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THE EFFECTS OF BACKPACKS OF DIFFERENT STRUCTURES WITH DIFFERENT LOADS ON SHOULDER TO BACK PRESSURE IN PRIMARY SCHOOL STUDENTS

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INTRODUCTION

The backpack issue has aroused attention from all sectors of society. Unreasonable structure design of backpacks and overload might cause students vertebral, shoulder and back and musculoskeletal pain, and therefore impact the growth and development of students directly or indirectly [1, 2]. Investigation shows that back pain is very common among primary school students [3].

Among the current research studies, scholars have started to consider health problems caused by the process of carrying backpacks and have analyzed the impact of bag weight and the way of wearing it on the bodies of primary school students, including plantar pressure, angle of inclination of the body, muscle tone, etc. Based on test results, some papers suggested that the load of the backpack should be no more than 10% of human body weight [4], or 15% as critical

MOTS-CLÉS: sac à dos, charge, structure, pression sur les épaules et le dos, élèves de l'enseignement primaire

THE EFFECTS OF BACKPACKS OF DIFFERENT STRUCTURES WITH DIFFERENT LOADS ON SHOULDER TO BACK PRESSURE IN PRIMARY SCHOOL STUDENTS

ABSTRACT. The main purpose of this study was to evaluate the difference between soft and hard backpacks in pressure transmission effect and decompression with increased weight. mFLEX was used to measure shoulder to back pressure on 100 primary school students (male-female ratio 4:6) wearing different bag loads (equivalent to 5%, 10%, 15%, 20% and 25% of their body weights). Meanwhile, a comparative analysis test was done between backpacks of different structures (red backpack A with shoulder and back cushion design and regular yellow backpack B without shoulder and back cushion design). The conclusion is, along with the increase of backpack load, shoulder to back pressure value increased significantly, among them shoulder pressure value increased linearly, and back pressure value increased exponentially. Pressure values of the cushion bag (A) in three areas were all significantly larger than those of control bag (B). The results of the study are contrary to our hypothesis. Instead of effectively alleviating the concentration of pressure in three stress areas, left shoulder, right shoulder and lower back (LS, RS and LB), the buffer structure increases the pressure values. Therefore, in main pressure areas, we cannot simply rely on adding buffer structure to reduce the pressure generated by loading.

KEY WORDS: backpack, load, structure, shoulder-back pressure, primary school students

INFLUENȚA RUCSACURILOR CU DIFERITE STRUCTURI ŞI SARCINI ASUPRA PRESIUNII ÎN ZONA UMERILOR ŞI A SPATELUI LA ELEVII DE ȘCOALĂ PRIMARĂ

REZUMAT. Scopul principal al acestui studiu a fost acela de a evalua diferenţa dintre rucsacurile moi şi dure în ceea ce priveşte transmiterea presiunii şi decomprimarea odată cu creşterea greutăţii. S-a utilizat sistemul mFLEX pentru a măsura presiunea în zona umeri-spate la 100 de elevi de școală primară (raportul băieţi:fete de 4:6) purtând rucsacuri cu diferite funcţii (rucsac roşu A cu pernuţe în zona umerilor şi a spatei şi rucsacul B obişnuit, de culoare galbenă, fără pernuţe în aceste zone). Concluzia este că, odată cu creşterea greutăţii rucsacului, valoarea presiunii în zona umeri-spate a crescut în mod semnificativ; valoarea presiunii în zona umerilor a crescut liniar, iar valoarea presiunii în zona spatei a crescut exponenţial. Valorile presiunii în cazul rucsacului cu pernuţe (A) în trei regiuni au fost în mod semnificativ mai mari decât cele obţinute în cazul rucsacului de referinţă (B). Rezultatele studiului sunt contraire ipotezei noastre. În loc să atenuize în mod eficient presiunea concentrată în trei regiuni importante - umărul stâng, umărul drept şi zona lombară (LS, RS şi LB), structura tampon duce la creşterea valorilor presiunii. Prin urmare, în regiunile principale de presiune nu ne putem baza pe adăugarea unei structuri tampon pentru a reduce presiunea generată de greutate.

CUVÂNTE CHEIE: rucsac, sarcină, structură, presiune umăr-spate, elevi de școală primară

LES EFFETS DES SACS À DOS AUX STRUCTURES ET CHARGES DIFFÉRENTES SUR LA PRESSION À L’ÉPAULE ET AU DOS CHEZ LES ÉLÈVES DE L’ÉCOLE PRIMAIRE

RÉSUMÉ. Le but principal de cette étude a été d'évaluer la différence entre les sacs à dos souples et durs en ce qui concerne l'effet de transmission de la pression et la decompression avec le gain de poids. On a utilisé le système mFLEX pour mesurer la pression dans la région des épaules et du dos chez 100 élèves de l'enseignement primaire (rapport garçons-filles de 4:6) portant des sacs à dos aux charges différentes (équivalent à 5%, 10%, 15%, 20% et 25% de leur poids corporel). Dans le même temps, On a effectuée une analyse comparative entre des sacs à dos aux différentes structures (un sac à dos rouge A avec des coussins dans les régions des épaules et du dos et un sac à dos jaune régulier B sans coussins dans les régions des épaules et du dos). La conclusion est que, avec l'augmentation de la charge du sac à dos, la pression dans les régions des épaules et du dos a augmenté de façon significative; la pression sur les épaules a augmenté exponentiellement, et la pression sur le dos a augmenté exponentiellement. Les valeurs de pression du sac à dos ont été significativement plus grandes que celles du sac de référence (B). Les résultats de l'étude sont contraires à notre hypothèse. Au lieu d'atténuer efficacement la concentration de pression dans trois régions importantes, l’épaule gauche, l’épaule droite et la région lombaire (LS, RS et LB), la structure tampon augmente les valeurs de pression. Par conséquent, dans les régions principales de pression, nous ne pouvons pas simplement compter sur l’ajout d’une structure tampon pour réduire la pression générée par la charge.

MOTS-CLEFS: sac à dos, charge, structure, pression sur les épaules et le dos, élèves de l’enseignement primaire
safety value [5]. School bags with symmetrical design should be selected [6]. But there are few research studies on the impact of backpacks of different design structures on human biomechanical properties during walking. Marsh et al. [7] analyzed the impact of backpacks on posture in adolescents wearing backpacks with and without abdominal supports, Mackie et al. [8] used questionnaires to compare four different school backpacks from perspectives such as appearance and function; Ramadan et al. [9] modified a backpack design for male school children, and compared the effect of modification on parameters such as muscle tone and heartbeat. Reports on the effect of different bag structures on shoulder to back pressure value have not been found yet. But few have paid attention to the impact of bags on human shoulder to back pressure. A few papers have paid attention to the reason for shoulder to back pain in certain groups of people doing special jobs, such as pilots, and mechanic troops [10, 11], some researchers have used questionnaires to analyze lower back pain [12], but rarely used instruments to measure quantitatively shoulder to back pressure. Suozzi et al. [13] used a pressure meter to measure shoulder pressure and compare the changes in shoulder pressure, and tests showed that with the increase of angle of inclination, shoulder pressure also increased. Martin and Hooper [14] used Tekscan pressure sensor to measure shoulder pressure, and this method has been adopted by subsequent scholars. Jones and Hooper [15] compared the impact of single- or multiple-layered garments on shoulder pressure when wearing backpacks, and tests showed that the number of layers of garments had no impact on interface pressure. Mackie et al. [16] used a simulative backpack load to measure interface pressure on a model’s shoulders, and found out that load had significant impact on shoulder interface pressure. But there has been no paper to analyze the link between changes in shoulder to back pressure value and bag structure, as well as to analyze changes in back pressure value under different loadings. Meanwhile, there is a lack of research supporting how shoulder to back pressure in primary school students changes under the impact of both soft and hard bags with increased load weight.

Therefore, the main aim of the research is to evaluate the difference in pressure transmission effect and decompression between soft and hard bags with increased load weight. Our hypothesis is as follows: compared with hard bags, soft bags with cushion structures on the shoulder and back area have better decompression effect.

**METHODS**

Participants

Altogether 100 healthy children (age: 7-12; grade: 1-6) were recruited. Inclusion criteria were:

1. No foot operation history, no cerebral palsy;
2. Not suffering from scoliosis;
3. No foot injury;
4. Able to walk independently, normal gait.

Prior to the test, the staff communicated thoroughly with the guardians of subjects about the test flow and precautions, and written consents were obtained from them prior to data collection. All tests were approved by the local Ethics Committee, and were conducted according to the Declaration of Helsinki.

Test Bags

In the test, students wore two types of backpacks, the red backpack with honeycomb cushion structure on both shoulder and back areas (cushion bag (A), see Fig. 1a), and regular yellow backpack without honeycomb cushion structure on shoulder and back areas (control bag (B), see Fig. 1b).

Firstly, the load weight was determined by each subject’s body weight. Load weights were 5%, 10%, 15%, 20% and 25% of body weight respectively. In the test, subjects wore the school bag starting from 5% of body weight, increasing the load weight in order until reaching 25% of body weight.

Test Methods

The mFLEX pressure measuring system (mFlex, RSscan International, Belgium) was utilized to record the contact pressure between the body and the backpack. In total 24 pressure sensors were used, number 1-6 on the left shoulder, 7-12 on the right shoulder and 13-24 on the lower back. The area of pressure sensors is 0.96 cm² and the frequency is 5 Hz. Data partition was divided into three areas based on sensors’ positions: Left shoulder, Right shoulder and Lower back. Maximum pressure (mmHg) in each area needed to be calculated.
Prior to each test, strap length and sensor position are adjusted according to each primary school student’s body condition. Installation method of mFLEX pressure sensor in the test is shown in Fig. 1. Prior to the test, subjects walked across the test area at a self-preferred speed in natural gait for a 2-3 minute warm-up practice trial wearing the backpack equipped with sensor. Starting from formal collection of pressure data using mFLEX pressure distribution test system, subjects needed to be guided to wear bags of different loads to record pressure distribution on left and right shoulder and back during walking. Effective data of each load group needed to be collected successfully three times, each lasting 10 seconds, each time a total of 50 data points was collected. Interval between various bag loads was 1 min.

Data Processing and Statistical Analysis
Firstly 50 data points from each test were averaged, then three test data were averaged. All of the data were verified using 1-sample K-S test to check its normal distribution situation. Difference in cushion bag (A) and control bag (B) under different loading conditions was verified by paired samples. All analytical models of the research were performed using SPSS (V20, SPSS Inc., Chicago, USA), significance was defined as 0.05, confidence interval 95%.

RESULTS
Of 100 samples in the test, male-female ratio is 4:6, mean height 133±20.5 cm, mean weight 28.6±14.1 Kg. Subjects’ basic information is given in Table 1.

First the analysis of the impact of loading on test results, and the result of impact of loading on pressure value was shown in Fig. 2. With increased load weight, shoulder to back maximum pressure values of both bag A and B increased significantly. Among them, left shoulder maximum pressure value increased linearly along with the increase of load (cushion bag (A) R²=0.9963, control bag (B) R²=0.9909), right shoulder maximum pressure value

| Sample | 7yr | 8yr | 9yr | 10yr | 11yr | 12yr |
|--------|-----|-----|-----|------|------|------|
| Height/cm | 121±9 | 127±10 | 131±11 | 137±16 | 142±10 | 145±6 |
| Weight/kg | 22.0±6.4 | 27.8±12.6 | 27.3±11.2 | 30.5±11.4 | 32.0±9.7 | 34.7±7.6 |
| BMI | 14.9±3.6 | 16.9±6.3 | 15.9±4.1 | 16.2±5.3 | 15.9±2.8 | 16.5±2.7 |

Note: BMI, body mass index.
increased linearly along with the increase of load (cushion bag (A) $R^2=0.9956$, control bag (B) $R^2=0.9987$), back maximum pressure value increased exponentially along with the increase of load (cushion bag (A) $R^2=0.9910$, control bag (B) $R^2=0.9851$). Under most loading conditions, pressure values of the cushion bag (A) in 3 areas were all significantly larger than those of the control bag (B) (Table 2).

The data in the test does not comply with normal distribution, therefore all analytical models use non-parametric analytical model.

**DISCUSSION**

In the test, we did comparative analysis on the changes of pressure in areas LS, RS and LB of the cushion bag (A) and the control bag (B) with increased load weight, and the results showed that pressure values of the cushion bag (A) in three areas were all significantly larger than those of the control bag (B).

The results of this test is contrary to our hypothesis, as well as subverts people’s imagination of decompression structure of traditional bags. After analyzing the reasons, we believe that when a backpack is carried, LS, RS and LB form a structure of pressure in 3 areas, at this time a bag without cushion has larger contact surface with the human body, therefore the pressure is not high; but with the adding of decompression materials, e.g. sponge cushion, such as in the case of the cushion bag (A), on one hand this sponge cushion seems to have a buffer effect, in reality it reduces the contact surface of the bag to the body and the human body therefore concentrates the pressure, resulting in higher pressure. Therefore we believe that in backpack design, in the main pressure areas...
such as LS, RS and LB, we cannot simply rely on adding a buffer structure to alleviate the pressure generated by loading, instead we can alleviate the discomfort of loading by adjusting the center of gravity of the whole bag, increasing waist zone support, etc. Meanwhile, due to the lack of reports on similar tests, appropriate conditions and ranges need to be taken into consideration when comparing with other test results on backpack loading or bag structure design.

CONCLUSIONS

Instead of effectively alleviating the concentration of pressure in LS, RS and LB, the buffer structure increases the pressure values. Therefore, in the main pressure areas, we cannot simply rely on adding buffer structure to alleviate the pressure generated by loading, instead we can alleviate the discomfort of loading by adjusting the center of gravity of the whole bag, increasing waist area support, etc.

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THE INFLUENCE OF NEW PRESERVATION PRODUCTS ON VEGETABLE TANNED LEATHER FOR HERITAGE OBJECT RESTORATION

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INTRODUCTION

Cultural heritage is an infinite source of information of historical and anthropological value. By preserving this heritage we are giving back to society a glimpse to our history and transfer our traditions to future generation.

Traditionally, conservation and restoration work was considered an empirical, handicraft activity practiced by people with manual skills who passed secret techniques and materials on to younger generations. However, under the influence of modern theories on art history and the impact of technological and scientific revolution on social life, these interventions cannot be perceived today as a process of restoration; even if they met certain requirements regarding restoration, they were not a reflection of a scientific concept.

Conservation represents the full range of measures aimed at keeping the object in good condition and maximizing its life [1]. Conservation encompasses a vast series of operations that

ABSTRACT. The paper studied the effect of four materials for the preservation of collagen-based heritage objects. The products developed were applied to new leather samples tanned with vegetable tanning agents such as quebracho and mimosa, which were then subjected to accelerated ageing for 24, 48 and 72 hours, at the temperature of 50°C. The effects of the new environmentally-friendly materials applied to leather were assessed according to a characterisation protocol specific for preservation and restoration of collagen-based heritage objects. The effects of the new formulations on vegetable tanned leather were assessed using the characterisation protocol that includes physical-chemical and organoleptic analyses in terms of colour change, handle, uniform spread, hydrophobisation (resistance to water drop and penetration time). Colour change was determined and assessed using Datacolor CHECK II portable spectrophotometer, and CIEL*a*b* and CIEL*C*h software, obtaining chromatic coordinates for each leather sample treated with the studied formulations. Treatments have caused some changes in leather characteristics, depending on the product applied.

KEY WORDS: vegetable tanned leather, preservation, restoration.

INFLUENŢA UNOR NOI PRODUSE DE CONSERVARE ASUPRA PIEILOR TĂBĂCITE VEGETAL DESTINATE RESTAURĂRII OBIECTELOR DE PATRIMONIU

REZUMAT. În această lucrare a fost studiat efectul a patru materiale pentru conservarea obiectelor de patrimoniu pe suport colagen. Produsele elaborate au fost aplicate pe eșantioane de piei noi tăbăcite cu tanașii vegetali precum quebracho și mimoza, care apoi au fost supuse unui proces de îmbătrânire accelerată pentru 24, 48 și 72 de ore, la temperatura de 50°C. Evaluarea efectelor noilor materiale ecologice aplicate pe piei a fost efectuată cu ajutorul unui protocol de caracterizare specific domeniului conservării și restaurării obiectelor de patrimoniu pe suport colagenic. Evaluarea efectelor noilor recepții asupra pieilor tăbăcăți cu extracte tanante vegetale s-a realizat utilizând protocolul de caracterizare care cuprinde analize fizico-chimice și organoleptice privind modificările de culoare, tuseu, gradul de etalare, gradul de hidrofobilizare (rezistența la picătura de apă și timpul de pătrundere). De asemenea, determinarea și evaluarea modificărilor culorii s-a efectuat cu spectrototometrul portabil Datacolor CHECK II și cu sistemul software CIEL*a*b* și CIEL*C*h, obținându-se coordonatele cromatic ale culorii pentru fiecare probă de piele tratată cu recepturile studiate. Tratamentele efectuate au produs unele modificări ale caracteristicilor pieilor, în funcție de produsul aplicat.

CUVINTE CHEIE: piele tăbăcită vegetal, conservare, restaurare

L’INFLUENCE DE NOUVEAUX PRODUITS POUR LA CONSERVATION DES CUIRS AU TANNAGE VÉGÉTAL SUR LA RESTAURATION DES OBJETS DU PATRIMOINE

RÉSUMÉ. Dans ce travail, on a étudié l’effet de quatre matériaux pour la conservation des objets du patrimoine à base de collagène. Les produits développés ont été appliqués à des échantillons de cuir nouveau au tannage végétal tel que quebracho et mimoza, qui ont ensuite été soumis à un vieillissement accéléré de 24, 48 et 72 heures à 50°C. Les effets des nouveaux matériaux écologiques appliqués sur la peau ont été évalués selon un protocole de caractérisation spécifique pour la conservation et la restauration des objets du patrimoine à base de collagène. Les effets des nouvelles recettes sur le cuir tanné avec des extraits végétaux ont été évalués en utilisant le protocole de caractérisation qui inclut des analyses physico-chimiques et organoleptiques en ce qui concerne les changements de couleur, le toucher, l’étalage, le degré d’hydrophobisation (résistance à la goutte d’eau et le temps de pénétration). En outre, la détermination et l’évaluation du changement de couleur ont été réalisées avec le spectrophotomètre portable Datacolor CHECK II et le logiciel CIEL*a*b* et CIEL*C*h pour obtenir les coordonnées chromatiques de la couleur pour chaque échantillon de cuir traité avec les formulations étudiées. Les traitements ont produit des changements dans les caractéristiques du cuir, selon le produit appliqué.

MOTS-CLEFS: cuir tanné végétal, conservation, restauration
do not alter the appearance of the artifact but retain its original shape.

Preventive conservation is defined by the combination of measures and indirect actions that do not interact with the physical structure of the object in question and aim at preventing the factors involved in the mechanism of deterioration processes of the object.

Active conservation is directed to the object in question, interacts with the material structure and is meant to fight the effects of physical, chemical and biological degradation.

Despite increased interest in techniques to improve conservation and decontamination, leather and parchment artifacts are not always treated with due respect and are largely neglected also because of their less interesting appearance compared to other types of artifacts.

Collagen objects and artifacts are an essential part of archival and library collections, ethnographic and military collections, furniture collections, but also of natural sciences collections (paleozoology, ornithology, mammalogy, etc.). The intrinsic resistance of historical collagenous materials determined, on the one hand, minor restoration interventions over time, and special attention in terms of aggressiveness of substances and techniques used in conservation and restoration of such objects, sometimes with dramatic consequences. The study of deterioration mechanisms of these materials has been initiated very recently, both in European and in national studies [2-6], only in the last decade of the last century [7-8], but there are very few studies for validation of current substances, materials and protocols for conservation and restoration [9], still based on empirical knowledge, without a real scientific basis. Moreover, products for the conservation and restoration of collagen, especially leather and parchment, specified in the guidelines elaborated by the national institutions responsible for protecting cultural heritage [10, 11], are natural products (whose use has been perpetuated by tradition, but has not yet been validated by scientific methods) and synthetic substances (solvents, adhesives, insecticides and fungicides) created for the industry, which were adopted by restorers for lack of anything more appropriate or created specifically for their field.

The effect of conservation-restoration materials was analyzed in various specialized studies [12-16]. Rushdya Rabee Ali Hassan [15] evaluated the effect of linseed oil and glycerine emulsion for surface treatment on the chemical composition of archaeological leather samples, which were taken from a historical leather book cover. The samples were treated with a linseed oil emulsion (7 g glycerine, 20 ml linseed oil, 5 g cetyl alcohol, 5 g stearic acid, 100 ml distilled water) and were then visually evaluated, pH value was measured, thermal analysis (TGA) and infrared spectroscopy (FTIR) were used and physical-mechanical studies were conducted to determine structural and chemical differences between treated and untreated leather samples. Research has shown that there were no major changes in functional groups on the surface of leather, monitored by infrared spectroscopy; pH values showed that the emulsion led to improvements by reducing the acidity of the treated leather, also improving thermal and mechanical properties of treated samples.

Flavia Pinzari et al. [16] conducted a study of biodeterioration on a parchment representing an ancient manuscript. To observe the physical and chemical changes that occur in a parchment infested with bacteria and fungi, analyses (SEM-EDX) were performed and purple spots caused by bacterial attack were noticed.

In the paper “Evaluation of consolidants for the treatment of red rot on vegetable tanned leather: the search for a natural material alternative” [13], C.C. Mahony compares four consolidants: Cellugel, Klucel G with acrylic wax (SC6000), neri (consolidant extracted from aibika plant roots, traditionally used in the manufacturing of Japanese paper) and chitosan to assess their impact on vegetable tanned leather objects that had undergone red rot degradations (acid degradation of leather tanned with vegetable extracts, attacked by “red rot”). Compared to oxidative degradation of vegetable tanned leather, this acid degradation is much faster and more aggressive. Damaged leather shows low hydrothermal resistance and stability, acidity of the leather increases, often reaching pH values in the range of 3.0-4.0.

EXPERIMENTAL PART

Materials

In order to test new materials for the conservation of collagen-based heritage objects, new leathers were tanned with vegetable tanning agents such as quebracho and mimosa.

The effect of new formulations on leather
was assessed by characteristic physico-chemical and organoleptic methods.

Technological operations were performed in the pilot station of INCDTP-ICPI on goat skins of B category, in accordance with the technological principles of patent RO122098 (2007) - “Method for producing natural leather for heritage bookbinding”. The starting point for the preliminary study was patent 127958/2016 “Active and preventive conservation product for treating heritage leather” and four new compositions were developed for preventive conservation of collagen objects, presented in Table 1.

The developed products were applied to vegetable tanned goat skin samples which were then subjected to accelerated ageing for 24, 48 and 72 hours at 50°C.

As seen in Table 1, the four variants proposed are based on natural oils (cedar, wax), natural waxes (beeswax), natural fats (lanolin), emulsifiers, solvents/thinners (distilled water, hexane) protein components (hydrolyzed collagen) and essential oils (lavender, melilot, basil).

T1.1 and T1.2 products contain no water and were made by modern principles of treating old leather objects, using only natural ingredients to ensure both penetration of treatment into leather structure and good behavior over time.

T1.3 and T2 products are water-in-oil emulsions (have low water content) that were made for uniform spreading, dermal penetration and distribution of the greasing/emulsifying active substance in the substrate.

Fatty materials were selected taking into account both the HLB value (Hydrophil-Lipophil Balance) indicating material affinity to fat and water, and the surface electrical charge of the material to be treated (old leather objects).

In creating formulations for conservations, the principles of obtaining cationic, anionic, amphoteric and “multicharge” emulsions (combining compatible anionic and cationic oils) were taken into account.

**Characterisation Protocol**

The protocol for characterization and assessment of the effects of new environmentally-friendly materials applied on leather samples was carried out after accelerated ageing at different time intervals, namely 24, 48 and 72 hours.

This characterization protocol included the following:

- Assessment of grain handle;
- Uniform spreading/penetration of materials;
- Emulsification / softness;
- Hydrophobisation;
- The degree of colour change.

The compositions were applied by dabbing the leather samples (Fig. 1) and, after drying and ageing, tests were performed according to established protocol.

| Code variations recipes | T1.1 | T1.2 | T1.3 | T2 |
|-------------------------|------|------|------|----|
| Materials used          | Basic formulation: lanolin, cedar oil, beeswax, hexane, volatile oils (melilot, basil, lavender) | T1.1+15-25% hexane | T1.1+15-25% hexane, 2-4% emulsifier, 13-18% distilled water | lanolin, paraffin oil, collagen hydrolysate, wax, distilled water, triethanolamine |

Figure 1. Application of treatment to leather
RESULTS AND DISCUSSION

Organoleptic Assessment

To assess the degree of penetration, softening, spreading, uniformity, handle, and colour change were conducted at various time intervals, after 1, 2 and 3 days of ageing (Table 2).

Table 2: Assessment of penetration, softening, spreading, uniformity, handle and colour change of treated leather samples

| Treatment/Observations | T1.1 | T1.2 | T1.3 | T2 |
|------------------------|------|------|------|----|
| Initial                | Weak spreading, Moderate penetration, Sticky handle, Weak uniformity | Weak spreading, Moderate penetration, Sticky handle, Moderate uniformity | Good spreading, Moderate penetration, Sticky handle, Moderate uniformity | Very good spreading, Good penetration, Slightly greasy handle, Moderate uniformity |
| After 24 h             | Weak spreading, Moderate penetration, Sticky handle, Moderate uniformity | Weak spreading, Moderate penetration, Slightly sticky handle, Moderate uniformity | Good spreading, Moderate penetration, Slightly sticky handle, Moderate uniformity | Very good spreading, Good penetration, Dry handle, Good uniformity |
| After 48 h             | Moderate spreading, Moderate penetration, Good uniformity, Uniform handle, strongly waxy | Moderate spreading, Moderate penetration, Good uniformity, Uniform waxy handle | Good spreading, Moderate penetration, Good uniformity, Uniform waxy handle | Very good spreading, Good penetration, Good uniformity, Uniform slightly greasy handle |
| After 3 days           | Good spreading, Good penetration, Sticky handle, Good uniformity, Uniform waxy handle, Slightly intense colour | Good spreading, Moderate penetration, Slightly sticky handle, Good uniformity, Uniform waxy handle, Slightly intense colour | Good spreading, Moderate penetration, Slightly sticky handle, Good uniformity, Uniform slightly waxy handle, Very slightly intense colour | Very good spreading, Good penetration, Dry handle, Good uniformity, Exudate handle, but with powdery surface, Very slightly intense colour |

As Table 2 shows, organoleptic assessment (degree of penetration, softness, spreading, uniformity, handle and colour change) of the treated leather indicated that some treatments have produced changes in the characteristics of leathers. However, leather appearance was not altered in the case of T1.3 product composition, observing thus, the principles of conservation norms. This product can be successfully used in the conservation of heritage objects.

Assessment of the Hydrophobisation Degree

The degree of hydrophobisation was assessed using standard 221, STAS 8259/3-68, which refers to the method for determining the resistance of leather to the action of water droplets in order to measure penetration time, assess colour contrast between the control sample and treated samples using the greyscale and to assess the contrast between the portion where the water drop fell and the rest of the specimen, also using the greyscale. The tested leather samples were treated with the formulations T1.1, T1.2, T1.3 and T2 and aged at 50°C. The results are shown in Figure 2 and Table 3.

Table 3 shows that the most hydrophilic sample is T2, which fully absorbs water in 2 minutes, and hydrophobic samples are T1.1 and T1.3, with a water absorption time of 10-15 minutes. The best values for colour change after 24h were obtained for leather samples T1.1 and T1.3 tanned with mimosa and leather samples T1.2 and T1.3 tanned with quebracho, respectively. The most pronounced contrast between the control sample and the treated samples is best seen in sample T1.3.

Colour Determination and Assessment

In order to determine and assess colour, leathers were measured using a portable Datacolor CHECK II spectrophotometer, equipped with software for colour measurement [17-18]. Using CIEL*a*b* and CIEL*C*h dedicated software, chromaticity coordinates were obtained for each leather sample.

The significance of the parameters is as follows:

- $L^*$ represents the lightness, the maximum value for $L^*$ is 100 (perfect white), while the minimum is 0 (perfect black);
THE INFLUENCE OF NEW PRESERVATION PRODUCTS ON VEGETABLE TANNED LEATHER FOR HERITAGE OBJECT RESTORATION

CONCLUSIONS

Leather conservation is a constantly changing area as new methods of research and evaluation of artifacts are developed. This research illustrates the difficulties specialists in the field are facing and the need to find new suitable materials for conservation of heritage leather objects.

Developing environmentally-friendly products for conservation and restoration of historical collagenous materials will enable a substantial reduction in exposure to risk factors for workers and the environment, limiting or eliminating the use of mixtures of chemicals responsible for possible toxic or carcinogenic effects.

As a result of experiments to obtain and use new formulations for the conservation and

Table 3. Hydrophobisation degree assessment tests

| Treatment/Characteristics                                      | Reference | T1.1 | T1.2 | T1.3 | T2 | /UM |
|---------------------------------------------------------------|-----------|------|------|------|----|-----|
| Leather tanned with mimosa extract                            |           |      |      |      |    |     |
| Penetration time (STAS 8259/3-68)                             | 1         | 15   | 10   | 4    | 2  | min |
| Initial colour change, contrast between control sample and treated samples | -         | 2    | 2    | 1/2  | 2/3| Marks |
| Colour change after 24 h, contrast between drop mark and the rest of the sample | 3         | 4/5  | 4    | 4/5  | 4  | Marks |
| Leather tanned with quebracho extract                         | 2.5       | 9    | 10   | 5    | 1,5| min |
| Penetration time (STAS 8259/3-68)                             | -         | 3/4  | 2/3  | 1    | 4  | Marks |
| Initial colour change, contrast between control sample and treated samples | 4/5       | 3    | 4/5  | 3/4  | 3/4| Marks |
| Colour change after 24 h, contrast between drop mark and the rest of the sample |           |      |      |      |    |     |

- \( a^* \) represents the shade between green (-\( a^* \)) and red (+\( a^* \));
- the negative value of \( b^* \) is blue, while the positive one, yellow;
- \( C^* \) (chroma) provides clues on purity (higher values) or complexity (lower values) of the mixture;
- \( h \) is the hue angle, reflects the proportion of the chromatic components \( a^* \) and \( b^* \).

As Figures 3-4 show, values have a linear direction without significant changes, although the decrease of parameter \( L^* \) and increase of \( a^* \) indicate a slightly darker shade, particularly of leather treated with the formulation T1.1.
Figure 3. Colour parameters for mimosa-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)

Figure 4. Colour parameters for quebracho-tanned leather - treatment T1.1 (a), T1.2 (b), T1.3 (c) and T2 (d)
restoration of collagen-based heritage objects the following were found:

- The proposed formulations meet the requirements of national conservation and restoration standards;
- Four variants of formulations were developed and tested (T1.1, T1.2, T1.3, T2) based on oils, natural waxes and fats, with the addition of emulsifiers, solvents, volatile oils, and protein components;
- T1.1 and T1.2 variants do not contain water;
- T1.3 and T2 variants are water-in-oil emulsions with low water content;
- All of the proposed formulation variants can be categorized as eco-friendly;
- The effects of the new formulations on leather tanned with vegetable tanning extracts were assessed using a characterization protocol that includes physical-chemical and organoleptic analyses regarding the colour changes, handle, uniform spreading, hydrophobisation degree (resistance to water droplets and time penetration). Also, colour change was determined and assessed using the portable Datacolor CHECK II spectrophotometer and CIEL*a*b* and CIEL*C*h software, yielding chromaticity coordinates of colour for every leather sample treated with the studied formulations.
- After applying the characterization protocol, T1.3 was found the best variant for the conservation of heritage leather objects.

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SUPPLIER INVOLVEMENT IN NEW PRODUCT DEVELOPMENT: A STUDY IN THE BRAZILIAN FOOTWEAR INDUSTRY

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ABSTRACT. The supplier involvement in the New Product Development (NPD) has become an important contribution to the solution of problems, which causes the process to be faster and more productive. However, it is still difficult to manage the supplier involvement during the NPD process. This study evaluates benefits and success factors of the supplier involvement during the process of NPD among three companies from the footwear industry in Sinos Valley/Brazil. The method developed indicates which items must be implemented as common objectives between company and supplier, as well as the most influential points for the success of the partnership. The results present an array of opportunities for the improvement of the partnership between company and suppliers.

KEY WORDS: success factors, Sinos Valley, supply chain management

INTRODUCTION

The efficient integration of competences and resources between companies has become a requirement in order to compete in a globalized economy [1]. At first, such integration activities were centered in the agility of product delivery, in the quality guarantee during production, in logistics and in cost reduction. However, given the fact that these issues tend to be standardized, the focus shifted on to New Product Development (NPD), mainly to the relations that the company establishes with its suppliers [2-4]. Therefore, the reduction in product lifecycles and the competitive pressures caused by technology update also lead the company to integrate both clients and suppliers, especially as a way to add value to its supply chain [5].

There is still a growing participation of suppliers in the company results, mainly because the purchase of raw materials determines an estimate of 50% of its cost [6, 7]. Moreover, more than 70% of the final cost in the world automotive industry is generated by the suppliers [8]. In addition to the pressures for cost reduction made by the manufacturers on their suppliers, which varies from 5 to 8% a year, the continuous improvement of product quality and the reduction in time development demand...
The supplier involvement in the NPD has become an important contribution to the solution of problems, which causes the process to be faster and more productive [6, 7]. However, it has not yet been made clear how and when it is appropriate to cooperate with the suppliers during the development process [10-12], this issue being one of the most important areas to be developed within the scope of NPD [13]. Recent studies have brought little understanding on how the suppliers should contribute to the process as well as the aspects to ensure the positive results for such relationship [14, 15].

Therefore, this study evaluates benefits and success factors of the relationship between company and supplier during the process of NPD. This contribution starts with the identification and measurement of the importance of all benefits as well as the success factors that influence the performance of a cooperative relationship with the supplier during NPD. In order to carry out this study, three companies from the footwear sector in Brazil have been selected along with their most strategic suppliers for the establishment of such partnership.

Brazil is the third largest footwear manufacturer in the world after China and India and the sixth among the largest exporters [16]. The Brazilian footwear cluster of the Sinos Valley was chosen because it is a showcase for successful integrations into global chains from a developing country [17, 18]. Therefore, this case is based also on the depth of the cooperation between companies and their suppliers [16, 19].

BENEFITS AND THE SUCCESS FACTORS OF THE COOPERATIVE RELATIONSHIP WITH THE SUPPLIER DURING NPD

The benefits and the success factors that match the performance of the cooperative process have been researched in order to provide a better NPD cooperative performance between companies and their suppliers. Such benefits and factors have been classified according to the subsystems that make up the social-technical system [20]. These authors regarded sociotechnical systems as subdivided into four interrelated subsystems: personnel, technological, work design and external environment. In this study, the social-technical system approach is used to classify the issues related to the work system between the company and its suppliers, more specifically to the cooperative relationship during NPD.

Technological Subsystem

Among the subsystems that make up the social-technical system, the technological one aims to identify the way in which technology influences the organizations’ work system [20]. In this study, the issues related to the technological development as well as the tools used during the cooperative relationship with the supplier in NPD are classified (Table 1).

Personal Subsystem

This subsystem focuses on the influences by which the work system participants’ characteristics and qualification determine the result of the project. According to Pasmore [45], this is the subsystem that allows the creation, modification and the improvements within the organization, because human beings are the sources for adaptation, innovation, idealization and inspiration inside the organization. Thus, the issues towards the agents’ qualification and knowledge who take part of the cooperation are grouped in the personal subsystem (Table 2).

External Environment Subsystem

Being an open system, the social-technical one holds a close relationship with the environment in which it is inserted through a constant exchange of information and influences. Therefore, the organization depends on its capacity to adapt to the external context constantly in addition to the monitoring of the environment as to provide the necessary adjustments to these modifications [20]. According to Pasmore [45], the influences the organization receives from the external environment can be classified within the external environment subsystem as follows: governmental, regulatory, ecological, logistic, commercial, financial, among others (Table 3).

Work Project Subsystem

As stated by Hendrik and Kleiner [20], the variables the other three subsystems comprise (technological, personal, and external environment) exert influences upon themselves and upon work structure, considering that the work design subsystem is capable of interacting with the variables in the other subsystems in
order for the company to achieve better results. In this study, the issues related to the procedures used in the cooperation with the supplier during NPD are grouped in the work design subsystem (Table 4).

The benefits and the success factors mentioned in the references were used to develop a close-end questionnaire in order to identify the importance of company’s perception and its strategic suppliers in relation to each benefit and success factor. The classification of these questions in the subsystems of the socio-technical system allows the comprehensive identification of the subsystems that exert greater

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### Table 1: Benefits and success factors classified in the technological subsystem

| Benefits of the cooperation | References |
|-----------------------------|------------|
| B1  Increase the number of patents | [21] |
| B2  Improve product quality    | [2, 5-8, 22-37] |
| B3  Develop better manufacturing | [31, 38] |
| B4  Product cost reduction     | [6-8, 25, 28, 30-32, 34-37, 39, 40] |
| B5  Process cost reduction     | [6, 8, 25, 28, 30, 32, 34-36, 39, 40] |

| Success Factors of the cooperation | References |
|------------------------------------|------------|
| S1  Supplier’s component costs in the product final value | [34, 41] |
| S2  Product greater complexity     | [5, 33, 42] |
| S3  Use of FMEA and QFD with the supplier | [32, 42] |
| S4  Use of DFDM and DFA with the supplier | [32, 42] |
| S5  Use of a supplier’s ranking system | [6, 23, 24, 31, 32, 44] |
| S6  CAD/CAE compatible systems     | [6, 31, 34, 44] |

### Table 2: Benefits and success factors classified in the personal subsystem

| Benefits of the cooperation | References |
|-----------------------------|------------|
| B6  Learning opportunities in the cooperation | [46] |
| B7  Increase the supplier’s motivation | [32] |
| B8  Access to competences and knowledge | [7, 8, 24, 29, 31, 32, 36, 46, 48-55] |
| B9  Innovation source        | [7, 11, 29, 34, 36, 46, 48, 52, 54] |
| B10 Development time reduction | [7, 22, 23, 25, 27-30, 32-36, 39, 52, 54] |

| Success factors of the cooperation | References |
|------------------------------------|------------|
| S7  Suppliers’ knowledge/technology | [7, 23, 40, 43, 56] |
| S8  Cultural similarity            | [22, 23, 29, 49, 57] |
| S9  Information/control of the supplier’s operations | [35, 52] |
| S10 Use of Guest engineers         | [3, 23, 35] |
| S11 Low Asymmetric Information between Companies | [50, 51] |

### Table 3: Benefits and success factors classified in the external environment subsystem

| Benefits of the cooperation | References |
|-----------------------------|------------|
| B11 Joint investments in R&D  | [24, 36] |
| B12 Comply with environmental and governmental rules | [7] |
| B13 Reduction of risk/uncertainty in NPD | [7, 24, 31, 36, 47, 48, 52, 58] |

| Success factors of the cooperation | References |
|------------------------------------|------------|
| S12 Low differences between company sizes | [34] |
| S13 Low uncertainty of environment | [7, 24, 31, 50, 56] |
| S14 Type of relationship governance | [11, 24, 46, 59] |
| S15 High integration of the production chain | [34, 59] |
| S16 Confidence in the supplier’s performance | [7, 31] |
| S17 Low risk of loss of copyright  | [52] |
| S18 Low pressure for cost reduction | [24, 25, 27, 35, 60] |
Table 4: Benefits and success factors classified in the work project subsystem

| Benefits of the cooperation | References |
|----------------------------|------------|
| B14 Workload decrease in DP | [8, 23, 30, 61] |
| B15 Flexibility in NPD | [7, 22, 23] |

| Success factors of the cooperation | References |
|-----------------------------------|------------|
| S19 Physical proximity | [27, 34] |
| S20 Relationship with a few suppliers | [3, 7, 24, 25, 29, 43, 46, 50, 60] |
| S21 Long-term relationship with the supplier | [7, 24, 25, 27, 29, 46, 51, 53, 60, 61] |
| S22 High flow of information exchange | [5, 24, 28, 31, 34, 35, 52, 56, 61] |
| S23 Communication with direct contacts | [27, 52] |
| S24 Informal meeting for the Exchange of information | [24, 64] |
| S25 Managing the cooperation between client and supplier | [6, 26, 36] |
| S26 Integration of the project team | [6, 23, 24, 26, 28, 34, 36, 39, 42, 49, 56, 61, 63, 64] |
| S27 Articulate common goals and objectives | [7, 31, 52, 65] |
| S28 Moment when the supplier must cooperate in NPD | [7, 13, 22, 43, 66] |
| S29 Company’s internal integration | [65] |
| S30 No use of poor communication | [27, 28, 52] |
| S31 Frequent communication | [22, 38] |
| S32 Use of Concurrent engineering | [28, 32] |
| S33 Increase of NPD complexity with supplier participation | [28, 51] |
| S34 Possibility of cooperation inefficiency | [58, 21] |
| S35 Information dispersion | [28, 50] |

RESEARCH METHOD

The multiple-case study method with a theoretical replication [67] was due to the diversity of shoe companies in Sinos Valley, Brazil and to the lack of similar studies about this sector. Three companies were selected, and their size was used as the criterion for the differentiation between them. For the company case study, interviews with product and supply chain manager were used which also identify the suppliers that already develop any sort of cooperative relationship with the company during its NPD. Subsequently, part of the analysis developed in the company is also replicated in the identified suppliers, which completes the company study. The case study format both in the company and in its respective suppliers is illustrated in Figure 1.

A close-end questionnaire has been applied in order to measure the importance of benefits and success factors for the cooperative relationship between client and supplier during NPD, pointing out each benefit and success factor identified in the referenced literature (Tables 1-4). Respondents are then invited to express their opinions on each benefit and success factor through a 15 cm continuous assessment scale, as proposed by Stone et al. [68]. The intensity of each response may vary between 0 and 15.
SUPPLIER INVOLVEMENT IN NEW PRODUCT DEVELOPMENT: A STUDY IN THE BRAZILIAN FOOTWEAR INDUSTRY

The analysis of the data collected from questionnaire follows three phases: questionnaire reliability, intra-group analysis and performance of subsystems. In the first phase, the analysis of the questionnaire reliability was carried out through Cronbach’s alpha [69, 70], which aims to evaluate the questionnaire internal reliability.

As a means of identifying the tendency towards the difference or the similarity between the company’s and its suppliers’ answers, the intra-group analysis, it has been developed a descriptive statistics method made up of three phases: i) calculate the mean between each company’s suppliers, ii) for each question compare the difference in module between the suppliers’ mean and the company’s answers; iii) calculate the quartiles for the difference result of the company’s answers in module and the suppliers’ questions mean. The result is the identification of 25% of the greatest and the smallest differences between the company’s answers to each question and the suppliers’ mean, that is, the questions where it is possible to identify a greater agreement and disagreement tendency between the company’s opinion and its suppliers’.

RESULTS

Both Company A (small size) and Company C (big size) exclusively produce women’s shoes, whereas Company B (medium size) mainly produces children’s shoes but also women’s and sports shoes in smaller quantities. All companies only trade their products using their own brands, and Companies A (small) and C (big) own only one brand. Company B (medium) owns seven different brands, and it happens because this company is a branch of a bigger and older textile group, which has the legal rights. The characterization of these three companies is illustrated in Table 5.

| Company A (small size) | Company B (medium size) | Company C (big size) |
|------------------------|-------------------------|----------------------|
| Daily production       | 1300 pairs/day          | 45000 pairs/day      |
| Number of employees    | 40 employees            | 2500 employees       |
| Start of activities    | 1998                    | 1955                 |
| Main product           | Feminine                | Feminine             |
| Materials most used in the upper | Leather, Polyurethane (PU) and Polyvinyl chloride (PVC) | Polyvinyl chloride (PVC) and cloth |
| Materials most used in the outsole | Polyurethane (PU) and Polyvinyl chloride (PVC) | Polyurethane (PU) |

The third phase, the performance of subsystems (technological, personal, external environment and work design) seeks to identify the subsystems exerting the greater influence upon the performance of the cooperative relationship between company and supplier during NPD. In order to identify the significant differences in the importance of the questions inserted in each subsystem, the Analysis of Variance (ANOVA) has been used. In case the tendency towards the influence difference of subsystems in the benefits or success factors is found, the multiple comparison test (LSD) is applied in order to identify which subsystems tend to exert greater influence upon the benefits and the success factors.

Table 5: Characterization of the three companies

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RESULTS

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Company A (small size) identified three suppliers as potential partners in order to establish a cooperative relationship during NPD, and these suppliers have maintained a relationship with the company since the start of the activities. Moreover, they are located near the company and have similar number of employees. Company B selected four suppliers to take part in the research, which have also maintained a relationship with the company since the start of the activities. The selected suppliers are located in Sinos Valley and have fewer employees than the company. Company C (big size) selected three suppliers, which are located in Sinos Valley and have a varied number of employees.
of employees, being greater than the company in one case. The description of the raw materials the selected suppliers deliver as well as the start of the activities with the company are represented in Table 6.

| Suppliers  | Company A (small size) | Company B (medium size) | Company C (big size) |
|------------|------------------------|-------------------------|----------------------|
| Raw material Start | Raw material Start | Raw material Start |
| Packaging 1999 | Components 2000 | Chemicals 1992 |
| PU Outsoles 1999 | Fabrics 2000 | Outsoles 1992 |
| Components 1999 | Liners 2000 | Liners 1994 |
| Components 2000 |

The amplitude of the inter-quartile difference between the company’s answers and its suppliers’ indicates, in a broader way, a tendency towards a greater agreement or disagreement in relation to the importance of the benefits and the success factors of the cooperative relationship. In this sense, Company B (medium size) is the one with a greater tendency towards the agreement in relation to the importance of the benefits of the supplier involvement during NPD (Figure 2), precisely the company from which it was possible to raise more evidence of a cooperative relationship with its suppliers. However, regarding the success factors, this measure indicates that Company B (medium size) is the one tending to greater disagreement with its suppliers, which points to a greater diversity in the way to achieve the success in the supplier involvement, as it can be observed in the dispersion graph illustrated in Figure 3.

Table 6: Suppliers the companies selected to take part in the study

| Suppliers | Company A (small size) | Company B (medium size) | Company C (big size) |
|-----------|------------------------|-------------------------|----------------------|
| Raw material Start | Raw material Start | Raw material Start |
| Packaging 1999 | Components 2000 | Chemicals 1992 |
| PU Outsoles 1999 | Fabrics 2000 | Outsoles 1992 |
| Components 1999 | Liners 2000 | Liners 1994 |
| Components 2000 |

Questionnaire Reliability

The answers of the questionnaire have been submitted to a reliability test, which have been well interpreted both by the three companies and by their respective suppliers. This can be verified through a Cronbach alpha greater than 0.6, which according to Hair Jr. et al. [70] represents the acceptable coefficient for exploratory research (Table 7).

Table 7: Cronbach alpha coefficients for the questionnaire

| N | Benefits of the supplier involvement | Success factors of the supplier involvement |
|---|-------------------------------------|---------------------------------------------|
| 13 | 0.932 | 0.699 |

Intra-Group Analysis

The result of the descriptive statistics method proposed for the interpretation of the data collected from the companies’ and their suppliers’ answers related to the importance of the questions raised in the literature is illustrated in Table 8.

Table 8: Difference between the company’s answers and its suppliers’ separated in quartiles

| Benefits of the supplier involvement | Valid Questions | Quartile |
|-------------------------------------|----------------|----------|
| Company A and suppliers 15 | 1.4807 | 5.4240 | 3.9433 |
| Company B and suppliers 15 | 1.2693 | 2.3000 | 1.0307 |
| Company C and suppliers 15 | 2.3243 | 4.6875 | 2.3632 |

| Success factors of the supplier involvement | Valid Questions | Quartile |
|---------------------------------------------|----------------|----------|
| Company A and suppliers 36 | 0.9133 | 3.7647 | 2.4606 |
| Company B and suppliers 36 | 0.8066 | 5.1271 | 5.9337 |
| Company C and suppliers 36 | 0.9228 | 4.6875 | 3.7647 |
To the benefits of the supplier involvement, the questions where it can be seen the tendency towards disagreement between company and supplier contribute as to diagnose the company’s and its supplier’s frame of mind. In questions where a greater tendency to agreement (Q1) can be found as well as a greater qualification than the average score, it is recommended that these should be used as potential benefits for the company and its suppliers in the establishment of the cooperative relationship during NPD. The tendencies towards the agreement and the disagreement between company and its suppliers in the questions regarding the benefits of the cooperation are presented in Table 9.

In Company A (small size), the suppliers develop, almost independently, all the components for the company products, and its work consists of adapting the products to fashion tendencies. This company’s behavior contributes to the understanding of the tendency towards disagreement regarding the workload decrease in NPD (B14) and the possibility of joint investments in R&D (B11). Among the questions that tend to agreement, patent development (B1) and reduction of risk in NPD (B13) are points that should be approached as possibilities of gain in the cooperative relationship. However, the possibility of flexibility in NPD (B15), despite the tendency towards agreement between company and suppliers, its qualification did not reach the minimum score of 7.5 in order to be included as an agreement objective for the relationship.

Company B (medium size) is, among the studied companies, the one that is more open to innovation and to the development of technologies for its products. However, a tendency has been found towards disagreement between its suppliers regarding the joint investments in R&D (B11), in spite of representing an opportunity for development of new materials and techniques [24, 36]. Process cost reduction (B4), development time (B10) and innovation source (B9) are among the questions where there is the tendency towards agreement between company and supplier and can be considered as common objectives.

Company C (big size), as well as the small size company, is also more directed to following fashion tendencies. Nevertheless, it has a much more developed structure, which is able to carry out tests and to develop some components and raw materials. This greater independence contributes to the understanding of the tendency towards disagreement with its suppliers regarding questions about process
cost reduction (B4), product (B5), and the risk in NPD (B13). Among the questions that should be approached as possibilities of gain from the supplier involvement during NPD, are development of new product manufacturing (B3), access to knowledge (B8), development time reduction (B10) and the possibility of more flexibility in NPD (B15).

Regarding the success factors of the supplier involvement, the questions that show greater disagreement between company and supplier can also be used as a way to diagnose the cooperation with its suppliers, whereas the ones indicating greater tendency to agreement, since all have an average score greater than 7.5, can be used as opportunities of improving the supplier involvement cooperation in NPD. Both the tendencies towards agreement and disagreement regarding the success factors are illustrated in Table 10.

In Company A (small size), the tendency towards agreement comprises mainly questions related to communication (S24, S25, S31, S32) and, indirectly, the long-term relationship with supplier (S22), which according to Ward et al. [61], positively contributes to the communication between company and supplier during NPD. Thus Company A (small size) should prioritize the improvements related to the communication with its suppliers in order to better the performance of its relationship with them during NPD. Since the company does not have more sophisticated mechanisms for the exchange of information with its suppliers, and its communication consists mainly of visits of commercial representatives and the requests for the purchase of raw materials, the implementation of projects focused on the establishment of procedures during the contact between companies, the frequency of these contacts, its quality in addition to better retaining the suppliers, represent potential possibilities of improvement in the supplier involvement during NPD.

In Company B (medium size), there is a greater variety between the success factors that tend towards the agreement between company and supplier. Generally speaking, a predominance of questions regarding NPD (S4, S29, S30) has been found. Despite the fact that the company already uses a suppliers’ qualification system, such system does not comprise questions related to NPD. The inclusion of these questions could contribute to improvements in the identification of the moment when the suppliers should take part in the process and in the identification of technologies the supplier has in order to add value to the product. In the questions related to communication, there is also the tendency towards agreement between company and its suppliers (S25,S32). In this case, granting the suppliers access to the existing information...
management system during NPD, besides projects allowing a greater integration with its partners, such as joint training courses to the company’s and suppliers’ development team. The other questions where tendency towards agreement can be found are directed to relationship risk reduction (S14, S15). In this sense, setting more complete contracts and showing the supplier the planning of cooperation activities and objectives contribute to some better understanding of the relationship and a gradual risk reduction. The long-term relationship with suppliers also represents an alternative to increase the supplier’s confidence when it comes to keeping the partnership [24].

In Company C (big size), a tendency has been found towards agreement with the success factors related to NPD (S2, S6, S7, S33, S35). Given the fact that a company’s product development is a fairly restricted process even to employees, not to mention to suppliers, opening this process to key suppliers could help foster participation. Setting a system of hierarchy and selection of suppliers, which includes in its assessment the capacity to cooperate during NPD would contribute for the company to consider the supplier’s technology, as well as the use of compatible mechanisms, such as CAD/CAE, in addition to minimizing the chances of failure of the relationship. The other success factors where there is a tendency towards agreement are directed to the integration between companies (S11, S16, S20). In this sense, the company’s capacity to conduct the majority of activities internally, reduces the suppliers’ participation in the process. However, projects that intensify the relations between companies, such as the exchange of technical information, the practice of guest engineers, as well as the intensification of the relationship with local suppliers would

| Success factors of the supplier involvement | Companies and their suppliers | Company A | Company B | Company C |
|--------------------------------------------|------------------------------|-----------|-----------|-----------|
| S1-Supplier’s component costs in the product final value | 3.646 | 3.695 | 3.335 |
| S2-Product greater complexity | 1.911 | 2.100 | 0.903 |
| S3-Use of FMEA and QFD with supplier | 1.045 | 3.450 | 1.220 |
| S4-Use of DFM and DFA with supplier | 1.755 | 0.702 | 1.467 |
| S5-Use of suppliers’ ranking system | 1.150 | 4.734 | 1.770 |
| S6-CAD/CAE compatible systems | 0.752 | 3.398 | 0.331 |
| S7-Suppliers’ knowledge/technology | 1.650 | 0.537 | 0.273 |
| S8-Cultural similarity | 2.210 | 2.998 | 0.929 |
| S9-Information/control of the supplier’s operations | 6.266 | 6.633 | 1.071 |
| S10-Use of guest engineers | 3.847 | 3.562 | 0.314 |
| S11-Low asymmetric information between companies | 0.549 | 2.620 | 1.326 |
| S12-Low differences between company size | 3.040 | 1.457 | 1.815 |
| S13-Low uncertainty of environment | 1.786 | 0.762 | 1.190 |
| S14-Type of relationship governance | 0.546 | 0.336 | 2.721 |
| S15-High integration of the supply chain | 1.985 | 2.014 | 0.323 |
| S16-Confidence in the supplier’s performance | 0.194 | 0.939 | 1.149 |
| S17-Low risk of loss of copyright | 2.185 | 9.618 | 6.707 |
| S18-Low pressure for cost reduction | 2.709 | 9.674 | 9.836 |
| S19-Physical proximity | 1.143 | 5.825 | 0.127 |
| S20-Relationship with a few suppliers | 5.359 | 7.363 | 1.731 |
| S21-Long-term relationship with the supplier | 0.224 | 0.236 | 0.982 |
| S22-High flow of information exchange | 1.014 | 1.096 | 1.448 |
| S23-Communication with direct contacts | 0.154 | 1.103 | 5.164 |
| S24-Informal meeting for the exchange of information | 0.823 | 0.561 | 8.678 |
| S25-Managing the cooperation between client and supplier | 1.414 | 2.833 | 7.333 |
| S26-Integration of the project team | 1.394 | 2.161 | 6.397 |
| S27-Articulate common goals and objectives | 3.804 | 1.877 | 3.763 |
| S28-Moment when the supplier must cooperate in NPD | 1.004 | 0.762 | 6.363 |
| S29-Company’s internal integration | 3.308 | 0.566 | 2.697 |
| S30-No use of poor communication | 0.540 | 2.907 | 2.035 |
| S31-Frequent communication | 0.219 | 0.143 | 3.774 |
| S32-Use of concurrent engineering | 1.432 | 1.916 | 0.730 |
| S33-Increase of NPD complexity with supplier participation | 1.876 | 6.962 | 2.707 |
| S34-Possibility of cooperation inefficiency | 4.762 | 7.155 | 0.204 |
| S35-Information dispersion | 1.531 | 6.572 | 4.303 |

Company and supplier tend to disagree (Q3)
Company and supplier tend to agree (Q1)
contribute to a better performance of the supplier involvement during NPD.

**Performance of Subsystems**

In order to carry out this analysis, all respondents’ answers to the close-end questionnaire have been included (N=13). The questionnaire is made up of 15 questions related to the benefits and other 35 related to success factors. The ANOVA [71, 72] result shows that there are significant differences between the influence of the subsystems in the relationship both in the benefits (F=7,767; p value<0,000) and in the success factors (F=11,340; p value<0,000). Regarding the benefits of the supplier involvement, the test of multiple comparisons (LSD) shows that the questions comprised in the personal and technological subsystems tend to be more valued by the companies and their suppliers (Table 11).

In relation to the success factors of the supplier involvement, it was identified a tendency to which the questions comprised in the work design and technological subsystems have greater influence over the result of the cooperative relationship during NPD (Table 12).

In this sense, it is suggested that in the studied cases, the companies focus more on the questions comprised in these subsystems in order to achieve their objectives during the supplier involvement. The technological subsystem is used in this study to include the questions related to technology and the use of tools in the relationship with the supplier during NPD. The work design subsystem comprises questions directed to the procedures adopted during the performance of activities, in other words, to the work structure. This tendency towards the valuation of the questions comprised in the technological subsystem and work design should not be seen as a means of reducing the importance of the other subsystems. However, they can point to the priority of the questions included in these subsystems.

**CONCLUSIONS**

The analytical method used was considered effective in order for the companies to identify the possibilities of improving the performance of the supplier involvement during NPD, as well as the setting of common goals during the process. On the one hand, the benefits on which the companies tend to agree are presented as synergy possibilities that should be adopted during the cooperative NPD. On the other hand, the success factors on which the companies

**Table 11: Test of multiple comparisons (LSD) for the benefits of the supplier involvement**

| Subsystem                | Average | Personal subsystem | Technological subsystem | External environment subsystem |
|--------------------------|---------|--------------------|-------------------------|-------------------------------|
| Work design subsystem    | 8.70    | -2.95**            | -2.29**                 | -1.1246                       |
| Personal subsystem       | 11.66   | -                  | 0.66                    | 1.8333**                      |
| Technological subsystem  | 11.00   |                    |                         | 1.1733*                       |
| External environment subsystem | 9.82   |                     |                         |                               |

* significant at 5% - **significant at 1%

**Table 12: Test of multiple comparisons (LSD) for the success factors of the supplier involvement**

| Subsystem                | Average | Personal subsystem | Technological subsystem | External environment subsystem |
|--------------------------|---------|--------------------|-------------------------|-------------------------------|
| Work design subsystem    | 10.87   | 2.24**             | -0.29                   | 1.25**                        |
| Personal subsystem       | 8.62    |                    | -2.54**                 | -0.99                         |
| Technological subsystem  | 11.16   |                    |                         | 1.54**                        |
| External environment subsystem | 9.61   |                     |                         |                               |

* significant at 5% - **significant at 1%
agreed tend to indicate the questions that have stronger impact on the result of the supplier involvement during NPD process.

It was found a higher valuation of questions related to communication and NPD by the studied companies and suppliers, which shows that these points should be worked on as to better such companies’ cooperative NPD performance. It was also possible to identify a higher valuation of questions comprised in the work project and technological subsystems, the ones towards the procedures included in the development process and in the tools used during the process, respectively.

The application of the questionnaire and the data analysis gave the companies a diagnosis of the relationship they have with their suppliers during the NPD process. This analytical method also offers the companies a way to monitor the main factors that influence the supplier involvement in addition to allowing for the possibility of developing projects that cause the improvement of the performance of the relationships that companies have with their suppliers during NPD.

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FINISHING PRODUCT FOR IMPROVING ANTIFUNGAL PROPERTIES OF LEATHER

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ABSTRACT. Some biocides used in the leather industry have a certain toxicity and are prohibited by the directives in force. A product with antifungal properties containing coriander essential oil was tested as finishing auxiliary for bovine shoe upper leather. The paper presents the results obtained in leather finishing using the new product AF-C and evaluation of its antifungal activity against Aspergillus niger strain. For maximum efficiency, the concentration of AF-C antifungal product must not decrease below 65% in the final dressing for leather finishing.

KEY WORDS: leather, finishing, coriander essential oil, antifungal product

INTRODUCTION

Biological factors (fungi, bacteria) may damage leather and leather items by degradation of the grain (stains, matting, etc.). The cost of raw materials for leather production is significant. So, the preservation of stock is still fundamental to good quality control and making a living for tanners. Yet biocides by their very nature are environmentally unfriendly. However, help may be at hand, with research into new ecofriendly brands of bacterial control [1].

Biocides based on beta-naphthol, benzothiazole and sulfone derivatives, organic sulfur compounds, etc. used in the leather industry have a certain toxicity to humans and the environment, some of which are prohibited by the directives in force, i.e. pentachlorophenol, polyhalogenated phenolic compounds [2-5].

Many studies were aimed at replacing potentially hazardous substances used in the processing of hides, skins and furs:
- Synthesis of new classes of biocides based on derivatives of 2-amino-benzothiazole-6-substituted with methyl, methoxy, chloro, nitro, modified chemically by sulphonation [6] and used in cattle leather processing [7] which have shown to be effective against Aspergillus niger species, but not against the Trichoderma viride species;
- Synthesis of new classes of tanning agents to replace chromium in tanning hides and furs [8-15].

Several studies have been conducted on the use of natural products derived from plants for the treatment of leather and fur:
- Bayramoglu et al. [16, 17] from Ege University in Turkey used Origanum species to extract essential oils from plants through steam distillation process. It has been found that utilization of the essential
Oil of \textit{Origanum minutiflorum} during pickling has antifungal activity and that its effect is improved with increasing concentration. As a result of this study, it was found that the wet blue leather specimens treated with 1\% \textit{Origanum} sp. essential oil showed antibacterial effect on Gram-positive bacteria. \textit{Origanum minutiflorum} essential oil had an antifungal effect on wet blue. The bacteria are more resistant to the essential oils than yeasts and moulds. A concentration of 21\% relative to the float of the essential oils of oregano from three different species and fennel oil was tested for their antimicrobial activity along with 7-25\% of phenol and 4-chloro-3-methyl-phenol as a commercial bactericide commonly used in the leather industry. The results showed that the three essential oils of oregano had a much stronger bactericidal activity than the commercial product and may find use as antibacterial agents in the leather industry.

- Use of essential oils in finishing leather and fur [18-20];
- Use of essential oils to stop the growth of fungi [21].

Essential oils from aromatic and medicinal plants have been known to possess potential as natural agents for leather preservation, including antibacterial and antifungal; in fact, many essential oils have been qualified as natural biocides and offered as potential substitutes of synthetic biocides in specific steps of leather processing. Many studies revealed utilization of essential oils for leather and leather objects protection against fungi [22-32].

Coriander (\textit{Coriandrum sativum} L.) is an annual herbaceous plant originally from the Mediterranean and Middle Eastern regions, cultivated for its culinary, aromatic and medicinal use. This plant is of economic importance since it has been used as a flavoring agent in food products, perfumes, cosmetics and drugs. This culinary and medicinal plant is widely distributed and mainly cultivated for the seeds which contain an essential oil (ranges between 0.3\% and 1.1\%) [33]. The essential oil and various extracts from coriander have been shown to possess antibacterial, antidiabetic, anticancerous, antimutagenic, antioxidant and free radical scavenging activities [34, 35]. In addition to its culinary value, coriander is known for its wide range of healing properties.

Coriander essential oil contains 60-70\% \textit{d}-linalool (or coriandrol, geraniol, cimol, pinene, terpinene, phellandrene, dipentene, petroselinic acid, etc.), 15-20\% lipids, 10\% starch, 4-5\% mineral substances, pectins, etc. [36, 37]. Coriander essential oil has bactericidal and fungicidal properties [38-41].

Coriander seed essential oil is high in linalool. European oils show monoterpene hydrocarbon content between 16 to 30\%, linalool 60 to 75\%, whereas a considerable amount of other oxygenated monoterpenes is also present. The main monoterpene hydrocarbon components detected in these oils are \(\gamma\)-terpinene (up to 10\%), and limonene, \(\rho\)-cymene, \(\alpha\)-pinene up to 7\% each. The most prominent non-linalool oxygenated monoterpenes reported are geranyl acetate up to levels of 5\%, borneol up to 7\%, camphor and geraniol up to 4\% each and geranol up to 2\% [42].

Linalool is a tertiary alcohol isomer of geraniol and nerol, containing an asymmetrical carbon atom; it is found in nature preponderantly in isopropylidene form; it is a component of over 200 essential oils of various origins (herbs, leaves, flowers, fruits, wood); the dextrorotatory form (+) was isolated from coriander essential oil and is found in a proportion of 60-70\%.

![Linalool structure](image)

A new leather finishing auxiliary with antifungal properties (AF-C) was prepared based on beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide and coriander essential oil [18, 19].

The aims of this study are as follows: (i) to study utilization of the new product, AF-C, in leather finishing; (ii) to evaluate its antifungal activity.

**EXPERIMENTAL**

**Materials**

The chrome tanned bovine leathers, finished and crust for shoe upper: 1.2-1.4 mm
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thickness; brown; obtained in the facilities of INCDTP – Division Leather and Footwear Research Institute Bucharest, Romania.

Auxiliary materials for leather finishing from TFL Company, Germany.

Roda Casicolor Brown R: viscous and homogenous fluid, dry substance 38%; pH (10% solution) 7; ash – 28%;
Roda wax MONO: dry substance 36.87%; pH (10% solution) 4.2; Ford cup viscosity Ф4, 12; kinematic viscosity 8.97 cSt; density 0.957 g/cm³;
Roda-cryl 87: dry substance 34.50%; pH (10% solution) 6.0; Ford cup viscosity Ф4, 14; density 1.025 g/cm³;
Roda-pure 302, polyurethane binder for ground coat: dry substance 30.87%; pH (10% solution) 7.5; Ford cup viscosity Ф4, 15; density 1.076 g/cm³;
Roda-pure 5011, polyurethane binder: dry substance 40%; pH (10% solution) 5.5; Ford cup viscosity Ф4 7; density 1.053 g/cm³;
Product AF-C with antifungal properties, prepared from coriander essential oil, beeswax, lanolin, ethanol and lauryl alcohol ethoxylated with 7 moles of ethylene oxide [18, 19] with the following characteristics: dry substance 12%; pH (10% solution) 4.5; density 0.820 g/cm³.

Methods

Chemical characteristics of shoe upper leather were determined according to the following standards:

- SR EN ISO 4684:2006; Leather - Chemical tests - Determination of volatile matter;
- EN ISO 4048: 2008 - Determination of matter soluble in dichloromethane and free fatty acid content;
- SR EN ISO 5398:2008 - Leather - Determination of chromic oxide content; Part 1: Quantification by titration;
- EN ISO 4045:2008 - Determination of pH and difference figure;
- SR EN ISO 11640:2002 - Strength to dry and wet abrasion (1-5 ranking);
- SR EN ISO 5402:2012 - Resistance to repeated bending, number of flexions.

Antifungal activity against Aspergillus niger: The tests were made following standard ASTM D 4576-2013, Standard Test Method for Mold Growth Resistance of Wet Blue.

Petri dishes were placed in thermo-hygrostat at 30°C temperature and were observed and evaluated after 3, 7, 14, 21 and 28 days.

Optical microscopy images were captured using a Leica stereomicroscope S8AP0 model with optic fiber cold light source, L2, with three levels of intensity and magnification 40X.

Obtaining Bovine Shoe Upper Leather

Two series of experiments were performed in order to obtain cattle shoe upper leather using finishing auxiliary with antifungal properties (AF-C):

- Series I prepared with technology presented in Table 1 and with different quantities of product AF-C according to Table 2: Samples AF-1; AF-2; AF-3; control sample - M1;

| Table 1: Finishing technology for bovine shoe upper leather |

| Operation                              | Composition of dispersion/Method of application |
|----------------------------------------|------------------------------------------------|
| Basecoat (Applying Dispersion I)       | 60-80 g/L Roda Casicolor Brown                  |
|                                        | 20 g/L Roda wax MONO                             |
|                                        | 125 g/L Roda-cryl 87                             |
|                                        | 125 g/L Roda-pure 302                            |
|                                        | 650-670 g/L water                                |
|                                        | Application by spraying 2 times                  |
| Intermediate pressing                  | Hydraulic press using mirror or steam plate, parameters: |
|                                        | - temperature – 50-60°C                          |
|                                        | - pressure – 50-100 bar                          |
| Applying Dispersion I                  | By spraying 2-3 times                            |
| Antifungal treatment / fixing          | Applying Dispersion II (see Table 2)            |
|                                        | Spraying 2 times                                 |
| Final pressing                         | Hydraulic press using mirror plate, parameters:  |
|                                        | - temperature – 70-80°C                          |
|                                        | - pressure – 50-100 bar                          |
Table 2: Composition of dispersion II

| No. | Sample | Composition of dispersion II |
|-----|--------|-----------------------------|
| 1   | AF-1   | 1000 g/L product AF-C       |
| 2   | AF-2   | 750 g/L product AF-C        |
|     |        | 250 g/L RODA pur 5011       |
| 3   | AF-3   | 650 g/L product AF-C        |
|     |        | 350 g/L RODA pur 5011       |
| 4   | M1 Control | 700 g/L Roda pur 5011    |
|     |        | 300 g/L water               |
| 5   | AF-4   | 1000 g/L product AF-C       |
| 6   | M2 Control | Not finished               |

- Series II in which only finishing auxiliary with antifungal properties AF-C was used for leather finishing according to Table 2: Samples AF-4; unfinished leather was used for control sample M2.

Product AF-C was compatible with the materials used in the final dressing. Leather from Experiment AF-1 was sticky after pressing.

AF-C product can be used as such in surface finishing of buffed bovine hides such as suede, buffo or nubuck to obtain a fatty/waxy feel and a better resistance to fungi of the dermal substrate.

RESULTS AND DISCUSSION

Characterization of Leather Finishing

Chemical characteristics of the leathers were determined in accordance with standard STAS 1619:1994: Leather for uppers and leather goods. Cattle skins tanned with chrome, grain finished. General technical conditions (Table 3).

Chemical and physical-mechanical characteristics of leather were within the limits specified in standard 1619:1994.

Evaluation of Antifungal Effect of Leather Finished with AF-C Product

The experiment examines how the growth of mold is influenced by existing treatment on the leather sample treated with biocides through mold resistance under simulated contamination.

Leather untreated with the AF-C product was used as a control: M1 – finished leather and M2 – not finished (crust) leather. Incubation duration was 28 days and fungal observations were performed at intervals of 7, 14, 21 and 28 days. Mold development on leather samples was evaluated by ranking according to the notation used in the standard method used: mark 0 indicates the absence of stems and a strong fungitoxic effect, and mark 5 indicates no fungitoxic effect, the mold covering the entire surface of the specimen.

Development of the *Aspergillus niger* strain on leather samples over time, i.e. macroscopic images of the samples are shown in Table 4.

Table 3: Chemical characteristics of bovine shoe upper leather

| Sample/Characteristic | AF-1 | AF-2 | AF-3 | M 1  | AF-4 | M 2  | STAS 1619:1994 |
|-----------------------|------|------|------|------|------|------|----------------|
| Volatile matter, %    | 13.97| 14.76| 13.78| 13.80| 13.88| 14.09| 14-15          |
| Extractibles, %       | 7.88 | 7.67 | 7.57 | 7.44 | 7.87 | 7.96 | Max. 8         |
| The content of chromium oxide, % | 5.93 | 5.74 | 5.66 | 5.47 | 5.77 | 6.10 | Min. 3.5       |
| pH                    |      |      |      |      |      |      |                |
| Dry and wet abrasion strength, rank | 5/4  | 5/4  | 5/4  | 5/5  | 5/4  | 5/4  |                |
| Resistance to repeated bending, number of flexions | 250.000 | 250.000 | 250.000 | 250.000 | 250.000 | 250.000 |            |
Table 4: Images of leather samples within Series I experiment

| Sample | 7 days | 14 days | 21 days | 28 days |
|--------|--------|---------|---------|---------|
| AF-1   | ![Image](af1_7d.png) | ![Image](af1_14d.png) | ![Image](af1_21d.png) | ![Image](af1_28d.png) |
| mark   | 0      | 0       | 0       | 0       |
| AF-2   | ![Image](af2_7d.png) | ![Image](af2_14d.png) | ![Image](af2_21d.png) | ![Image](af2_28d.png) |
| mark   | 0      | 0       | 0       | 2       |
| AF-3   | ![Image](af3_7d.png) | ![Image](af3_14d.png) | ![Image](af3_21d.png) | ![Image](af3_28d.png) |
| mark   | 2      | 2       | 4       | 4       |
| Control| ![Image](control_7d.png) | ![Image](control_14d.png) | ![Image](control_21d.png) | ![Image](control_28d.png) |
| mark   | 4      | 5       | 5       | 5       |

Table 5: Images of leather samples within Series II experiment

| Sample | 7 days | 14 days | 21 days | 28 days |
|--------|--------|---------|---------|---------|
| AF-4   | ![Image](af4_7d.png) | ![Image](af4_14d.png) | ![Image](af4_21d.png) | ![Image](af4_28d.png) |
| mark   | 0      | 0       | 0       | 0       |
| Control| ![Image](control_7d.png) | ![Image](control_14d.png) | ![Image](control_21d.png) | ![Image](control_28d.png) |
| mark   | 4      | 5       | 5       | 5       |

In the two series of experiments, the leather samples AF-1 and AF-4 were the most resistant to mold, the samples did not develop fungi for 28 days - mark 0; the leather sample AF2 did not develop fungi for 21 days - mark 0; the leather sample AF3 developed fungi after 7 days - mark 2. It can be observed that the fungitoxic effect decreased with reduced quantities of AF-C used in the final dressing composition.

The negative control leather M1 and M2 (without product AF-C) already failed in the first week and received marks ranging between 4 after 7 days and 5 after 14 days.

Moisture content and pH of the leather have been reported as the main biotic factors affecting the fungal deterioration. In the present investigation, the volatile matter content and pH of leather ranged between 13.78 and 14.76%, and between 4.5 and 6, respectively. So, the fungal distribution on the samples was not influenced by their moisture content and pH.

The finishing auxiliary with antifungal
properties AF-C improved resistance of finished leather to biological factors (fungi). For maximum efficiency, the concentration of the antifungal product must not decrease below 65%.

CONCLUSIONS

Results showed that the AF-C product containing coriander essential oil could be used as natural antifungal in leather finishing. The AF-C product can be used in surface treatment of bovine finished leather for shoe upper and in surface finishing of buffed bovine hides such as suede, buffo or nubuck to obtain a fatty/waxy feel and a better resistance to fungi of the dermal substrate. The AF-C product improved resistance of finished leather to biological factors (fungi) and can complement treatment with biocides used to treat natural leather in wet processing operations. For maximum efficiency, the concentration of the antifungal product must not decrease below 65% in the final dressing for leather finishing.

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ABSTRACT. The purpose of this paper is to develop an antibacterial polymer nanocompound based on silicone rubber reinforced with TiO$_2$ nanoparticles and with added crosslinkers - dicumyl peroxide. The antibacterial nanocompound polymer was developed by vulcanization on a laboratory roll mill, so as to be further processed by means of molding using the electric press, with preset parameters for optimum processing. The antibacterial polymer nanocompound obtained was characterized in terms of physical-chemical properties in normal condition and after accelerated aging at 70°C for 168 hours; it was also characterized in terms of immersion in specific environments for the food and pharmaceutical industries according to standards in force, and structurally by FT-IR. The new advanced material based on silicone elastomer (silicone rubber) helps to improve product quality, protects human health, sterilizes products against bacteria and microbes and last but not least protects the environment, but also increases the turnover of domestic and international companies. Following physical-chemical and chemical characterization of polymer nanocompounds, two variants were selected (P$_5$ and P$_6$) which have potential applications in food and pharmaceutical industries.

KEY WORDS: silicone rubber, polymer nanocompound, vulcanization, antibacterial nanocompound

INTRODUCTION

Worldwide there is a need to develop new advanced materials based on silicone elastomers (silicone rubber) with enhanced properties, reinforced with nanopowders with antimicrobial, antibacterial, and antifungal properties (ZnO and TiO$_2$) [1, 2]. Vulcanization process as the main stage has a major impact on the final properties of the product, including determination of the optimal amount of nanometric reinforcing filler and crosslinking agent used (peroxides) [3-6].

Reinforcing agents in the nanometric range provide antibacterial, antiseptic and antifungal properties, help initialize the vulcanization process, and also improve physical, mechanical and chemical properties, especially elasticity, tensile strength, resistance to aggressive chemical agents, etc.

Silicone elastomers are polymers with special characteristics due to their high resistance to temperatures from (-100°C) to above (+300°C) [7, 8]. These are high temperatures specific to nanocomposites.
sterilization, used to make products for the food, pharmaceutical and medical industries. Items made of silicone elastomers (silicone rubber) are preferred in medicine because they do not contain substances such as antioxidants and other restricted ingredients [9-12].

This paper presents the development of polymer nanocompounds based on silicone rubber, reinforced with TiO\textsubscript{2} nanoparticles filled with chalk (CaCO\textsubscript{3}), with stearin as plasticizer and crosslinked with dicumyl peroxide (PD), which were characterized in terms of physico-mechanical and chemical properties by immersion in specific environments for the pharmaceutical and food industries (alcohol, distilled water, cooking oil - sunflower oil) according to standards in force and structurally analysed by FT-IR.

EXPERIMENTAL

Materials

The following materials were used in order to make the antibacterial polymer nanocompound:

1. silicone rubber (Elastosil R701/70-OH: polydimethylsiloxane with vinyl groups, (dynamic) viscosity above 9.000.000 mPa x s, in the form of paste, density – 1.32 g/cm\textsuperscript{2}, colour – opaque);
2. stearin (in the form of white flakes, moisture – 0.5% max, ash – 0.025 % max);
3. active zinc oxide (ZnO –93-95% precipitate, white powder, density – 5.5 g/cm, specific area – 45-55 m\textsuperscript{2}/g);
4. titanium dioxide nanoparticles (TiO\textsubscript{2} – white nanopowder, assay ≥ 99.5 % trace metals basis);
5. chalk (CaCO\textsubscript{3} precipitate – white powder, molecular weight 100.09);
6. di(tert-butylperoxyisopropyl) benzene, powder 40% with calcium carbonate and silica (PD) - Perkadox 14-40B (1.65 g/cm\textsuperscript{3} density, 3.8% active oxygen content, pH 7, assay: 39.0-41.0%).

Preparation of Composites

The antibacterial polymer nanocompound based on silicone rubber, reinforced with nanometric particles (TiO\textsubscript{2}), filled with CaCO\textsubscript{3} (chalk) and crosslinked with dicumyl peroxide (Perkadox – PD) was developed by electric laboratory roll mill mixing (with temperature adjustment), of 1 kg capacity, with cooling (rolls are water-cooled). Mixing was performed without heating the rolls. The order of adding ingredients was strictly observed, according to Table 1. Silicone rubber was plasticized between the rolls for approximately 3 minutes, the plasticizer – stearin – was added and mixing continued for 1.5 minutes; zinc oxide was then added (microparticle) and embedded into the mixture until homogenisation; TiO\textsubscript{2} nanoparticles were added, continuing to mix for 3 minutes until the nanometric component was embedded; the filler (CaCO\textsubscript{3}) was then added and mixing continued for 2-2.5 minutes; the last ingredient – dicumyl peroxide – is embedded into the mixture for 2 minutes. After adding all the ingredients, the mixture is homogenized on the roll mill for 1 to maximum 3 minutes and taken off in the form of a 3-4 mm thick sheet. The resulting nanocompound is tested rheologically to determine the optimal vulcanization time, in order to set the optimal parameters for electric press processing, TP 600, by compression between its plates at a temperature of 170°C and preset times. Work stages and conditions are as follows:

- Pressing at 300 KN pressure - depending on rheological values (2 min. pressing);
- Cooling - 10 min.

After 24-hour conditioning at room temperature, samples were cut out from the sheets and tested in terms of physical-mechanical properties: normal condition – at room temperature – and accelerated ageing at 70°C for 168 hours.

| Symbol | MU | CS\textsubscript{i} (control) | P\textsubscript{5} | P\textsubscript{6} | P\textsubscript{7} |
|--------|----|-----------------------------|-----------------|----------------|----------------|
| Silicone rubber | g | 150 | 150 | 150 | 150 |
| Stearin | g | 7.5 | 7.5 | 7.5 | 7.5 |
| Zinc oxide (microparticles) | g | 6 | 4.5 | 3 | 1.5 |
| Titanium dioxide (nanoparticles) | g | - | 1.5 | 3 | 4.5 |
| Chalk (CaCO\textsubscript{3}) | g | 15 | 15 | 15 | 15 |
| PD (dicumyl peroxide – 40% - on silica and CaCO\textsubscript{3} substrate) | g | 11.25 | 11.25 | 11.25 | 11.25 |
The technological process for developing antibacterial polymer nanocompounds based on silicone rubber, reinforced with TiO₂ nanoparticles is illustrated in Figure 1.

The analysis of physical-mechanical characteristics of antibacterial polymer nanocompounds were tested and characterized according to standards in force. Table 2 presents values for physical-mechanical testing.

**Table 2: Physical-mechanical testing of polymer nanocompounds based on silicone rubber reinforced with TiO₂ nanoparticles**

| Material | CS₁ (control) | P₅ | P₆ | P₇ |
|----------|---------------|-----|-----|-----|
| **Physical-mechanical characterization: normal condition** | | | | |
| Hardness, °Sh A | 65 | 64 | 54 | 53 |
| Elasticity, % | 12 | 10 | 08 | 07 |
| Tensile strength, N/mm² | 3.4 | 3.8 | 3.3 | 3.0 |
| **Physical-mechanical characterization: accelerated ageing at 70°C and 168 h** | | | | |
| Hardness, °Sh A | 71 | 70 | 68 | 63 |
| Elasticity, % | 12 | 09 | 08 | 07 |
| Tensile strength, N/mm² | 3.4 | 3.0 | 3.1 | 2.5 |

Immersion in liquids was performed according to ISO 1817:2015 monitoring volume and mass variation. Samples used for immersion were 2±0.2 mm thick and their volume was 1-3 cm³. Samples were immersed in tightly sealed recipients, for 24 hours.

Structural investigations were performed by FT-IR spectroscopy. Spectral determinations were performed using a double beam molecular absorption IR spectrometer, in the 4000-600 cm⁻¹ range, using an FT-IR Able Jasco 4200 device coupled with ATR cu diamond crystal and sapphire head, Figure 2.
characteristics (Table 2) shows the following:

- The hardness of antibacterial polymer nanocompounds based on silicone rubber reinforced with TiO$_2$ nanoparticles shows changes compared to control sample CS$_1$, and after accelerated ageing, hardness increases significantly compared to normal condition for all samples, due to plasticizer loss.
- Elasticity. Due to nanoparticle addition, a decrease in elasticity is noticed compared to the control sample. After accelerated ageing, elasticity decreases in all studied samples.
- Tensile strength. With the addition of reinforcing agent (TiO$_2$) and crosslinker (dicumyl peroxide), tensile strength shows values ranging from 3.0 N/mm$^2$ to 3.8 N/mm$^2$. Tensile strength therefore increases compared to control sample CS$_1$ depending on the percentage of reinforcing agent added to the mixtures, and after accelerated ageing at 70°C for 168 h, tensile strength shows much lower values compared to the control sample.

### Chemical Characterisation – Immersion of Antibacterial Polymer Nanocompounds

The behaviour of mixtures was tested after immersion into various working environments – ethyl alcohol (70% ethyl alcohol concentration), distilled water, vegetable fat (sunflower cooking oil) for 24 hours at room temperature, in brown coloured tightly sealed recipients. Mass variation, $\Delta M$, and volumetric variation, $\Delta V$, were determined.

Values resulting from immersion are given in Table 3.

Values obtained for immersion of silicone rubber-based mixtures reinforced with TiO$_2$ nanoparticles in various specific environments lead to the following conclusions:

- concentration of the nanometric reinforcing agent, TiO$_2$, influences mass variation ($\Delta M$) and volume variation ($\Delta V$), both decreasing proportionally with the TiO$_2$ percentage added to the antibacterial polymer compounds;
- in distilled water very good behaviour is noticed, below 1% for mass variation ($\Delta M$) and 1.5% for volume variation ($\Delta V$), indicating very low swelling in water;
- in ethyl alcohol and cooling oil (sunflower oil) variations are negative, below ±4%, indicating that in ethyl alcohol the extraction of a substance such as stearin, unreacted crosslinkers and chalk occurs, including in the vegetable oil immersion environment (sunflower oil).

### FT-IR Spectrometric Analysis

The silicone rubber sample – ELASTOSIL R701/70-OH, control sample – CS$_1$, and antibacterial polymer nanocompounds – P$_5$ and P$_6$ were analysed by FT-IR spectroscopy.

As a result of determinations, the following were found:

1) The spectrum (Figure 3) recorded for the silicone rubber sample – ELASTOSIL R701/70-OH – shows IR frequencies (cm$^{-1}$) and vibration attributions given in Table 4.

2) The spectrum recorded for the

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### Table 3: Mass variation ($\Delta M$) and volume variation ($\Delta V$) of polymer nanocompounds based on silicone rubber reinforced with TiO$_2$ nanoparticles in various environments

| Material                     | $\Delta M$ | $\Delta V$ | $\Delta M$ | $\Delta V$ | $\Delta M$ | $\Delta V$ | $\Delta M$ | $\Delta V$ |
|------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Ethyl alcohol (70%)          | -0.76      | -1.11      | -1.52      | -2.07      | -1.21      | -1.71      | -0.77      | -1.66      |
| Distilled water              | 0.17       | 0.69       | 0.44       | 1.52       | 0.3        | 0.71       | 0.28       | 0.41       |
| Cooking oil (sunflower oil)  | -1.23      | -1.65      | -2.15      | -3.31      | -2.22      | -2.94      | -2.32      | -2.43      |

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### Table 4: Frequencies and vibration attributions for the silicone rubber sample

| Frequency | Vibration attributions |
|-----------|------------------------|
| 696       | $\nu$ Si(CH$_3$)$_3$   |
| 787.271   | $\nu$ Si(CH$_2$)      |
| 866.338   | Si(CH$_3$)$_2$, (r)    |
| 1007.12   | Si(-CH$_3$ = CH$_2$)   |
| 1258.78   | $\delta$ SiCH$_3$     |
ANTIBACTERIAL NANOCOMPOUND BASED ON SILICONE RUBBER. PART I – OBTAINING AND CHARACTERISATION

Table 5: Frequencies and vibration attributions for the control sample

| Frequency  | Vibration attributions                        |
|------------|------------------------------------------------|
| 697.141    | \( \nu \text{Si(CH}_3\text{)}_3 \)           |
| 786.815    | \( \nu \text{Si(CH}_3\text{)} \)             |
| 871.667    | \( \text{Si(CH}_3\text{)}_2 + \text{Si(CH}_2\text{)}_2 \) |
| 1006.66    | \( \text{Si} - \text{CH} = \text{CH}_3 \)     |
| 1258.32    | \( \delta \text{SiCH}_3 \)                    |
| 1451.17    | \( \nu \text{CH}_3(\text{CH}_2)_{16} - \text{CO} \) (stearic acid) |
| 2849.31    | \( \delta \text{SiCH}_3 \)                    |
| 3361.32    | \( \nu \text{Si(CH}_3\text{)}_3 \)           |

Figure 3. IR spectrum recorded for silicone rubber – ELASTOSIL R701/70-OH

Table 6: Frequencies and vibration attributions for antibacterial polymer nanocompound P5

| Frequency  | Vibration attributions                        |
|------------|------------------------------------------------|
| 694.458    | \( \nu \text{Si(CH}_3\text{)}_3 \)           |
| 787.002    | \( \nu \text{Si(CH}_3\text{)} \)             |
| 870.911    | \( \text{Si(CH}_3\text{)}_2 + \text{Si(CH}_2\text{)}_2 \) |
| 1005.9     | \( \text{Si} - \text{CH} = \text{CH}_3 \)     |
| 1258.53    | \( \delta \text{SiCH}_3 \)                    |
| 1459.09    | \( \nu \text{CH}_3(\text{CH}_2)_{16} - \text{CO} \) (stearic acid) |
| 2849.52    | \( \delta \text{SiCH}_3 \)                    |

Figure 4. IR spectrum recorded for antibacterial polymer compound, control sample – CS1

Table 7: Frequencies and vibration attributions for antibacterial polymer nanocompound P6

| Frequency  | Vibration attributions                        |
|------------|------------------------------------------------|
| 694.459    | \( \nu \text{Si(CH}_3\text{)}_3 \)           |
| 787.002    | \( \nu \text{Si(CH}_3\text{)} \)             |
| 870.911    | \( \text{Si(CH}_3\text{)}_2 + \text{Si(CH}_2\text{)}_2 \) |
| 1005.9     | \( \text{Si} - \text{CH} = \text{CH}_3 \)     |
| 1258.53    | \( \delta \text{SiCH}_3 \)                    |
| 1459.09    | \( \nu \text{CH}_3(\text{CH}_2)_{16} - \text{CO} \) (stearic acid) |
| 2849.52    | \( \delta \text{SiCH}_3 \)                    |

Figure 5. IR spectrum recorded for antibacterial polymer nanocompound, sample P5

Figure 6. IR spectrum recorded for antibacterial polymer nanocompound, sample P6

antibacterial polymer compound CS1 – control sample – is given in Table 5.

3) The spectrum recorded for the antibacterial polymer nanocompound P5 is given in Table 6.

4) The spectrum recorded for the antibacterial polymer nanocompound P6 is given in Table 7.

IR spectra recorded for each nanocompound show that the disperse phase – silicone rubber (silicone elastomer) is in
the highest amount, as it is the materials into which all other ingredients are embedded (the predominant material). The reinforcing agent in the form of nanoparticles – TiO$_2$ – does not stand out due to its low amount and to its uniform embedding in the disperse phase.

Conclusions
This paper presents the technology for developing antibacterial polymer nanocompounds based on silicone rubber (silicone elastomer), plasticizer – stearin, filled with chalk, reinforced with TiO$_2$ nanoparticles (with antifungal, antibacterial and antimicrobial properties) and crosslinked with dicumyl peroxide (PD).

After immersing samples in specific work environments, formulations do not undergo surface modifications in terms of colour change and cracking, which indicates that the technologies and processing parameters are optimal.

FT-IR spectra confirm the presence of silicone rubber by the intensity of the characteristic peaks of the predominant material (the material in which the other ingredients are embedded).

Given the resistance of nanometric reinforcing agent – TiO$_2$ (with antimicrobial, antibacterial and antifungal role) to high temperatures, over +300°C, specific to sterilization, the polymer compounds based on silicone rubber may be used in the food and pharmaceutical industries.

Based on the values of physical-mechanical and chemical characteristics of antibacterial polymer nanocompounds based on silicone rubber, reinforced with TiO$_2$ nanoparticles, variants P$_5$ and P$_6$ were selected for potential applications in the food and pharmaceutical industries.

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CHARACTERISTICS OF CHROME COMPLEXES IN NEUTRALIZING EFFLUENT

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ABSTRACT. In order to explain the reason of chromium released from chrome tanned leather to effluent in neutralizing, the chromium complex composition, structure and property in neutralizing effluent were characterized. Hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the tanned hide powder was treated by conventional neutralizing to prepare neutralizing effluent (NE). Ion exchange chromatography (IEC) and gel filtration chromatography (GFC) were used to separate NE to study its chromium composition firstly; then ultraviolet-visible absorption spectroscopy (UV) and Fourier Transform Infrared Spectroscopy (FT-IR) were combined to analyze the structure of chrome complexes in NE; at last, chromium from NE was used for tanning and the thermal properties of the tanned hide powder were measured by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The results indicated that NE mainly consisted of anionic-zero valent, monovalent and bivalent chrome complexes and the molecular volume was small also. The Cr(III) complexes in NE were mainly combined with ligands like SO$_4$$^{2-}$ and HCOO$^-$ through single point coordination. Compared with the control, higher weightlessness rate but lower maximum thermal decomposition temperature ($T_{\text{max}}$), thermal denaturation temperature ($T_{\text{D}}$) and enthalpy ($\Delta H$) of NE chrome tanned hide powder demonstrated poor tanning ability of the chromium. In short, the characteristics of chromium complexes released from neutralizing process were: anionic-zero valent and low positive charge composition, small molecular volume, mainly combined with ligands through single point coordination and poor tanning ability. The study would provide foundation and reference for developing chromium solidifying methods in neutralizing.

KEY WORDS: neutralizing effluent, chromium complex, composition, structure, tanning property

CARACTERISTICILE COMPLECŞILOR DE CROM DIN EFLOUENTUL DE LA NEUTRALIZARE

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CARACTERISTICAS DE COMPLEJOS DE CHROME DE LOS EFUENTES RESULTANTES DE LA NEUTRALIZACIÓN

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RESUMÉ. Pour expliquer la libération de complexes de chrome dans les effluents résultats de l’opération de neutralisation des cuirs tannés au chrome, on a caractérisé la composition, la structure et les propriétés des complexes de chrome dans les effluents de neutralisation. On a tanné du cuir en poudre en utilisant une solution de chrome à une basicité de 33% (BCS), puis le cuir en poudre est soumis à un procédé classique de neutralisation pour préparer l’effluent résultant de cette opération (NE). On a d’abord utilisé la chromatographie par échange d’ions (CEI) et la chromatographie par filtration sur gel (GFC) pour séparer le NE afin d’étudier sa composition de chrome, et puis on a combiné la spectroscopie d’absorption ultraviolet-visible (UV) et la spectroscopie infrarouge à transformée de Fourier (FT-IR) pour analyser la structure des complexes de chrome dans le NE; enfin, le chrome résultant du NE a été utilisé dans le tannage et les propriétés thermiques de la poudre de cuir tanné ont été mesurées par l’analyse thermogravimétrique (TG) et par la calorimétrie différentielle à balayage (DSC). Les résultats indiquent que le NE se composait principalement de complexes de chrome anioniques zérovalents, monovalents et bivalents, et que le volume moléculaire était faible. Les complexes de Cr(III) du NE ont été combinés principalement avec des ligands, tels que SO$_4$$^{2-}$ et HCOO$^-$ par un point unique de coordination. Concernant le rapport du tannage, on a mesuré le taux de perte de poids plus élevé et la température maximale de décomposition thermique ($T_{\text{max}}$), la température de dénatisation thermique ($T_{\text{D}}$) et l’enthalpie ($\Delta H$) plus diminuées du cuir en poudre tanné au chrome résultant du NE démontrant la faible capacité de tannage du chrome. En bref, les caractéristiques des complexes de chrome libérés par le processus de neutralisation étaient: des complexes anioniques zérovalents, à faible charge positive et au volume moléculaire faible, combinés principalement avec les ligands par un point unique de coordination et avec une faible capacité de tannage. La présente étude est un point de départ et de référence pour l’élaboration de méthodes de solubilisation du chrome dans le processus de neutralisation.

MOTS CLÉS: effluent de neutralisation, complexe de chrome, composition, structure, capacité de tannage

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INTRODUCTION

Chrome tanned leather has excellent performance, so chrome tanning is still dominant in the leather industry, however the chromium pollution problem is increasingly brought to the attention. Therefore minimizing chromium pollution has significant environmental benefits and is important for sustainable chrome tanning technology. To reduce chromium discharge, cleaner chrome tanning methods like pickle free, high exhaustion, reversing process, organic solvent and adding auxiliary chrome tanning technologies and so on were studied [1-5]. In order to decrease chromium pollution further, recycle and reuse chrome tanning effluent technologies were also developed [6, 7]. However, chromium will release in post-tanning process such as rewetting, neutralizing, retanning, dyeing and fatliquoring effluents, leading to Cr₂O₃ content in post-tanning effluents reaching 10-450 mg/L which is higher than wastewater disposal limit standard [8, 9]. It is great trouble as chrome content in the effluents is too low to reuse or recycle in tanning but too high to use as float in corresponding processes at the same time. Thus, chrome releasing in post-tanning processes must be paid more attention and needs effort to minimize for clean chrome tanning process and high chromium exhaustion in whole leather making.

Organic retanning agents, dyestuffs and fatliquoring agents are mainly anionic materials used in subsequent processes for improving wet blue properties. The neutralizing process is usually used to raise the pH and diminish wet blue positive charge to facilitate anionic materials penetration. Whether alkaline, like sodium bicarbonate, or organic acid salts like sodium formate or sodium acetate, they all have strong affinity to chromium, therefore, the chrome release in neutralizing process is the highest in wet end except chrome tanning [10, 11]. Realizing why chromium is easily released in neutralizing is important and essential to reduce chrome discharge in the process and increase chrome comprehensive exhaustion in leather making. Although chromium complex structure and composition in rewetting process were studied [12], chromium characteristics in neutralizing had not been studied in detail.

In this work, the research grade hide powder was tanned by chromium sulfate liquor with 33% basicity (BCS), and then the leather was rewetted and neutralized to prepare neutralizing effluent (NE). The NE was separated by ion exchange chromatography (IEC) and gel filtration chromatography (GFC) and to study the chrome complex composition; then both ultraviolet-visible absorption spectroscopy (UV) and Fourier Transform Infrared Spectroscopy (FT-IR) were used to analyze the structure of the chromium complexes in NE; finally, hide powder was tanned by the chrome recovered from NE and thermal stability of the hide powder was characterized by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) to present the chrome complex property. The study would help illustrate the reason why chromium is released in neutralizing as well as provide foundation and reference for developing chromium solidifying methods in the process.

EXPERIMENTAL

Materials

Hide powder was research grade product from Tanning Chemical Lab of Chinese Academy of Forestry Sciences in Nanjing. Chromium sulphate was bought from Shanghai Aladdin Reagents Company. SP Sephadex C-25 cation exchange resin and SP Sephadex G-25 glucan gel resin were obtained from GE Healthcare. Other chemicals in the study were research grade and purchased from Chengdu Kelong chemical reagent factory, China.

Preparation of Basic Chromium Sulphate

1000mL 0.2mol/L chromium sulphate solution was prepared at first, and then 0.067mol sodium bicarbonate was added after 30min under stirring to obtain chromium sulfate liquor with 33% basicity (BCS).

Preparation of Neutralizing Effluent

20.00g hide powder was soaked with 100mL water in a 500mL flask at 25°C for 30min. A 100mL BCS was put in the system and interacted with hide powder in a thermostatic water bath oscillator at 25°C for 120min. Then, sodium bicarbonate was used to adjust the tanning liquor pH to 3.8-4.0 and then ran at 38 for 60min. At last, the tanned hide powder was dried in a vacuum drying oven at 40°C to constant weight.

0.2% formic acid and 150% water were added in dried hide powder, and then put in constant
temperature bath oscillator for 2h (38°C, 200r/min). Then, the hide powder was washed with running water for 10min. 2% sodium formate and 150% water were added and put in constant temperature bath oscillator for 90min (35°C, 200r/min). After filtering with nylon filter cloth, NE was collected. All the chemicals used for rewetting and neutralizing were based on dried hide powder weight.

Chromium Composition Determination by IEC and GFC

5 mL BCS and NE were filtered by microporous membranes (pore size, 450nm), and then added into pretreated SP Sephadex C-25 cation exchange chromatographic column (inner diameter 2.0 cm, packed 20.0 cm). Elution conditions were selected as follows: flow velocity of eluent 2.5 mL/min, followed by using H₂O, NaClO₄ (0.5mol/L), NaClO₄ (1.0mol/L), NaClO₄ (2.0mol/L), HCl (2.0mol/L) and HCl (3.0mol/L) to elute. UV1900 UV-Vis spectrophotometer (Shanghai Jinghua technology instrument co., LTD, China) was used to detect the absorbance at 420 nm [12, 13].

5 mL BCS and NE were filtered by microporous membranes (pore size, 450nm), and then added into pretreated SP Sephadex G-25 gel filtration chromatographic column (inner diameter 2.0 cm, packed 80.0 cm). H₂O with flow velocity of 2.5 mL/min was used to elute. UV-Vis spectrophotometer was used to detect the absorbance at 420 nm [12].

Chromium Structure Determination by UV and FT-IR

After IEC separation, each composition was lyophilized and then dissolved by distilled water. UV-Vis spectrophotometer was used to scan obtained liquor at 300-800 nm. R values were calculated by formula (1) as follows:

\[ R = \frac{\varepsilon_1}{\varepsilon_2} \]

where \( \varepsilon_1 \) - molar absorption coefficient of chrome at about 420nm and \( \varepsilon_2 \) - molar absorption coefficient of chrome at about 580nm.

Lyophilized chromium complexes were ground with KBr and made into thin sheets, then a Nicolet 10 FT-IR (American Thermo Scientific Corporation) was used to scan in wavelength range of 500-4000 cm⁻¹ for 32 times, and the data was recorded.

Chromium Property Determination

1.00g hide powder was tanned by 100mL 10g/L chrome solution prepared by dissolving lyophilized NE in a thermostatic water bath oscillator at 25°C for 120min. Then, sodium bicarbonate was used to adjust the tanning liquor pH to 3.8-4.0 and then ran at 38°C for 60min. Then, the tanned hide powder was dried in a vacuum drying oven at 40°C to constant weight. The dried hide powder was put in a dryer with saturated sodium sulphite to keep the temperature at 25°C and the air relative humidity of 65% before DSC and TG test [14]. The hide powder tanned by BCS was used as control.

The hide powder samples were put into ceramic crucibles and heated with 10°C min⁻¹ heating rate in a N₂ atmosphere (flow N₂:100mL min⁻¹); the range of temperature was from 50 to 650°C. A NETZSCH TG 209 F1 thermal gravimetric analyzer (Germany) was used for the determination, and the TG and DTG curves were recorded. Then the weightlessness rate at 200-600°C and maximum thermal decomposition temperature (Tₘₐₓ) was calculated.

The hide powder samples were put into Aluminum crucibles and heated with 10°C min⁻¹ heating rate in a N₂ atmosphere (flow N₂: 100mL min⁻¹); the range of temperature was from 25 to 250°C. A DSC 200 PC differential scanning calorimeter (Germany) was used for the determination, and the DSC curves were recorded. Then thermal denaturation temperature (Tₜₜ) and enthalpy (ΔH) was calculated.

RESULTS AND DISCUSSIONS

Chromium Complex Composition in Neutralizing Effluent

Charge Characteristics of Chrome Complexes in Neutralizing Effluent

According to the results of Li et al. [13], peak I, II, III, IV and V represented anionic-zero valent, monovalent, bivalent, trivalent and tetravalent chromium complexes, respectively. Notably, NE consists of anionic-zero valent, monovalent and bivalent chrome complexes (as shown in Figure 1b) only, however, BCS is separated into five components (in Figure 1a). The chrome complexes composition in BCS and NE are calculated based on the area of IEC peak (listed in Table 1). Moreover, the content difference of each composition between NE and BCS is also calculated in Table 1.
As shown in Table 2, charge distribution of BCS is more uniform, and composition is abundant. However, only anionic-zero valent, monovalent and bivalent chrome complexes exist in NE, in addition, the anionic-zero valent composition is dominant (47.44%) while high positive charge compositions cannot be detected. The results indicate that low-positive electricity chrome complexes are easy to be released in neutralizing, because the binding capacity between anionic-zero valent, low positive electricity chrome complexes and collagen are weak [15].

Molecular Volume of Chrome Complexes in Neutralizing Effluent

GFC is often used to analyze the molecular volume distribution to study the composition of coordination compounds. The retention time of the large molecular volume complexes is shorter while the small molecular volume is longer in the GFC separation process. GFC results of BCS and NE are shown in Figure 2. As shown in Fig. 2, chrome complexes in BCS are washed off completely during 172min and 280min, (Figure 2a); however, chrome complexes in NE are totally washed off between 368min and 408min (Figure 2b). Accordingly, the chrome complexes molecular volume in NE is far less than BCS. Smaller molecular volume means there is rarely polynuclear complexes, thus, the chromium complexes volume are too small to combine collagen through multiple crosslink [15].

In short, some measures should be taken to enlarge positive charge and increase size of chromium complex for forming stable and multi-crosslink between collagen and itself, it would be the foundation of reducing chromium releasing in neutralizing.

Chromium Complex Structure in Neutralizing Effluent

UV Results of Chrome Complex in Neutralizing Effluent

The R value of chrome complex compositions of I, II, III, IV and V in BCS is 1.08, 1.10, 1.09, 1.15 and 1.36 respectively, while only anionic-zero valent, monovalent and bivalent chrome complexes with R value 0.95, 0.80 and 0.83 are in NE. Composition with 1.36 R value being in BCS means Cr(III) combines with ligands mainly through a multi-point coordination mode which has better affinity and binding stability with collagen. Nevertheless, coordination patterns of chrome complexes combined with ligands in NE are mainly single as R values are always lower than 1.19 [15]. In consequence, chromium releasing in neutralizing should ascribe to lacking sufficient combination between chrome and ligands.
Table 2: R values of each composition in NE and BCS

| R values | I  | II | III | IV | V  |
|----------|----|----|-----|----|----|
| BCS      | 1.08 | 1.10 | 1.09 | 1.15 | 1.36 |
| NE       | 0.95 | 0.80 | 0.83 | -   | -   |

**FT-IR Results of Chrome Complex in Neutralizing Effluent**

Characteristic absorption peak and coordination mode of chrome complexes in NE are shown in Table 3. There are four absorption peaks in 900-1300cm\(^{-1}\) for chromium complex in composition I, which indicates that combination mode for SO\(_4^{2-}\) and central ion Cr(III) is two-point coordination. In the same way, two and three absorption peaks in composition II and III demonstrate that SO\(_4^{2-}\) is in free state and coordinates with Cr(III) by single point coordination [15].

Table 3: FT-IR absorption peak and coordination mode of chromium complex in NE

| Composition | Scope (cm\(^{-1}\)) | Peak (cm\(^{-1}\)) | Num. Ligand | Coordination mode |
|-------------|---------------------|-------------------|-------------|-------------------|
| I           | 900-1300            | 995,1048, 1148,1114 | 4 SO\(_4^{2-}\) | two-point         |
|             | 1680-1550           | 1633              | 2 HCOO      | single point      |
|             | 1465-1370           | 1405              |             |                   |
|             | 3400                | 3439              | 1 OH        | ----              |
|             | 900-1300            | 941,1088          | 2 SO\(_4^{2-}\) | free             |
| II          | 1680-1550           | 1630              | 1 HCOO      | single point      |
|             | 1465-1370           | 1430              |             |                   |
|             | 3400                | 3423              | 1 OH        | ----              |
|             | 900-1300            | 941,1087, 1141    | 3 SO\(_4^{2-}\) | single point      |
| III         | 1680-1550           | 1631              | 1 HCOO      | single point      |
|             | 1465-1370           | 1422              |             |                   |
|             | 3400                | 3441              | 1 OH        | ----              |

One asymmetric and one symmetric stretching vibration absorption peak are respectively found in 1550-1680cm\(^{-1}\) and 1370-1465cm\(^{-1}\) of chrome complex in composition I, II and III, moreover, the interval of these two absorption peaks are small. Therefore single point coordination is speculated between Cr(III) and HCOO [15]. Based on the UV, FT-IR and IEC results, chromium complexes structure in neutralizing effluent are speculated and shown in Figure 3.

The weightlessness rate, T\(_{max}\), T\(_d\) and ΔH of BCS and chromium from NE tanned hide powder are presented in Table 4. As shown in Table 4, weightlessness rate of NE tanned hide powder is 46.82%, which is higher than BCS tanned sample; however, T\(_{max}\) of NE tanned hide powder is lower than control. These results indicate that NE tanned hide powder could be decomposed easily under high temperature. In addition, T\(_d\) and ΔH of NE tanned hide powder are 70.71°C and 386.27 J/g which are lower than corresponding value of BCS tanned hide powder too; they demonstrate inferior thermal stability of NE tanned hide powder. Given the lower charge and molecular volume as well as lacking of multi-combination between chrome and ligands, tanning ability of chromium in NE is too poor to improve collagen thermal resistance representing as easier decomposed under high temperature and thermal stability showing as low energy being needed for leather denature.

**CONCLUSIONS**

Chromium in neutralizing effluent mainly consists of anionic-zero valent and low-positive electricity (+1 and +2) chrome complexes, and the molecular volume is far less than the chromium sulfate liquor with 33% basicity. The basic structure character of chromium in neutralizing effluent are speculated and shown in Figure 3.
effluent is chromium combined with SO$_4^{2-}$ and HCOO$^-$ by single point coordinate bond. Tanning ability of chromium in neutralizing effluent is still poor. To sum up, the characteristics of chromium complexes released from neutralizing process are anionic-zero valent and low positive charge composition, small molecular volume, mainly combined with ligands through single point coordination and poor tanning ability. The study may have important hints for improving the tanning and post-tanning process to reduce chromium discharge in wet end and promote chromium comprehension exhaustion in leather making.

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THE INFLUENCE OF COMPATIBILISER ON THE PROPERTIES OF POLYMER COMPOSITES

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ABSTRACT. Thermoplastic polymers are materials of the future, with special properties, depending on the type of elastomer, the degree of reinforcement, the type of reinforcement material, the functionalization of the reinforcing material, the type of functionalization agent, the elastomer-compatibiliser-reinforcing agent ratio, etc. Polycarbonate (PC) and polyamide (PA) are two elastomers with high hardness, immiscible due to differences in polarity, processing temperature, and solubility. These factors lead to a poor dispersion of PC in the PA matrix and vice versa. Mechanical and physical properties of these polymer blends come not only from the combination of polymeric compounds, but also from the developed morphological forms (interface). Therefore, an additive is required to act as a compatibiliser able to effectively reduce elastomer viscosity. In order to observe the influence of the selected compatibiliser on the properties of polymer composites, the latter were characterized physico-mechanically and morphologically. Thus, compatibilisers chosen for this study were polycaprolactone and polyalkylloxazoline. These compatibilisers, with specific surface and free energy, intervene in polymer-polymer interactions, increasing compatibility, forming polymer-compatibiliser-polymer bonds. Considering these properties formulations of polymercompounds were established (P1-P13) based on polyamide/compatibiliser/polycarbonate/fibreglass. Tested polymer composites contain different percentages of polyamide and polycarbonate (90, 70, 50, 30, 10), compatibilisers (caprolactone and oxazoline) 3-7%, and 10-30% fibreglass.

KEY WORDS: composites, polymers, polyamide, polycarbonate, compatibilisers

INFLUENȚA AGENTULUI DE COMPATIBILIZARE ASUPRA CARACTERISTICILOR COMPOZITELOR POLIMERICE

REZUMAT. Materialele polimerice termoplaste sunt materiale de viitor, având proprietăți speciale, în funcție de tipul de elastomeri, gradul de armare, tipul de material de armare, funcționalizarea materialului de armare, tipul de agent de funcționalizare, raportul elastomer-agent de compatibilizare-agent de armare etc. Poli carbonateul (PC) și poliamida (PA) sunt doi elastomeri cu duritate mare, nemiscibili datorită diferențelor de polaritate, temperatură de prelucrare și solubilitate. Acești factori conduc la o slabă dispersie a PC în matricea de PA și invers. Proprietățile mecanice și fizice ale acestor amestecuri polimerice nu provin doar de la combinația de compuși polimerici, ci și de la formele morfologice dezvoltate (interfață). Prin urmare, este necesar un aditiv care să acționeze ca un compatibilizator capabil să reducă în mod eficient viscositatea elastomerilor. În vederea observării influenței compatibilizatorului ales asupra proprietăților compozitelor polimerice, acestea au fost caracterizate prin punct de vedere fizico-mecanic și morfologic. Astfel, compatibilizatorii aleși pentru acest studiu au fost poliacaprolactona și polialchiloxazolina. Acești compatibilizatori, cu suprafață specifică și energie liberă, interven în interacțiunile polimer-poli mer, măriind gradul de compatibilizare, realizând legături de tip polimer-compatible-polimer. Având în vedere aceste proprietăți, s-au stabilit recepturi de compounding polimerice (P1-P13) pe bază de poliamidă/compatibiliser/ polycarbonat/fibreglass. Compotizele polimerice testate conțin procente diferite de poliamidă și polycarbonat (90, 70, 50, 30, 10), compatibilizator (caprolactonă și oxazolină) 3-7% și fibreglass de sticlă 10-30%.

CUVINTE CHEIE: compozite, polimeri, poliamidă, polycarbonat, compatibilizatori

L’INFLUENCE DE L’AGENT COMPATIBILISANT SUR LES CARACTÉRISTIQUES DES COMPOSITES POLYMÉRIQUES

RÉSUMÉ. Les polymères thermoplastiques sont des matériaux d’avenir, ayant des propriétés particulières, en fonction du type d’élastomère, du degré de renforcement, du type de matériau de renforcement, de la fonctionnalisation du matériau de renforcement, du type d’agent de fonctionnalisation, du rapport de l’agent compatibilisant-élastomère-agent de renforcement, etc. Le polycarbonate (PC) et la polyamide (PA) sont deux polymères avec une dureté élevée, immiscibles à raison de différences dans la polarité, la température de traitement et la solubilité. Ces facteurs conduisent à une faible dispersion de PC dans la matrice de PA et vice versa. Les propriétés physiques et mécaniques de ces mélanges de polymères ne proviennent pas seulement de la combinaison des composés polymères, mais aussi des formes morphologiques développées (interface). Par conséquent, un additif est nécessaire pour agir comme un agent compatibilisant qui peut réduire effectivement la viscosité des élastomères. Afin d’observer l’influence de l’agent compatibilisant choisi sur les propriétés des composites polymère, ceux-ci ont été caractérisés de point de vue physico-mécanique et morphologique. Ainsi, les agents compatibilisants choisis pour cette étude ont été la polycaprolactone et la polyalkylloxazoline. Ceux-ci, avec leur surface spécifique et leur énergie libre, interviennent dans les interactions polymère-polymère, ce qui augmente la compatibilité, en formant des liens de type polymère-compabiliser-polymère. Compte tenu de ces propriétés on a établi des formulations de composés polymères (P1-P13) à base de polyamide/compatibiliser/polycarbonate/fibre de verre. Les composites polymères testés contiennent différents pourcentages de polyamide et de polycarbonate (90, 70, 50, 30, 10), de l’agent compatibilisant (caprolactone et oxazoline) 3-7% et 10-30% fibre de verre.

MOTS CLÉS : composites, polymères, polyamide, polycarbonate, agents compatibilisants

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INTRODUCTION

A wide variety of new multicomponent polymeric materials have been developed in the last two decades. In the field of polymeric materials, leading companies have oriented towards the development of modified polymer structure with superior physical and mechanical properties compared to those of the base constituents taken individually, which offer superior versatility.

Thermoplastic polymeric composites are novelty materials, with special properties, depending on the type of elastomer, degree of reinforcement, the type of reinforcement material, the functionalization of the reinforcing material, the type of functionalization agent, the elastomer-compatibiliser-reinforcing agent ratio etc. These properties offer high use value in fields which require materials with advanced characteristics: dimensional stability, resistance to UV radiation, solvents, aggressive chemical agents [1-7], impact resistance, and possibility of use in a wide range of temperatures etc. Properties result from a set of summed specific characteristics of individual materials, which arise from physical, mechanical and chemical interactions that occur during manufacturing processes that result in a polymer nanostructure.

Grafted copolymers are currently widely used with the role of compatibility agents in blends with other plastic materials and are generally obtained by grafting free radicals in the melt onto the polymer chains. Most commonly used monomers are maleic anhydride, glycidyl methacrylate and acrylic and vinyl monomers containing reactive functionalized groups.

Based on the above, compatibiliser choice for mixed PA/PC requires special attention. Mechanical and physical properties of these polymer blends arise not only from the combination of polymeric compounds, but also from developed morphological forms (interface).

In this paper polyamide (PA) was used as dispersion phase, due to its processing property at high temperatures (200-230°C), which confers thermal resistance to the composite, and polycarbonate (PC), a polymer with wide industrial application [8, 9] due to its high impact resistance, was used as the dispersed phase. Compatibiliser (polycaprolactone or polyalkyloxazoline) with specific surface and free energy is involved in polymer-polymer interactions, enhancing compatibility degree [10] and creating polymer-compatibiliser-polymer bonds. The interface can also serve as a nucleation center, as a preferential adsorption place and as a space for chemical reactions. The use of such composite systems is required by features such as heat resistance, mechanical strength, resistance to aggressive agents, low weight, processability, etc.

By establishing optimal types and amounts of polycarbonate, polyamide, compatibiliser (polycaprolactone or polyanlyloxyazoline), and optimum processing technological parameters, high performance properties can be achieved, such as: impact and thermal resistance.

The formulations were designed to have predetermined physical (hardness, thermal stability, impact resistance), chemical (vapor, aggressive chemical agents resistance), technological (processing by injection/ extrusion, at controlled temperature and pressure, recyclable, optimized processing time, etc.), and fireproof properties.

MATERIALS AND METHODS

Polycarbonate and polyamide are two very hard elastomers, immiscible due to polarity, processing temperature, and solubility differences. These factors lead to a poor dispersion of PC in the PA matrix and vice-versa. In this situation, an additive is required [11, 12], that can act as a compatibiliser, which can effectively reduce the elastomer’s viscosity.

Multiphase polymeric composites need an adequate dispersion and compatibility method. Thus, the employed compatibiliser has to meet three essential requirements:

• To reduce interfacial tensions, thus achieving a fine dispersion;
• To stabilise the thermal and shearing effect morphology in the obtaining process;
To make possible the adhesion between phases, in solid state. In this regard, the role of the additives, such as compatibilisers, was investigated. The compatibilisers are necessary to adjust the mechanical properties or to promote miscibility in complex systems.

Thus, the compatibiliser (polycaprolactone or polyalkyloxazoline) with specific surface and free energy is involved in polymer-polymer interactions, enhancing compatibility degree, creating polymer-compatibiliser-polymer bonds. The interface can also serve as a nucleation center, as a preferential adsorption place and as a space for chemical reactions. The use of such composite systems is required by features such as heat resistance, mechanical strength, resistance to aggressive agents, low weight, processability, etc.

Materials

In order to achieve hybrid composites with thermal resistance, the following materials were used:

- (1) Polyamide - standard PA for injection - Sebamid 6 s3c (Basplast),
- (2) Polycarbonate - CALIBRET™ polycarbonate resin, density 1.2g/cm³ (Trinseo Gmb),
- (3) Polycaprolactone, mp: 60°C (lit), density: 1.145 g/cm³ (Sigma-Aldrich Chemistry, USA),
- (4) 2-ethyl-2-oxazoline – Mw-500.000, density: 1.14g/cm³ (lit) (Sigma-Aldrich Chemistry, USA),
- (5) simple fibreglass - BMC3 4.5 mm,
- (6) (Organosilane-3-Aminopropyl) trimethoxysilane, Mw-179.29 g/mol, bp: 91-92°C (lit) (Sigma-Aldrich Chemistry, USA).

Tables 1 and 2 show the multiphase polymeric composite formulations, based on PA/PC, with two types of compatibiliser (polycaprolactone, polyalkyloxazoline) and reinforced with simple and treated fibreglass. In order to make the comparison between composites possible, the base simple polymers PA, and PC, were shown in the table. The ratio between the components of the polymeric composites is as follows: 90-70% PA, 10-30% PC, 3-7% compatibiliser and 10-30% reinforced fibreglass.

### Table 1: Formulations of polymer composites based on PA/PC compatibilised with polycaprolactone

| Sample    | UM | PA | PC | P₁ | P₂ | P₃ | P₄ | P₅ | P₆ | P₇ | P₈ |
|-----------|----|----|----|----|----|----|----|----|----|----|----|
| Polyamide | %  | 100| -  | 90 | 50 | 70 | 70 | 70 | 70 | 70 | 70 |
| Polycarbonate | % | -  | 100| 10 | 50 | 30 | 30 | 30 | 30 | 30 | 30 |
| Polycaprolactone | % | -  | -  | -  | -  | -  | 3  | 3  | 5  | 5  | 7  |
| Fibreglass (treated) | % | -  | -  | -  | -  | -  | -  | -  | -  | 10 | -  |
| Fibreglass (simple) | % | -  | -  | -  | -  | -  | -  | -  | -  | 30 | -  |

### Table 2: Formulations of polymer composites based on PA/PC compatibilised with polyalkyloxazoline

| Sample     | UM | P₉ | P₁₀ | P₁₁ | P₁₂ | P₁₃ |
|------------|----|----|-----|-----|-----|-----|
| Polyamide  | %  | 70 | 70  | 70  | 70  | 70  |
| Polycarbonate | % | 30 | 30  | 30  | 30  | 30  |
| Polyalkyloxazoline | % | 3  | 3   | 5   | 5   | 7   |
| Fibreglass (treated) | % | -  | -   | 10  | -   | 30  |
| Fibreglass (simple) | % | -  | 10  | -   | 30  | -   |
In order to select the optimal variants, these new materials were characterized according to the rubber and plastic specific standards.

**Method**

Regarding obtaining polymeric composites with resistance to high temperature, flame, and impact, a processing technology and formulations for these materials were designed. Thus, the laboratory-scale technological process for polymeric composites based on polyamide and polycarbonate compatibilised with polycaprolactone or polyalkyloxazoline (3-7%) and reinforced with fibreglass, is detailed in Figure 1.

The formulations in Tables 1 and 2 were processed in a Brabender mixer, shown in Figure 2. The method for achieving multiphase polymer composites is as follows:

- Weighing the raw materials, according to the formulations;
- Base components, PA and PC, along with the compatibiliser (polycaprolactone or polyalkyloxazoline) are mixed together;
- Setting up the processing parameters through the dedicated software. Temperature was 200°C (zone 1) / 200°C (zone 2) / 200°C (zone 3);
- The previous obtained mix is introduced in the mixing chamber, and depending on the formulation, the fibreglass is added.

Depending on the formulation, the simple or treated fibreglass was added to the mixture in minute 8 and 13, respectively, continuing the mixing in the Brabender chamber. The total mixing time is 15 minutes/formulation.
THE INFLUENCE OF COMPATIBILISER ON THE PROPERTIES OF POLYMER COMPOSITES

Characterisation

**FT-IR Spectrometry Characterisation**

IR spectrums represent the radiant energy absorption curve in the IR domain by the sample molecule, depending on the wavelength or radiation frequency. The infrared domain of the electromagnetic radiation is between 0.8 and 200 μm. IR domain for usual organic chemistry is between 2.5 and 25 μm.

The structural determinations were carried out on an IR molecular absorption spectrometer with double beam, in the range of 4000-600 cm$^{-1}$, using 4200 FT-IR equipped with ATR diamond crystal and sapphire head. The solid state samples were set in the ATR and the equipment recorded the transmittance spectra of the sample and then compared it with the background spectra previously recorded. The recorded spectra of the samples were compared with the pure elastomer spectrum, and with the spectra found in the literature or with the equipment’s spectra library.

Overlapping spectra show the presence of PA and PC in the polymeric composites in variable percentages, by the intensity of characteristic peaks. The presence of polycaprolactone and polyalkyloxazoline compatibilisers in composites is outlined at 1040 cm$^{-1}$ and 801 cm$^{-1}$, respectively, in IR spectra. Note that the plastomer (PA and PC) is in excess of the other components, being the main ingredient, thus the fibreglass cannot be distinguished very well in this image, due to its small amount (fibreglass 10%wt of plastomer).

**Physical-Mechanical Characterisation**

The results of the physical-mechanical properties of the samples obtained for the polymer composites based on PA, compatibiliser, PC, and reinforced with fibreglass, are shown in Table 3.

Physical-mechanical characterization was carried out according to standards in force. Following the basic composites characterisation, P3 variant was chosen (70% PA/30% PC) to obtain the composites with compatibiliser (3-7%), simple and treated fibreglass (10-30%).

**Hardness**

Hardness decreases when adding the polycaprolactone or polyalkyloxazoline compatibiliser. When adding simple fibreglass,

| Characteristic / Sample | P1 | P2 | P3 | P4 | P5 | P6 | P7 | P8 | P9 | P10 | P11 | P12 | P13 |
|-------------------------|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|
| Hardness °Sh D SR ISO 7619-1:2011 | 77 | 78 | 75 | 78 | 80 | 78 | 81 | 79 | 80 | 80 | 81 | 82 | 81 |
| Tensile strength, N/mm², (SR ISO 37:2012) | 15 | 19 | 21 | 24 | 27 | 31 | 26 | 38 | 23.8 | 31.7 | 40 | 38.6 | 47 |
hardness increases but using the treated fibreglass instead, the hardness decreases by 1-2°Sh D. Thus, for the polymeric composites containing compatibiliser and treated fibreglass this property decreases by 2-3°Sh D.

**Tensile Strength**

Tensile strength decreases when mixing the plastomers, PA and PC, based on the ratio used between them. The addition of compatibiliser improves the tensile strength compared to P3 composites. With the addition of simple fibreglass tensile strength increases compared to P4 formulations. When using treated fibreglass with the compatibiliser, the value of tensile strength greatly improves. In that sense the composites P8 and P13 with 30% fibreglass show the best values of the tensile strength, of 38 N/mm² and 47 N/mm², respectively.

**Melt Flow Index**

The materials used have different characteristics and properties, such as color, density, hardness, different processing temperature, etc. Thus, the melt flow index was determined at the same temperature, of 230°C, and a pressure force of 5 Kg. The values of the melt flow index obtained for the polymeric composites processed in the Brabender mixer are shown in Figure 6.

It is noted that there are considerable differences between the viscosities of the two base polymers (PA and PC) which affects the flow of material. Thus, the values obtained for PA were 60 g/10 min and for PC, 11.7 g/10 min. Melt flow index for the obtained composite materials varies widely between these two extremes, due to the base polymer ratio, absence/presence of compatibiliser, absence/presence and the type of fibreglass. Thus, the flow index of composites P1-P3 decreases with increasing percentage of PC. The addition of the polycaprolactone compatibilising agent in a proportion of 5% increases the melt index value from 43 to 50 g/10 min. While using the polyalkyloxazoline compatibiliser with the same amount of 5% increases the melt index value to 59 g/10 min.

This characteristic is important in establishing the processing parameters of the polymeric composites into finished products, on the industrial equipment.
CONCLUSIONS

After testing the composite samples the following were found:

The compounds based on PA, PC thermoplastic polymers, compatibiliser and treated fibreglass have been selected because they will take advantage of the synergy of the two polymers such as chemical resistance, low water permeability, high temperature, flame, and impact resistance;

The composite sheets were obtained in an electrical heated press, by means of compression, between its plates, at a temperature of 220°C and at a pressure of 300 kN;

Developed formulations for polymer compounds (P1-P13) based on PA/compatibiliser/PC/fibreglass with different amounts of PA and PC (90, 70, 50, 30, 10), compatibiliser (polycaprolactone or polyalkyloxazoline) 5%, and fibreglass 10-30%.

Hardness decreases when adding the compatibiliser, and for the polymeric composites containing compatibiliser and treated fibreglass this property decreases by 2-3°Sh D.

Tensile strength decreases when mixing the plastomers, PA and PC, based on the ratio used between them. The addition of compatibiliser improves the tensile strength compared to P3 composites. The composites P8 and P13 with 5% compatibilisers and 30% treated fibreglass show the best values of the tensile strength, of 38 N/mm² and 47 N/mm², respectively.

Melt flow index ranges vary widely for the obtained polymeric composites. Thus, the flow index of composites P1-P3 decreases with increasing percentage of PC. The addition of the polycaprolactone compatibilising agent in a proportion of 5% increases the melt index value from 43 to 50g/10min. The usage of the polyalkyloxazoline compatibiliser with the same amount of 5%, increases the melt index value to 59g/10min.

The data presented show that the polyalkyloxazoline compatibilising agent favorably influences physical-mechanical and processing properties compared to polycaprolactone.

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ABSTRACT. Orthopedic footwear is part of the category of medical devices used in the conservative treatment of foot and lower limbs pathomechanics. For the custom-made medical device the manufacturer has to perform the design based on the prescription of a duly qualified medical practitioner that sets the specific design characteristics of the device. Quality management standards in the field of medical devices govern the entire process (or parts thereof) from design and development to delivery and provide technical support for their implementation. In this respect, the prescription is constituted as an input, respectively an essential requirement of the design process and must be complete and unambiguous. This paper aims to analyse aspects of medical prescription as an essential requirement of the design and manufacturing process of custom-made orthopedic footwear.

KEY WORDS: orthopedic footwear, medical device, prescription, quality management

INTRODUCTION

The World Health Organization (WHO), includes therapeutic footwear (for diabetes, neuropathy and orthopedic) together with the orthoses for lower limb in Priority Assistive Products List (LPA) [1]. According to EN ISO 9999: 2016: “Assistive products for persons with disability — Classification and terminology” [2], orthopedic footwear together with foot orthoses are included in the Class “orthotics and prosthetics”, subclass “orthotics”, defined as devices applied on the surface of the considered anatomical segment with a purpose to change the structural and functional characteristics of the neuro-musculoskeletal system [3]. EN ISO 9999: 2016 defines three categories of orthopedic footwear, namely: “off-the-shelf”, “customized”, and “custom-made/bespoke”. According to existing legal regulations, medical devices (prostheses, orthoses) are used in a specialised activity “in order to overcome some organic or physiological deficiencies” [4]. Activities related to the manufacture of medical devices are supported by national insurance systems; in Romania the following categories
of devices are found, according to the purpose of this work [5]: foot orthoses, arch supports, orthopedic footwear (boots and shoes with the following types: deformities, with spring, amputations of metatarsus and phalanges, lower limb discrepancy).

Existing regulations on medical devices establish the following definitions [6, 7]:
- “medical device - any instrument, apparatus, appliance, software, material or other article, whether used alone or in combination, including the software intended by its manufacturer to be used specifically for diagnostic and/or therapeutic purposes and necessary for its proper application, intended by the manufacturer to be used for human being for the purpose of:
  a) diagnosis, prevention, monitoring, treatment or alleviation of disease;
  b) diagnosis, monitoring, treatment, alleviation of or compensation for an injury or handicap;
  c) investigation, replacement or modification of the anatomy or of a physiological process”;
- “custom-made device - any device specifically made in accordance with a duly qualified medical practitioner’s written prescription which gives, under his responsibility, specific design characteristics and which is intended for the sole use of a particular patient. The above mentioned prescription may also be made out by any other person authorized by virtue of his professional qualifications to do so”.

The process by which a custom-made medical device is introduced in the conservative treatment of foot pathomechanics must be governed both by the regulations specific to each country and the requirements of quality management systems standards such as EN ISO 9001: 2015 or ISO 13485: 2016. For the purposes of these standards, a process is defined as the activity starting from an “input” which is transformed into an “output”. Analyzing the medical devices definitions mentioned above, we see that besides the “manufacturer”, in the case of custom-made medical device a “qualified medical practitioner” or “any other person authorized by virtue of his professional qualifications” are added. It is worth noting that the standard EN ISO 13485: 2016 includes in the section “Terms and definitions” a definition for medical device but does not include one for “custom-made device” [8].

For the purpose of standard EN ISO 13485:2016 and “Global Harmonization Task Force”- GHTF/SG1/N055:2009 (developed by IMDRF-International Medical Device Regulators Forum), the manufacturer is an entity that has both the responsibility of design and/or to manufacture the medical device with the intent to make it available for use, and to ensure compliance with applicable regulations except when the latter is in the duty of another entity in accordance with the existing laws [8, 9]. In the same sense, the design and/or manufacture process may also include, in addition to manufacturing, other activities such as “development of the specifications”. It can be seen that in the case of the custom-made device in the input data of the design process the prescription is determinant, being the responsibility of the medical practitioner or of any other person authorized by virtue of his professional qualifications that gives specific design characteristics. Thus, the prescription is considered as an input, respectively an essential requirement of the design process and it has to be in accordance with EN ISO 13485: 2016: complete, unambiguous, verifiable and validated [8].

Medical Prescription Definition

According to the Explanatory Dictionary of the Romanian Language and related with the medical act “prescription represents a recommendation given by the physician to a patient (through a recipe); recommendation for using a drug” [10]. In general terms, the prescription is an “obligation, disposition, provision” or a set of “written instructions including technical conditions to be followed in the design, verification or manufacturing of a technical system” [10]. According to Belknap, S. et al., “a prescription is a health-care program implemented by a physician or other qualified practitioner in the form of instructions that
govern the plan of care for an individual patient” [11].

A complete description of the “prescription” concept is provided by the pharmacology field, the stages of the magistral preparation/drugs’ prescribing process and the one of the custom-made medical devices could be considered similar. Thus, in the medicine field the prescription represents an instruction, respectively the mean of communication between the prescribing doctor and the pharmacist achieved through a written document [12].

Constitutive elements of the medical prescription and their definition may differ from country to country, there is not yet a unique standard [12] but basically, there are 7 elements [13-15]:

- “superscriptio” - contains the header,
- “inscriptio” - contains the patient data,
- “invocatio” - contains the abbreviation (Rp or Rx) of the word “Recipe”,
- “prescriptio” (“ordinatio” / “compositio”) - in the case of magistral drugs it contains data about the necessary ingredients to be used,
- “instructio” - contains information regarding the way of drugs’ administration,
- “subscriptio” - contains instructions for the magistral drug preparation,
- “adnotatio” - contains information provided by the pharmacist (added auxiliary substances, date, price, and others).

Whichever format is used, the prescription must be unambiguous [12], as this is an essential requirement of the quality management standards for which the prescription is an input document for the medical device design [8].

Practice of Medical Devices Prescription

Medical devices based on a prescription may be used only under the guidance and instructions of an authorized specialist [14, 16]. Prescription differs from country to country both in terms of its content and of the eligible prescribers, depending on how the prescribing competencies of the medical specialities who have the responsibility for the foot pathomechanics treatment are defined. The problem of communication between the medical practitioner and the medical device provider represents a continuing preoccupation [17] and it is topical especially in the countries where specialized segments of medical devices field are not sufficiently developed [18, 19]. As far back as 1969 Henderson discusses the problem of foot orthoses prescription in the context where difficulties were noted for the eligible prescribers in order to be up to date with the evolutions in the field of medical devices design [17]. These difficulties are hindering the effective communication between medical and technical specialists leading to an implicit transfer of the medical practitioner responsibilities to the technical one in relation to the establishing of the specific design characteristics for the medical device.

From the prescription definition results that in the case of medical devices “prescriptio” must contain the name, the type and the specific design characteristics of the medical device, which, according to the custom-made device definition are the prescriber’s responsibility and not the manufacturer’s. The general template of the medical prescription presented in the legal rules of the medical devices from Romania [20] only includes the name and the type of the recommended medical device where, for example, in the case of orthopedic footwear the name may be “boots” or “shoes” while the device type is described as: “deformities”, “amputations of metatarsus and phalanges” and “lower limb discrepancy”. In the same way in which the pharmacist must prepare the magistral drugs according to the physician’s prescription, the technical specialist in the field of custom-made orthopedic footwear (from allied health professions as: pedorthist, orthopaedic shoemaker meister, orthotist) have to manufacture the product according to specific design characteristics indicated by the prescriber. The World Health Organization (WHO) has developed a “Guide to Good Prescribing” for drugs which describe the implementation process of a medical treatment, as follows [21]:

1. definition of the patient problem,
2. specification of the therapeutic objective,
3. verifying the adequacy of the treatment for a given patient’s specific case,
4. writing a prescription - initiation of treatment,
5. informing the patient about the prescribed treatment,
6. monitoring the treatment.

Diagnosis, namely identification of the pathological condition [10] or defining the patient’s problem [21] represents a preliminary stage of the prescription writing. The steps to be followed for the use of foot orthoses in the treatment are [22, 23]:
1. clinical evaluation,
2. writing prescription & and conducting measurements,
3. orthosis fitting,
4. monitoring the evolution of the treatment.

A reference example in the nomination of the medical specialists with clearly defined competencies in the medical footwear prescription comes from Australia where the eligible prescribers are: physician in medical specialities as surgical ones (vascular surgery, orthopedics), physical and rehabilitation medicine, rheumatology, geriatrics, neurology, endocrinology; specialists in physiotherapy; specialists in occupational therapy; podiatrists; orthotists / prosthetists [24, 25]. It is worth noting that in the state of New South Wales in Australia the Certified pedorthists are considered eligible prescribers [25]. According to the Pedorthic Association of Canada (PAC), the Certified pedorthist develops the medical device prescription based on the referral received from the physicians, nurses or other medical practitioners. Orthoses prescription represents the detailed instructions on how to manufacture, containing information about the design parameters, materials, composition and production [26]. It is important to understand if the “prescription” as understood by PAC has the same meaning for insurers companies from Canada who reimburse for custom-made medical devices. It is also worth noting that in some countries a medical specialist who is not included in the list of eligible prescribers may be accredited on demand for this activity through a clearly defined process [24]. In the UK where pedorthics does not exist, footwear prescription is made by an orthotist being at least at the 6th qualification level (“Specialist/Senior Practitioner”) according to professional classification in this field [27, 28]. This qualification level is obtained in the UK based on studies at an university level (higher education) unlike the situation from Romania where the qualification of orthotist-prosthetist technician is obtained through studies at the third level (secondary or post-secondary education) [29]. Unlike the situation in UK where footwear prescription is included explicitly in the orthotist’s competencies, in Romania the occupational standard for the profession of orthotist-prosthetist technician makes no reference to orthopedic footwear [27-29].

WHO together with the International Society for Prosthetics and Orthotics (ISPO) define three categories (I, II, and III) of the specialists in the Orthotic & Prosthetic field [19, 30, 31]:
- Category I: Prosthetist-Orthotist - equivalent of a four-level training (higher education with a duration of 3-4 years),
- Category II: Orthopaedic Technologist - the equivalent of a three-level training (post-secondary school education with a duration of 3 years),
- Category III: Prosthetic/Orthotic Technician - the equivalent of a two-level training, qualification at the workplace. This category works only in the medical device manufacturing process under the guidance of specialists from the first two categories.

The WHO and ISPO documents show that in the Orthotic & Prosthetic field, specialists must have a university level education in accordance with professional standards of Category I. In developing countries, in the absence of Category I, its attributions can be shared by specialists from Category II for which, according to the specific casuistry, there is the possibility to obtain the qualifications only in certain subfields such as prosthetics or orthotics for upper or lower limb [19]. According to ISPO documents Category I specialists have the professional expertise in the area of orthopedic footwear while professional Category II has competences only for footwear.
REGULATIONS FOR THE PRESCRIPTION OF FOOTWEAR AS MEDICAL DEVICE

The cited ISPO documents note that there are difficulties in establishing professional designations because of the particularities found from country to country. This is true for Romania also where it is obvious that the Occupational Standard for qualification of orthotist-prosthetist technician designates the specialized personnel according to ISPO Category II.

The medical literature is reviewing many prescription variables or specific design characteristics of the medical devices especially for foot orthoses. There is information regarding the preferences related to prescribing habits in specific geographical areas [32], studies regarding recommendations based on specialists consensus for the prescription variables for certain pathologies [33-35] or comparisons between medical devices made by different categories of specialists in relation to the treatment objective achievement [36]. In the context of the continuously developing medical devices field the question arises whether the eligible prescriber's competencies are up to date with this evolution. Also an important issue is mentioned concerning the transfer of responsibility from the prescribing specialist to the medical device manufacturer in the case of an incomplete prescription. In this context, since 1969 Henderson and Lamoreux, recognized specialists for their involvement in the study and development of UCBL foot orthosis type (University of California Biomechanics Laboratory), have proposed an approach to medical devices prescription according to the following steps [17]:

1. establishing of the “diagnosis” by the physician,
2. establishing by the physician of the “medical objectives” for using the devices, based on the information provided by other members of the interdisciplinary team,
3. establishing “functional descriptions” by the physician where the “medical objectives” are transposed into the medical device objectives,
4. developing a “treatment program” by the physician, based on the information provided by interdisciplinary team where necessary.

Under the procedure proposed above, the orthotist (or another specialist in medical devices designing field) establishes “specific design characteristics” and manufacture the device following the objectives set for it. A good example of this can be considered the transposition in terms of the prescribing procedure described by Henderson and Lamoreux of the therapeutic footwear optimizing process for patients with diabetic neuropathy described by Sicco A. Bus and others [37]. Thus for therapeutic footwear prescribed by a specialist in physical and rehabilitation medicine the following elements can be formulated:

- “medical objective”: reducing the risk of ulceration,
- “functional description”: decreasing the pressures in the at risk areas from the plantar surface of the foot 25% below initial value (criterion no. 1) or below 200 kPa (criterion no. 2). Areas “at risk” were defined as those areas where peak pressure measured with an in-shoe measuring system are more than 200 kPa.

Based on this functional description the specialist in orthopedic footwear (the pedorthist) with a minimum of 4 years’ experience in the treatment of diabetic foot has made footwear modifications, respectively an “optimization” of specific design characteristics so as to meet one of the two criteria established in the “functional description”. The authors report that footwear “optimization” lasted 53 minutes on average. Optimization algorithm of therapeutic footwear meets the requirements of quality management standards through appropriate process documentation.

An ISPO report on education in the Orthotic & Prosthetic field at European level shows that for example in Belgium the medical devices prescription by a physician is an “open prescription”, containing only the “desired orthopedic effect” which can be assimilated with the “medical objective” described above. The same document shows the existence of different practices regarding prescription rights of Prosthetist-Orthotists stressing the importance of differentiating “medical prescription” (as an attribute of the medical practitioner) by the “technical prescription” (as an attribute of Prosthetist-Orthotists of Category I) [38].
example of establishing a medical objective and a functional description as part of the prescribing of a medical device comes from the podiatry field from USA through the development of a guidelines document regarding the prescription of foot orthoses [39]. According to the USA Medicare insurance system footwear made from the positive mold of the patient’s foot (“custom-molded”) may be prescribed by a podiatrist or other qualified doctor [40]. It is obvious that where there is duly qualification [6], the medical practitioner may indicate the device’s technical specifications. The orthotist/pedorthist may participate together with the physician to assess the effectiveness of the device obtained from this process. It is worth noting that both elements of this way of prescription and the need to develop it on the basis of team activities for complex devices are found in current practice of some countries [25].

CONCLUSIONS

The prescription problem is a sensitive issue especially in countries where specialized areas of foot conservative treatment based on specific medical devices such as podiatry or pedorthics are not developed. Through the lack of the “specific design characteristics” from custom-made medical device prescription, a transfer of responsibility from the eligible prescriber to the manufacturer is realised.

Considering the fact that in the current clinical practice there are many situations where the prescription is limited only to the indication of the name and the type of the medical device, a solution to this problem could be the introduction of a regulation where based on the “diagnosis”, “medical objectives” and “functional description” developed by the medical practitioner the technical specialist may establish the “specific design characteristics” in a technical prescription.

Open approach and finding practical solutions to the problem of medical devices prescription is the only solution through the responsibilities for conservative treatment of foot pathomechanics are properly shared among the members of the interdisciplinary team. Such a “win-win situation” approach can only be to the benefit of the specialists involved in the treatment and especially to the patient who has the right to benefit from an effective treatment.

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LEATHER FINISHING WITH NEW PIGMENT PASTE

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ABSTRACT. The paper presents obtaining and characterisation of full grain bovine shoe upper leather finished with new pigment pastes containing flax seed oil (brown colour) and poppy seed oil (yellow colour) as plasticizer instead of castor oil (reference). Nitrocellulose, polyurethane or acrylic dressing were used as final dressing. Finished leathers were characterized by physical-mechanical analysis and colorimetric method before and after aging. The leathers finished with polyurethane or acrylic final dressing had the highest resistance to light after aging under the influence of artificial light in comparison with those finished with nitrocellulose dressing. Flax and poppy seed oils used as plasticizers improved resistance to ageing of coating.

KEY WORDS: pigment paste, plasticizer, castor oil, flax seed oil, poppy seed oil

INTRODUCTION

The purpose of finishing is to improve the use properties of leather and to protect it from wetting and soiling, to level out patches and grain faults, furthermore to modify the surface properties (shade, lustre, handle, etc.).

The quality of pigment pastes used to develop finishing films impart some physical-mechanical, technological, aesthetical and ecological properties to the finished leather. Cumulated, they give value of use and commercial appearance to the manufactured products: footwear, clothing, handbags, etc. Pigments are inorganic or organic compounds constituting the colouring base of covering paints. In order to be used for leather finishing, pigments have to present some characteristics, the most important being: resistance to light, atmospheric agents and temperature, brilliant colour, great covering power, great degree of dispersion, compatibility with the other components of the finishing solution [1].

The formulations of pigment pastes for leather finishing usually contain castor oil as plasticizer. Castor oil is a vegetable oil obtained by pressing the seeds of the castor oil plant (Ricinus communis) [2]. It is a triglyceride in which approximately 90 percent of fatty acid chains are ricinoleates. Oleate and linoleate are the other significant components.

The castor seed contains ricin, a toxic protein. Heating during the oil extraction process denatures and deactivates the protein. However, harvesting castor beans may not be without risk [3]. Allergenic compounds found on the plant...
surface can cause permanent nerve damage, making the harvest of castor beans a human health risk. India, Brazil, and China are the major crop producers, and the workers suffer harmful side effects from working with these plants [4]. These health issues, in addition to concerns about the toxic by-product (ricin) from castor oil production, have encouraged the quest for alternative sources for hydroxy fatty acids [5, 6].

In order to increase health and environmental protection alternative materials with low toxicity are used to develop a finishing auxiliary – pigment paste [11-15].

Flax and poppy seed oils were reported to increase the films’ resistance to yellowing over time [7, 8].

Linseed oil, also known as flaxseed oil, is a colourless to yellowish oil obtained from the dried, ripened seeds of the flax plant (Linum usitatissimum). The oil is obtained by pressing, sometimes followed by solvent extraction. Linseed oil is a drying oil, meaning it can polymerize into a solid form. Due to its polymer-forming properties, linseed oil can be used on its own or blended with combinations of other oils, resins or solvents as an impregnator, drying oil finish or varnish in wood finishing, as a pigment binder in oil paints, as a plasticizer and hardener in putty, and in the manufacture of linoleum.

Linseed oil is a triglyceride, like other fats. Linseed oil is distinctive for its unusually large amount of α-linolenic acid, which has a distinctive reaction with oxygen in air [9].

Linseed oil is a common carrier used in oil paint. It can also be used as a painting medium, making oil paints more fluid, transparent and glossy. It is available in varieties such as cold pressed, alkali refined, sun bleached, sun thickened, and polymerised (stand oil).

Poppy seed oil is a drying oil. In oil painting, it is a popular oil for binding pigment, thinning paint, and varnishing finished paintings. Some users consider “sun-thickened” poppy seed oil to be the best painting medium [10]. While poppy seed oil does not cause as much yellowish tinting of paints as linseed oil, it dries slower and is less durable than linseed oil because the fat responsible for the yellowing also provides durability [10].

The paper presents obtaining and characterization of full grain bovine shoe upper leather finished with new pigment pastes [11-13] containing flax seed oil (brown colour) and poppy seed oil (yellow colour) as plasticizer instead of castor oil (reference). Nitrocellulose, polyurethane or acrylic dressing were used as final dressing. Finished leathers were characterized by physical-mechanical analysis and colorimetric method before and after aging.

EXPERIMENTAL

Materials

The chrome tanned bovine leathers, finished and crust for shoe upper: 1.2-1.4 mm thickness; brown; obtained in the facilities of INCDTTP – Division Leather and Footwear Research Institute Bucharest, Romania.

Auxiliary materials for leather finishing from TFL Company, Germany.

- Roda wax Mono: dry substance 36.87%; pH (10% solution) 4.2; Ford cup viscosity Ф4, 12; kinematic viscosity 8.97 cSt; density 0.957 g/cm³.
- Roda-cryl 87: dry substance 34.50%; pH (10% solution) 6.0; Ford cup viscosity Ф4, 14; density 1.025 g/cm³.
- Roda-pure 302, polyurethane binder for ground coat: dry substance 30.87%; pH (10% solution) 7.5; Ford cup viscosity Ф4, 15; density 1.076 g/cm³.
- Roda-pure 5011, polyurethane binder: dry substance 40%; pH (10% solution) 5.5; Ford cup viscosity Ф4 7; density 1.053 g/cm³.
- Roda lac 93, dry substance 15%.
- Roda pur 5011, dry substance – 41%, pH – 6.5.

Other auxiliary materials for leather finishing.

- Medacril EFP34, acrylic binder, ICPAO Mediaş, Romania, dry substance 39%, pH (10% solution) 5.5, Ford cup viscosity Ф4 12, kinematic viscosity, cSt 7, density 1.033 g/cm³.
- Wax-AGE 7, Feeling agent, INCDTTP – Division ICPI, Bucharest, Romania: dry substance 18.96, pH (10% solution) 7.3, Ford cup viscosity Ф4 27 s, kinematic viscosity, cSt 10.48, density 0.975 g/cm³.

Methods

Chemical characteristics of bovine shoe upper leather were determined according to the following standards: SR EN ISO 4684:2006; Leather - Chemical tests - Determination of volatile matter; EN ISO 4048: 2008 - Determination of matter soluble in dichloromethane and free fatty acid content; SR EN ISO 5398:2008 - Leather - Determination of chromic oxide content; Part 1: Quantification by
titration; SR EN ISO 11640:2013 - Leather. Tests for colour fastness. Colour fastness to cycles of to-and-fro rubbing; SR EN ISO 5402:2003 - Leather - Physical and mechanical tests - Determination of flex resistance by flexometer method (ISO 5402:2002).

Colorimetric measurements of leather finishing were performed using a MINOLTA spectrophotometer (CM 2002), with light impulses from a xenon lamp with 0.8 cm aperture. Light reflection is focused on a silicon photo diode with wavelengths between 400 and 700 nm (10 nm steps) and L*a*b* values (chromatic coordinates: brightness, red/green and yellow/blue). In the CIE L*a*b* space used in colorimetric analysis by reflection, the tint (represented by fundamental colours – red, green, yellow and blue), brightness or clarity (represented by the chromatic stimulus varying from black to white) and saturation (purity of colour) are expressed according to three coordinates: L*, a* and b*. On the X axis, a* parameter has values between red (a* > 0) and green (a* < 0) stimuli, on the Y axis, b* parameter varies between yellow (b* > 0) and blue (b* < 0) stimuli, and L* parameter, on polar Z axis, represents brightness (grey axis), varying between white and black.

Obtaining and Characterization of Pigment Pastes
Brown and yellow pigment pastes were obtained as described in [11-13]. The formulations are presented in Table 1. The reference sample for brown colour was considered the PPR1 formulation and for yellow colour, PPG1, for which castor oil was used as plasticizer. For the formulations PPR2 and PPG2, flax seed oil was used as plasticizer and for formulations PPR3 and PPG3, poppy seed oil was used as plasticizer.

New pigment pastes were characterized by physical-chemical analyses. Physical-chemical characteristics are presented in Table 2.

Physical-chemical characteristics of new pigment pastes are similar, no much differences were observed.

Obtaining of Finished Bovine Shoe Upper Leather
The framework technology for dry finishing of bovine leather into natural grain box assortments (brown and yellow), is presented in Table 3.

RESULTS AND DISCUSSION
Characterization of Finished Shoe Upper Leathers
The finished shoe upper leathers were characterized by physical-mechanical tests and results are presented in Tables 5-7.

Physical-mechanical characteristics of thermally aged samples (IT1 and IT2) are generally inferior compared to those of not aged leathers (NA) and depend on temperature of the treatment and type of final dressing.

| Formulation/ Components | PPR 1 reference | PPR 2 flax seed oil | PPR 3 poppy seed oil | PPR 1 reference | PPG 2 flax seed oil | PPG 3 poppy seed oil |
|-------------------------|-----------------|---------------------|---------------------|-----------------|---------------------|---------------------|
| Red iron oxide, (%)     | 30              | 30                  | 30                  | -               | -                   | -                   |
| Yellow oxide, (%)       | -               | -                   | -                   | 30              | 30                  | 30                  |
| Polyacrylic binder, %   | 40              | 40                  | 40                  | 40              | 40                  | 40                  |
| Ethoxylated lauric alcohol, % | 10           | 10                  | 10                  | 10              | 10                  | 10                  |
| Castor oil, %           | 10              | -                   | -                   | 10              | -                   | -                   |
| Flax oil, %             | -               | 10                  | -                   | -               | 10                  | -                   |
| Poppy seed oil, %       | -               | -                   | 10                  | -               | -                   | 10                  |
| Wax emulsion, %         | 3               | 3                   | 3                   | 3               | 3                   | 3                   |
| Water, %                | 7               | 7                   | 7                   | 7               | 7                   | 7                   |

| Sample/ Characteristics | PPR 1 reference | PPR 2 | PPR 3 | PPG 1 reference | PPG 2 | PPG 3 |
|------------------------|-----------------|-------|-------|-----------------|-------|-------|
| Dry substance, %       | 43.83           | 43.23 | 44.45 | 47.14           | 47.33 | 48.10 |
| pH solution 10%        | 6.9             | 7.2   | 7.3   | 6.8             | 7.0   | 7.1   |
| Ash, %                 | 56.45           | 56.67 | 56.94 | 57.19           | 57.38 | 58.21 |
Characterisation of Finished Leathers by Colorimetric Method

Finished leathers were tested according to the CIE LAB system; chromatic characteristics of leather are measured and presented in Table 8.

The finished leathers were artificially aged according to ISO 17228:2015 [17].

The following abbreviations were used: IT1 – leather aged at temperature of 50°C for 7 days; IT2 – leather aged at temperature of 70°C for 7 days; IL – leather aged in artificial light (Xenon lamp) for 7 days; IUV - leather aged in UV light for 7 days.

The colour difference parameters of the tested and reference leather samples are expressed by the following equations:

\[ \Delta H^* = [\Delta E^*]^2 - [\Delta L^*]^2 - [\Delta C^*]^2]^{1/2} \] (5)

Variation of colorimetric parameters for aged finished leathers are shown in Tables 9 and 10.

The first group of samples was finished using reddish brown pastes (CL 1-CL 9) containing castor oil (CL 1, CL 4 and CL 7), flax oil (CL 2, CL 5 and CL 8) or poppy seed oil (CL 3, CL 6 and CL 9) as plasticizers and nitrocellulose (CL 1-CL 3), acrylic (CL 4-CL 6) or polyurethane (CL 7-CL 9) dressing.

After irradiation and thermal treatment, samples CL 7 and CL 8 have positive values for brightness (\( \Delta L^* > 0 \)), i.e. they have lighter (brighter) colours than sample CL 9 that has a negative value for brightness (\( \Delta L^* < 0 \)), indicating the positive influence of poppy seed oil on the colour.

\[ \Delta a^* = a^*_p - a^*_r \] (1)

\[ \Delta L^* = L^*_p - L^*_r \] (2)

Based on these equations, the following parameters can be calculated:

- chromatic shifting, through the relation:
  \[ \Delta E^* = [\Delta a^*]^2 + [\Delta b^*]^2 + [\Delta L^*]^2]^{1/2} \] (3)

- saturation or purity difference, using the relation:
  \[ \Delta C^* = [a^*]^2 + [b^*]^2 - [a^*]^2 + [b^*]^2]^{1/2} \] (4)

Table 3: Finishing technology for bovine shoe upper leather

| Operation                  | Composition of dispersion/Method of application                                      |
|----------------------------|--------------------------------------------------------------------------------------|
| Application of dispersion I | 100 g/L pigment paste PPR1/PPR2/PPR3/PPG1/PPG2/PPG3                                  |
| (basecoat)                 | 30 g/L aqueous wax emulsion (Roda wax Mono)                                           |
|                            | 300 g/L aqueous acrylic dispersion (Roda-cryl 87)                                    |
|                            | 70 g/L water                                                                          |
|                            | Application by spraying (2 passes dispersion I)                                       |
| Intermediate pressing      | In hydraulic press with the mirror or fog plate, parameters:                          |
|                            | - temperature 50-60°C; pressure 50-100 atm                                            |
| Application of dispersion I | By spraying (2-3 passes dispersion I)                                                |
| Application of final dressing | Final dressing (3 variants) with the composition presented in Table 4.             |
| (fixing)                   | Application of the final dressing by spraying (2 passes)                              |
| Final ironing              | In hydraulic press with the mirror plate, parameters:                                |
|                            | - temperature 70-80°C; pressure 50-100 atm                                            |

Table 4: Variants for final dressing of leather finishing

| Variant / Components | FN (nitrocellulose) | FA (acrylic) | FP (polyurethane) |
|----------------------|---------------------|--------------|-------------------|
| Roda lac 93, g/L     | 700                 | -            | -                 |
| Medacril EFP34, g/L  | -                   | 700          | -                 |
| Roda pur 5011, g/L   | -                   | -            | 700               |
| Wax emulsion AGE 7, g/L | 20           | 20           | 20                |
| Water, g/L           | 280                 | 280          | 280               |

Samples CL 4-CL 9 aged by IL and IUV methods have \( \Delta L^* \) parameters lower than CL 1-CL 3, indicating the positive influence of acrylic and polyurethane dressing on fastness to light of leathers compared to the nitrocellulose dressing.

\( \Delta E^* \) colour difference is higher for leather sample CL 1 than for samples CL 2 and CL 3 aged using IT1 and IUV methods. Sample CL 4 has a higher colour difference than CL 5 and CL 6 aged
Table 5: Physical-mechanical characteristics of shoe upper leathers finished with new pigment pastes and nitrocellulose dressing

| Sample/Characteristic | Nitrocellulose dressing |
|-----------------------|-------------------------|
|                       | MI | CL 1 | CL 2 | CL 3 | CL 10 | CL 11 | CL 12 |
| Flex resistance, number | NA* | 200.000 | 200.000 | 200.000 | 200.000 | 200.000 | 200.000 |
|                        | IT1** | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 | 180.000 |
|                        | IT2*** | 170.000 | 160.000 | 160.000 | 160.000 | 160.000 | 160.000 |
| Colour fastness to cycles of to-and-fro rubbing, 1-5 | NA* | 5/4 | 5/4 | 5/4 | 5/4 | 5/4 | 5/4 |
|                        | IT1** | 4/3 | 4/3 | 4/3 | 4/3 | 4/3 | 4/3-4 |
|                        | IT2*** | 5/3 | 5/4 | 5/4 | 5/3-4 | 5/3-4 | 5/4 |

NA* - not aged;
IT1** - leather aged at temperature of 50°C for 7 days;
IT2*** – leather aged at temperature of 70°C for 7 days

Table 6: Physical-mechanical characteristics of shoe upper leathers finished with new pigment pastes and polyacrylic dressing

| Sample/Characteristic | Polyacrylic dressing |
|-----------------------|----------------------|
|                       | MI | CL 4 | CL 5 | CL 6 | CL 13 | CL 14 | CL 15 |
| Flex resistance, number | NA* | 200.000 | 200.000 | 210.000 | 200.000 | 200.000 | 210.000 |
|                        | IT1** | 180.000 | 180.000 | 190.000 | 180.000 | 180.000 | 190.000 |
|                        | IT2*** | 170.000 | 170.000 | 80.000 | 170.000 | 170.000 | 180.000 |
| Colour fastness to cycles of to-and-fro rubbing, 1-5 | NA* | 5/4 | 5/4 | 5/4-5 | 5/4 | 5/4 | 5/4 |
|                        | IT1** | 4/3 | 4/3 | 4/3 | 4/3 | 4/3 | 4/3 |
|                        | IT2*** | 5/3-4 | 5/3-4 | 5/4 | 5/3-4 | 5/3-4 | 5/4 |

NA* - not aged;
IT1** - leather aged at temperature of 50°C for 7 days;
IT2*** – leather aged at temperature of 70°C for 7 days

using IUV method; likewise, CL 7 has a $\Delta E^*$ value higher than CL 8 and CL 9 similarly aged.

The second group of samples was finished using ochre yellow pigment pastes (CL 10-CL 18) containing the same plasticizers: castor oil (samples CL 10, CL 13 and CL 16), flax oil (samples CL 11, CL 14 and CL 17) or poppy seed oil (samples CL 12, CL 15 and CL 18) and nitrocellulose (samples CL 10-CL 12), acrylic (samples CL 13-CL 15) or polyurethane (samples CL 16-CL 18) dressing. Samples CL 16-CL 18 aged using IT1 and IT2 methods have negative values for brightness ($\Delta L^*<0$), therefore are darker than CL 13-CL 15, with positive values, except for sample CL 14, with $\Delta L^*<0$, aged using IT2 method.

Samples CL 10-CL 13 have positive values for brightness, i.e. become brighter than the thermally aged ones in series II.

Therefore, leathers finished with acrylic and polyurethane dressing are more resistant to ageing than those finished with nitrocellulose dressing. Samples CL 13-CL 18 aged using IT1 and IUV methods have lower values of $\Delta L^*$ parameter compared to CL 10-C 12 and are darker, which indicates a positive influence of the acrylic and polyurethane dressing on fastness to light of leathers finished compared to nitrocellulose dressing.

The lower values of $\Delta L^*$ also indicate the positive influence of plasticizer poppy seed oil used on resistance to ageing.
Table 7: Physical-mechanical characteristics of shoe upper leathers finished with new pigment pastes and polyurethane dressing

| Sample/Characteristic                  | MI     | CL 7       | CL 8       | CL 9       | CL 16      | CL 17      | CL 18       |
|----------------------------------------|--------|------------|------------|------------|------------|------------|-------------|
| Flex resistance, number                | NA*    | 250.000    | 250.000    | 250.000    | 250.000    | 250.000    | 250.000     |
|                                        | IT1**  | 250.000    | 250.000    | 250.000    | 250.000    | 250.000    | 250.000     |
|                                        | IT2*** | 240.000    | 250.000    | 250.000    | 240.000    | 240.000    | 240.000     |
| Colour fastness to cycles of to-and-fro rubbing, 1-5 | NA*    | 5/4        | 5/4        | 5/4-5      | 5/4        | 5/5        | 5/5         |
|                                        | IT1**  | 5/4        | 5/4        | 5/5        | 5/4        | 5/5        | 5/5         |
|                                        | IT2*** | 5/4        | 5/4        | 5/5        | 5/4        | 5/5        | 5/5         |

NA* - not aged;  
IT1** - leather aged at temperature of 50°C for 7 days;  
IT2*** – leather aged at temperature of 70°C for 7 days

Table 8: Colorimetric parameters for finished shoe upper leathers

| Sample code | Technological variant                  | CIE L* | CIE a* | CIE b* | CIE C* | CIE H* |
|-------------|---------------------------------------|--------|--------|--------|--------|--------|
| Brown shoe upper leather                   |         |        |        |        |        |        |
| CL 1       | PPR1- FN (castor oil/ Nitrocellulose)  | 42.35  | 22.51  | 23.69  | 32.68  | 46.46  |
| CL 2       | PPR2- FN (flax oil/ Nitrocellulose)    | 42.64  | 22.58  | 23.96  | 32.92  | 46.70  |
| CL 3       | PPR3- FN (poppy seed oil/ Nitrocellulose) | 42.39 | 21.80  | 23.44  | 31.68  | 47.72  |
| CL 4       | PPR1- FA (castor oil/acrylic)          | 42.58  | 23.09  | 24.66  | 33.63  | 46.65  |
| CL 5       | PPR2- FA (flax oil/acrylic)            | 43.09  | 23.33  | 24.99  | 34.19  | 46.96  |
| CL 6       | PPR3- FA (poppy seed oil/ acrylic)     | 42.76  | 22.81  | 23.87  | 33.02  | 46.3   |
| CL 7       | PPR1- FP (castor oil/ polyurethane)    | 41.86  | 21.31  | 23.44  | 31.68  | 47.72  |
| CL 8       | PPR2- FP (flax oil/ polyurethane)      | 42.17  | 21.43  | 23.57  | 31.85  | 47.72  |
| CL 9       | PPR3- FP (poppy seed oil/ polyurethane) | 42.7   | 21.43  | 23.33  | 31.68  | 47.42  |
| Yellow shoe upper leather                  |         |        |        |        |        |        |
| CL 10      | PPG1- FN (castor oil/ Nitrocellulose)  | 35.23  | 21.40  | 13.79  | 25.46  | 32.80  |
| CL 11      | PPG2- FN (flax oil/ Nitrocellulose)    | 35.33  | 22.01  | 14.31  | 26.25  | 33.04  |
| CL 12      | PPG3- FN (poppy seed oil/ Nitrocellulose) | 35.64 | 21.45  | 13.71  | 25.45  | 32.59  |
| CL 13      | PPG1- FA (castor oil/acrylic)          | 34.71  | 21.93  | 14.01  | 26.03  | 32.56  |
| CL 14      | PPG2- FA (flax oil/acrylic)            | 34.59  | 22.84  | 14.72  | 27.17  | 32.80  |
| CL 15      | PPG3- FA (poppy seed oil/ acrylic)     | 35.26  | 21.53  | 13.65  | 25.49  | 32.38  |
| CL 16      | PPG1- FP (castor oil/ polyurethane)    | 34.36  | 21.23  | 13.56  | 25.19  | 32.56  |
| CL 17      | PPG2- FP (flax oil/ polyurethane)      | 34.42  | 21.79  | 14.00  | 25.90  | 32.73  |
| CL 18      | PPG3- FP (poppy seed oil/ polyurethane) | 34.74  | 20.86  | 13.34  | 24.76  | 32.59  |
Table 9: Variation of colorimetric parameters for aged brown finished leathers

| Sample code | Aged Method | ΔL* | Δa* | Δb* | ΔE* |
|-------------|-------------|-----|-----|-----|-----|
| IT1         | 0.30        | 0.52| 0.39| 0.72|
| IT2         | 0.32        | 0.35| 0.46| 0.66|
| IL          | 0.31        | -0.45| -0.73| 0.91|
| IUV         | 0.86        | -0.09| 0.15| 0.36|
| IT1         | 0.13        | 0.25| 0.29| 0.40|
| IT2         | 0.26        | -0.05| 0.07| 0.27|
| IL          | 0.61        | -0.41| -0.06| 0.31|
| IUV         | 0.29        | -0.20| -0.02| 0.31|
| IT1         | -0.29       | -0.01| -0.06| 0.30|
| IT2         | -0.29       | -0.35| -0.45| 0.64|
| IL          | -0.36       | -0.83| -0.89| 1.27|
| IUV         | -0.05       | -0.20| 0.02| 0.21|
| IT1         | 0.24        | 0.11| 0.38| 0.46|
| IT2         | 0.36        | -0.18| 0.21| 0.45|
| IL          | -0.15       | -0.29| -0.39| 0.51|
| IUV         | 1.08        | 0.37| 1.03| 1.54|
| IT1         | -0.20       | 0.08| -0.10| 0.24|
| IT2         | -0.12       | 0.20| 0.07| 0.24|
| IL          | -0.09       | 0.13| 0.07| 0.17|
| IUV         | 0.02        | -0.09| -0.2| 0.22|
| IT1         | -0.10       | 0.23| 0.88| 0.92|
| IT2         | 0.44        | -0.19| 0.76| 0.90|
| IL          | -0.14       | -0.43| -0.17| 0.48|
| IUV         | 0.18        | 0.05| -0.49| 0.54|
| IT1         | 0.65        | 0.53| 0.75| 1.13|
| IT2         | 0.74        | 0.37| 0.94| 1.25|
| IL          | 0.26        | -0.25| -0.36| 0.65|
| IUV         | 0.38        | -0.07| 0.24| 1.18|
| IT1         | -0.01       | 0.14| 0.08| 0.16|
| IT2         | 0.08        | 0.17| 0.29| 0.38|
| IL          | 0.41        | 0.28| 0.53| 0.73|
| IUV         | 1.15        | 0.24| 0.40| 0.45|
| IT1         | -0.21       | 0.06| -0.20| 0.30|
| IT2         | -0.19       | -0.09| 0.08| 0.24|
| IL          | 0.29        | 0.39| 0.62| 0.79|
| IUV         | 0.10        | -0.02| 0.25| 0.27|

Table 10: Variation of colorimetric parameters for aged yellow finished leathers

| Sample code | Aged Method | ΔL* | Δa* | Δb* | ΔE* |
|-------------|-------------|-----|-----|-----|-----|
| IT1         | 0.5         | 0.4 | 0.3 | 0.41|
| IT2         | 0.2         | -0.5| -0.83| 1.05|
| IL          | 0.7         | 0.2 | -0.2| 0.70|
| IUV         | 0.36        | 0.4 | 0.76| 0.94|
| IT1         | 0.9         | -0.8| 0.46| 0.61|
| IT2         | 0.9         | -0.3| -0.01| 0.30|
| IL          | 0.8         | 0.1 | -0.19| 0.61|
| IUV         | 0.81        | 0.4 | -0.01| 0.50|
| IT1         | 0.2         | -0.2| 0.22| 0.22|
| IT2         | 0.6         | -0.26| 0.32| 0.32|
| IL          | 0.9         | 0.7 | 0.74| 1.24|
| IUV         | 0.9         | 0.7 | 0.72| 0.72|
| IT1         | 0.5         | 0.09| 0.11| 0.21|
| IT2         | 0.03        | -0.07| -0.1| 0.13|
| IL          | 0.44        | -0.27| -0.39| 0.65|
| IUV         | 0.58        | 0.0 | -0.03| 0.12|
| IT1         | 0.09        | 0.07| -0.03| 0.12|
| IT2         | -0.06       | -0.55| -0.83| 1.00|
| IL          | 0.44        | -0.31| -0.51| 0.74|
| IUV         | 0.63        | -0.42| -0.73| 1.05|
| IT1         | 0.13        | -0.08| 0.24| 0.28|
| IT2         | 0.13        | -0.35| -0.48| 0.61|
| IL          | 0.61        | 0.32| -0.07| 0.69|
| IUV         | 0.27        | 0.23| -0.12| 0.37|
| IT1         | -0.08       | -0.09| -0.05| 0.13|
| IT2         | -0.12       | 0.38| 0.31| 0.50|
| IL          | 0.43        | -0.22| -0.48| 0.68|
| IUV         | 0.39        | 0.47| 0.37| 0.57|
| IT1         | -0.29       | -0.35| -0.66| 0.80|
| IT2         | -0.32       | 0.42| 1.09| 1.21|
| IL          | 0.23        | -0.08| -0.23| 0.36|
| IUV         | 0.24        | 0.37| 0.29| 0.53|
| IT1         | -0.51       | 0.8 | 1.07| 1.43|
| IT2         | -0.73       | 0.62| 1.33| 1.64|
| IL          | 0.11        | -0.5 | -0.51| 0.72|
| IUV         | 0.08        | -0.35| -0.56| 0.67|
CONCLUSIONS

The leathers finished with polyurethane or acrylic final dressing had the highest resistance to light after aging under the influence of artificial light in comparison with those finished with nitrocellulose dressing.

Flax and poppy seed oils used as plasticizers improved resistance to ageing of coating.

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EUROPEAN RESEARCH AREA

LEAMAN - MANAGER IN AN EFFICIENT AND INNOVATIVE LEATHER COMPANY

Programme: ERASMUS+ _ Key Action 2: Cooperation for Innovation and the Exchange of Good Practices - Strategic Partnerships for vocational education and training

Agreement No: 2016-1-PT01-KA202-022831

Duration: 24 Months (01.09.2016 – 31.08.2018)

PARTNERS

The partnership was established on the basis of combining the different backgrounds, experience and expertise of the partners. There are 7 partners from 6 different European countries (2 from Portugal, 1 from Italy, 1 from Spain, 1 from Greece, 1 from Romania and 1 from Poland). All of the partners are experienced in implementing transnational projects, in the field of vocational training, or in the field of leather industry, in order to complement one another regarding their role in the project.

The coordinator of LEAMAN is CTIC - Centro Tecnológico das Indústrias do Couro - Alcanena, Portugal. The Portuguese Technological Centre for the Leather Industry - CTIC has an extensive experience in training courses for the Leather sector in Portugal as well as in leading multinational training projects (among which several Leonardo projects) in the fields of leather and shoemaking.

INCDTP-ICPI is the Leather and Footwear Research Institute (ICPI) division of the National Research and Development Institute for Textiles and Leather (INCDTP) established in Bucharest, Romania. In Romania INCDTP-ICPI possesses unique expertise and R&D facilities in the field of leather processing, shoe manufacturing and allied fields, including training.

CIAPE is the Italian National Centre for Permanent Learning, a non-profit private organisation from Roma, Italy, with a strong experience in carrying out training activities, to develop and validate soft skills, as well as competences required in the future labour market.

Virtual Campus Lda is a development, training and consulting SME in the areas of Information Systems and Technology Enhanced Learning, located in Porto, Portugal.

CRE.THI.DEV - CREATIVE THINKING DEVELOPMENT, Rafina, Greece - is a non-profit company aiming at community development through the research and development of action plans, focused on the local and social economies, mainly in the fields of life-long learning, environmental protection, employment and local development.

INESCOP - INSTITUTO TECNOLOGICO DEL CALZADO Y CONEXAS, ELDA (ALICANTE), Spain - is a non-profit organisation developing scientific and technical activities addressing the needs of the footwear industry and related sectors, that cannot normally be solved individually by the companies due to their small size.

FRP - FUNDACJA ROZWOJ PRZEDSIĘBIORCZOŚCI – (Foundation for Promotion of Entrepreneurship) located in Lodz, Poland, is a private, non-profit foundation, providing training, consultancy and information services.

AIMS & OBJECTIVES

LEAMAN project aims to enhance providing knowledge to the leather sector workforce and upgrade the provided training so that it would be
in tune with the qualification requirements that will be the basis of the labour force of the future European Leather Industry. The training will be innovative in subject as well as in methodology. It will address issues of both technological and non-technological nature, given the increasing necessity to provide a combination of sector-specific and transversal skills and competences to the professionals in the industry.

Specific Objectives

LEAMAN proposes to develop a non-formal education tool for the Managers of the leather sector, being able to guide their companies to the necessary changes and become more easily adaptable to their new role in the market. LEAMAN seeks:

- to support the implementation of the European policy agenda for growth, jobs, equity and social inclusion;
- to tackle socio-economic changes relating to changes of the Leather sector in Europe;
- to contribute, through talent and innovation, to the enhancement of competitiveness of the Leather Companies and connected ones.

To facilitate learning, this educational tool called “Being a manager in an Efficient and Innovative Leather Company” will be based on the principles of transparency, permeability and recognition of qualifications and skills through the following characteristics:

1. The Massive Open Online Course (MOOC) that will be developed will be hosted by the platform of the project and it will be incorporated in the main MOOC platforms, thus allowing its use free of charge by everyone who is interested.

2. The definition of the European Qualifications Framework for the course aims to describe the qualifications based on learning outcomes, regardless of how or where these are achieved and with ECVET scores. This EQF will serve as a reference tool to compare the qualification levels of the different qualifications systems and it will promote permeability of education through lifelong learning and equal opportunities in the knowledge-based society, as well as the further integration of the European labour market, while respecting the rich diversity of national education systems.

3. The developed MOOC will be validated through a pilot testing in the form of Learning Labs in the six countries of the project. Participants in these Labs will be asked to test all learning units and provide feedback and comments about the quality, relevancy and attractiveness of the course.

TARGET GROUPS

- VETs, policy-makers, associations and organisations dealing with leathers, universities, research centres dealing with the project topics, companies (both the leather and the connected ones) and trainers;
- Managers of the leather industry and potential ones, managers of the leather connected industries and potential ones will be offered an up-to-date open access training course appropriate to their actual needs with technological and non-technological contents;
- 1500 persons in total are expected to be impacted, by one way or another, by the project results, either by their participation in multiplier events (6 Multiplier Events are envisaged – one in each participating country), learning labs and validation workshops or by registering to the Virtual Challenge Community, by using the EQF, by visiting and testing the MOOC and the platform, by getting informed by the newsletter and by participating in the innovative leather products competition.

ENVISAGED RESULTS

LEAMAN will produce concrete and transferable results (intellectual outputs – “O”), which can be exploited even after the project conclusion, both by the partners and by other stakeholders. LEAMAN shall deliver a set of instruments for the existing and aspiring managers of the leather and leather connected industries to receive the most up-to-date and according to the anticipations of required skills and training needs knowledge and information in order to be a manager in an Efficient and Innovative leather company, as follows:
- **O1 Need analysis and state of the art** for identifying and analysing those characteristics of the leather and its connected industries today, regarding the provided training, the existing trends in the industry, the anticipated skills, and the training needs, using desk and field research;

- **O2 EQF and Professional profile of the Manager of the leather industry** - based on the research report, a European Qualification Framework (EQF) of the New Manager for Efficient and Innovative leather MEs, will be produced;

- **O3 The MOOC “Being a manager in an Efficient and Innovative leather company”** - a Massive Open Online Course (freely accessible and open licensed) with the aim of improving the knowledge and skills of managers (and potential ones) of leather industries and connected ones will be developed;

- **O4 Virtual challenge community** – a platform for the community consisting of relevant stakeholders active in the sector of leather and connected ones, which will be active during the different phases of the project and also after its end. A Decalogue describing the 10 benefits deriving from the collaboration between companies, research and training centres in developing innovative leather products, will be also produced;

- **Dissemination and exploitation** of all stages of the project as well as the results of LEAMAN through social media (Facebook, Twitter) and periodic newsletters in order to ensure maximum multiplier effects;

- **Communication and dissemination** - whose the main goal is to create a level of involvement of relevant stakeholders and to assure that the project potential audience will be as large and relevant as possible.

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**News & Events**

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