The editors take no responsibility of the results, opinions and conclusion expressed in the published papers.