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Researching Properties of Gained Flame Retardancy on the Upholstery Leathers by Tributyl Phosphate Chemical

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Abstract

Tributyl Phosphate (TBP) is classified as organophosphorus compounds and shows a fire retardant effect in different materials. In this work, TBP was applied to the non-finished upholstery leathers at different concentrations. (0%, 8%, 16%, 24%) After the flame retardant mixture applied to the leathers, samples were finished with a standard finishing recipe. Fire retardant effect on TBP treated leathers was determined by LOI test. Also morphological properties of leathers by SEM, molecular binding characterization of leathers by ATR+FTIR Analysis and physical properties of leathers by Tensile Strength, Percentage Extension, Double Edge Tear Load, Thickness and Dry Rubbing Fastness were researched. The results showed that TBP treated leathers have a good flame retardant effect and caused to reduce physical properties in allowable values.

Keywords: Leather, Tributyl Phosphate, Flame Retardancy

1. INTRODUCTION

Nowadays, leather which is used in many different fields such as shoes, goods, garments, etc. because of some properties like porous structure, mechanical resistance, good chemical stabilization, air and water vapor permeability, water absorption and adiabaticity. However, customers expect that leather will be gained new features as waterproof, antimicrobial, flame retardancy in regard to area of usage by new technologies and chemical products. One of these features is flame retardant or non-flammable leather production and it have not still presented to the market due to the effective chemicals that are used in leather manufacturing processes or methods cause it to burn easily and also leather products contain some inflammable organic compounds. The production of flame retardant leather is important for some leather types as motorcyclist jackets, flight or automotive upholstery leathers. If these type leathers ignite lately, the retardant property of material will provide gain in time to rescue humans and animals during the fire. Flame retardants can have classified as halogen containing flame retardants and halogen-free flame retardants. However, textile or different industries as plastic, chemical, etc. have chosen halogen free flame retardants due to their advantages of low smoke, low toxicity, low corrosion, etc. Phosphorus based flame retardant chemicals are one of these categories and there are many written work about the effects of flame retardants in literature. Tributyl Phosphate (TBP) is classified as organophosphorus compounds and shows a fire retardant effect in different materials. In this work, TBP was applied to the non-finished leathers at different concentrations. (0%, 8%, 16%, 24%) After the flame retardant mixture applied to the leathers, samples were finished with a standard

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finishing recipe. Fire retardant effect on TBP treated leathers was determined by LOI test. Also morphological properties of leathers by SEM, molecular binding characterization of leathers by ATR+FTIR analysis and physical properties of leathers by tensile strength, percentage extension, double edge tear load, thickness and dry rubbing fastness were researched.

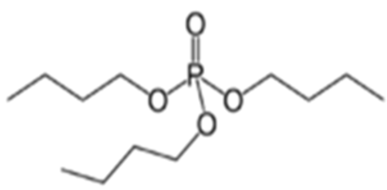


Figure 1. Chemical Formulation of TBP

2. MATERIAL AND METHODS

2.1. Material

Brown color cattle upholstery and natural floater type leathers which was not made finishing process and was dried by toggling machine, were supplied from a leather company.(Stahl Company, Turkey) Tributyl Phosphate- TBP (97%) was obtained from Sigma (St. Louis, USA), 2-Propanol (≥99.5%) was obtained from Sigma (St. Louis, USA). In the finishing recipe; different chemicals were used, Sarpur 317 and Sarpur 303 (Sarchem b.v.) as polyurethane binder, Saracryl 527 and Saracryl 588 (Sarchem b.v.) as acrylic binder, Sarfill 8537 (Sarchem b.v.) as filler, Sartop 111 as protein binder Sartop 1002 as casein binder, Sarkol K Dark Brown (Sarchem b.v.) as Pigment, Melio Wax 185 (Clariant b.v.) and Sarwaks 8147 (Sarchem b.v.) as wax, Supronil Dark Brown (Clariant b.v.) as anilin dye, Sartop 118 (Sarchem b.v.) as protein binder, Melio EW 348B (Clariant b.v.) as hydrolacque, Melio WF 5226 (Clariant b.v.) as feeling agent.

2.2. Methods

15 pieces leather samples (140 mm x 60 mm) were symmetrically cut from the part next to the back bone of the cattle for limit oxygen index (LOI) test. Tributyl Phosphate-2-Propanol (TBP-IPA) mixtures were prepared at different concentrations for the flame retardant application. (0%, 8%, 16%, 24%). Also 0% group leather samples were only applied IPA solution for the homogenous application. Surface of leather samples were treated with TBP-IPA solutions by Leather Padding Technique which is a kind of finishing technique, made by hand and is used for the intense or decorative pattern finishing applications. All leathers were dried in the room temperature for 24 h and then same application was repeated once again. After the proposed flame retardant mixture applied, samples were finished with a standard finishing recipe and the finishing recipe is given in Table I. Finsihing application; mixture of 1 number is applied to all groups as 2x Spray, Press (70 atm, 90 oC,1sn), 1 x Spray, Press (70 atm, 90 oC,1sn) and then mixture 2 number is applied as 1 x Spray, Press (70 atm, 90oC, 1 sn).

Table 1. Finishing Recipe of TBP Applied Leathers

Chemical	Rate
1)Polyurethane Binder (g)	100
Acrylic Binder (g)	100
Protein Binder (g)	25
Filler (g)	35
Casein Binder (g)	25
Waks (g)	30
Pigment Dye (g)	80
Anilin Dye (g)	20
Water (g)	500
2)Hydrolaque (g)	100
Feeling Agent (g)	10
Water (g)	150

2.3. Measurements

Limit oxygen index (LOI) tests were performed on a limiting oxygen index chamber with strips of fabrics according to ASTM D 2863-77 in Dokuz Eylül University Textile Department Test Laboratory. 15 pieces leather samples for each group (140 mm x 60 mm) were taken from flame-retardant leather and were used for parallel tests. For SEM analysis the samples were placed on a scanning electron microscope (Fei-Quanta Feg 250) and their images were taken at 100 µm and 20 µm magnifications. FTIR analysis was conducted in order to determine the differences in the chemical properties of leather treated with TBP and control group (0%). FTIR studies were conducted on Bruker-Vertex70 ATR device with ATR equipment. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-600 cm-1 and the results were evaluated in the FTIR Spectrum Software and compared with the spectrums in the literature. Leathers were conditioned under standard atmospheric conditions as recommended in EN ISO 2419 at a temperature of 23 °C ± 2 °C and 50% ± 5% relative humidity, and sampling locations were carried out according to EN ISO 2418. The dry rubbing fastness of the TBP treated samples was measured according to EN ISO 11640 (50 motions) using Otto Specht Bally Finish Tester 9029. Changes in the color of the leather and the felt were measured using a grey scale according to ISO 105-A02 and ISO 105-A03. Thickness identification of samples was made according to EN ISO 2589. Determination of tensile strength, percentage extension, double edge tear load of the samples were measured according to EN ISO 3376 and EN ISO 3377-2 respectively, using Shimadzu AG-IS Test Apparatus. Thermogravimetry/differential thermal analysis (TG/DTA) of flame retardant leathers (0%, 8%, 16% and 24%) were conducted at heating rates of 20 oC min-1 under air atmosphere (flow 60 mL min-1) between 35 oC and 800 oC temperatures using SII Exstar TG/DTA 6300 (Nanotechnology SII 6000). Sample mass was approximately 5 mg. TG/DTA curves were mapped by computer automatically.

3. RESULTS AND DISCUSSION

3.1. Limit Oxygen Index (LOI) Test

LOI results of TBP treated Leathers was given- in Table 2. The LOI value of leather samples treated with TBP increased with increasing content from 8% to 24%. The TBP treated leather has better flame retardant effect than control group and the highest LOI reaches 30.5%. Flame behavior of natural leather is generally higher than other protein fibers as silk, cotton or wool. While LOI values can be approximately 18-19% in cotton, 23% silk and 25% wool; LOI results of natural leather without flame retardant change around in 26-28% due to fact that leather manufacture be different industry than textile fibers. In addition, type of leather (garment, goods, upholstery, etc.), finished type, type of animal (goat, sheep, cattle, etc.); types and quantities chemicals used in leather processes influence the LOI test results. A little highest LOI results of control group can be related with this situation in Table I. When compared flame retardancy leather studies in literature; Lyu et al. used nanocomposite based on erucic acid modified montmorillonite/sulfited rapeseed oil in fatliquaring process for flame retardant leather product and they found maximum 27.9% LOI value in leather samples. Jiang et al. synthesized montmorillonite-amino resin and used in hide powder (collagen fiber) that is not a finished leather product. According to results they reached maximum 30.9% LOI test result. In a similar works Yang et al. searched melamine based flame retardant effect in goat skin fibers and they found maximum 34.8% LOI value. Xu et al. applied tetrakis hydroxymethyl phosphonium–melamine–pentaerythritol-diphosphorate (THPM) to semi-product wet blue leather and after treated, the LOI test results are showed maximum 32.9%. However finishing process in leather product can be reduced LOI values because of used finishing chemicals such as feel modifier, duller, anti-tack agents, waxes, etc. and so effect of different flame retardants in searches should be determine after leather manufacture was completed. So the decline of LOI values than other searches is found normally values due to fact that leathers was finished standard finishing recipe and LOI results are obtained from commercial leather product and TBP treated leathers can satisfy the requirements for flame-retardant leather and showed a real flame retardant effect in the finished leathers.

Table 2. LOI Results of TBP Treated Leathers

Group	LOI (%)
%0	28.5
%8	28.5
%16	29.9
%24	30.5

3.2. SEM Analysis of TBP treated leather

SEM results of 0%, 8%, 16% and 24% TBP treated leathers was shown in Figure 2, Figure 3, Figure 4. and Figure 5. According to result in all SEM imagines, surfaces of leathers have some impurities that can come from finishing chemicals. But grain structures of leathers are non-critical shrunk by increasing TBP rates.

Figure 2. SEM Imagines of 0% TBP Treated Leathers

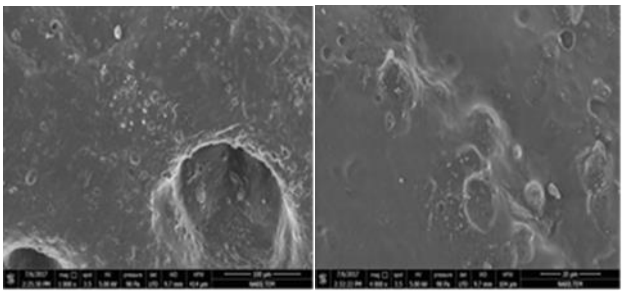


Figure 3. SEM Imagines of 8% TBP Treated Leathers

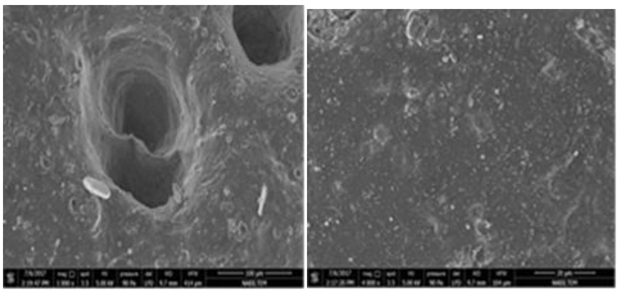


Figure 4. SEM Imagines of 16% TBP Treated Leathers

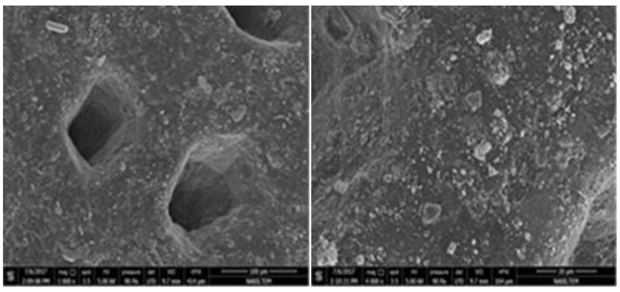
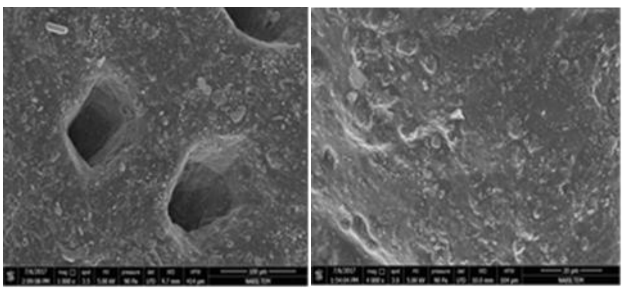


Figure 5. SEM Imagines of 24% TBP Treated Leathers



3.3. ATR-FTIR Analysis of TBP Treated Leathers

ATR-FTIR spectrum for finished leathers control group and 0%, 8%, 16% and 24% treated with TBP are given in Fig. 6. The spectral range of 3000-2800 cm-1 is typical for CH stretch in aliphatic compounds. While in FTIR spectrum 3299 cm-1, 2918 cm-1, 2851 cm-1 peaks are observed because of Amide B group (consists of asymmetric CH2 groups) of collagen protein structure; the stretching vibration band of 2958 cm-1 peak occurred the high intensity of the methyl asymmetric stretching by increasing TBP rates. This is related with butylene groups in TBP flame retardant chemical. [27] [28] As depending increasing TBP rates, peaks of 8%, 16% and 24% groups was comprised 1095 cm-1 which is related to be P=O stretching intensive vibration, while 1059 cm-1 peak was diminished because of binding of TBP to surface of leathers. [29] Similarly the stretching of 1276 cm-1 and 1643 cm-1 peaks which is represent C-N groups and the aromatic rings respectively in leather, are clearly decreased in 8%, 16% and 24% FTIR spectrums because of binding in reaction of phosphorous compounds and collagens, both P-C and C-O bonds. [30] Also the absorption peak at 539 cm-1 that corresponds to the bond of P-Cl, gave stronger stretching depend on increasing TBP rates. [4]

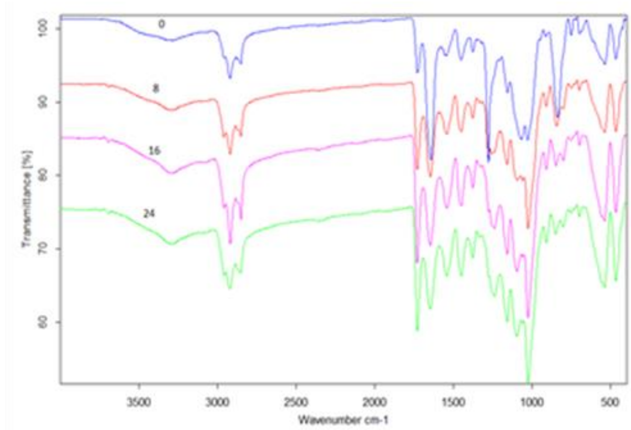


Figure 6. ATR-FTIR Results of TBP Treated Leathers

3.4. Thermogravimetric analysis (TGA) Analysis of TBP Treated Leathers

Figure 7. shows TG, DTG and DTA curves by graphical illustration untreated and TBP treated leather samples under air at a heating rate of 20 oC. According to TGA results; while 8%, 16% and 24% TBP treated leathers reached fractionally to maximum flame temperature because of flame retardant effect of TBP chemical, was seen that big part of 0% TBP treated leather sample burnt in maximum temperature.

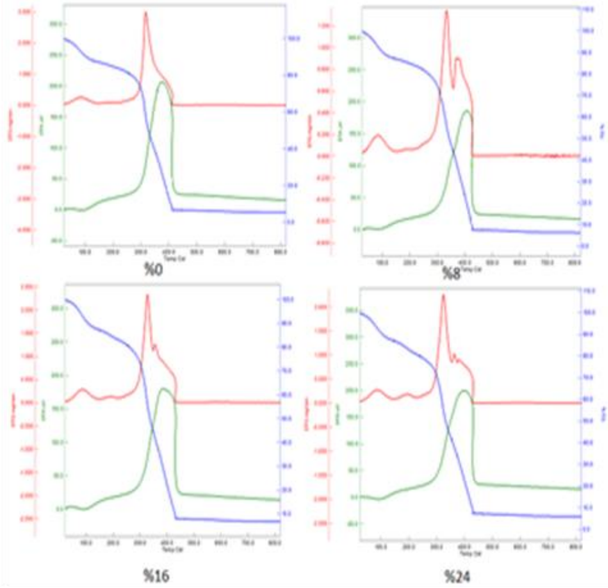


Figure 7. TGA Results of TBP Treated Leathers

In Table 3. the degradation temperatures of flame-retardant leather have increased, the temperature of maximum weight loss rate increases from 317.95oC to 328.76oC. Also it can be said that in TGA analysis of 16% and 24% TBP treated leathers, TBP did not cause the big differences values in order to reduce burning behavior of leathers.

Table 3. The Temperature of Maximum Weight Loss in TGA Analysis of TBP Treated Leathers

Group	0%	8%	16%	24%
T_{max} (°C)	317.95	322.82	327.98	328.76

3.5. Physical Properties of TBP Treated Leathers

Leathers should have enough strength properties, depending on the application field. Acceptable quality standards recommended by United Nations Industrial Development Organization (UNIDO), for upholstery leathers offers minimum of 20 N/mm2 of tensile strength, maximum of 75% tensile extension, minimum of 100 N of double edge tear load and minimum 4 rating in felt.[31] According to physical fastness results of TBP treated leather in given Table IV; all results showed that the increasing TBP amount cause to reduce physical properties at acceptable limiting values. The tensile strength values obtained from leather samples are varied from 34.06 N/mm2 to 19.7 N/mm2. However the value of 16% TBP treated group gave some lower than acceptable UNIDO value. But this result is associated with non-homogeneous structure of naturel leather products and it is considered to be at limiting tensile strength values. Tear extension values obtained from TBP treated leathers are higher than the elongation limit of 75 % as indicated by UNIDO. Also the increase of amount of TBP chemical at the leathers gave rise obviously to reduce the leather thickness. Dry rubbing fastness of 0%, 8% and 16%TBP treated leathers in felt resulted in 4/5 and 4 respectively and these results indicated that leathers meet the standards of UNIDO recommended for upholstery (furniture) leathers. However one sample in only 24% TBP treated group gave 3/4 rating results because of application mistake. All in all; it can be said Physical Properties of TBP Treated Leathers significantly fulfilled the requirements of UNIDO.

Table 4. Physical Properties of TBP Treated Leathers

Group	Tensile Strength (N/mm^2)	Percentage Extension (%)	Double Edge Tear Load (N/mm)	Thickness (mm)	Dry Rubbing Fastness (Felt)		
0%	34.06	70.4	201.8	1.51	4/5	4/5	4/5
8%	24.25	72.7	179.25	1.50	4/5	4	4/5
16%	19.7	73.6	120.7	1.47	4	4	4
24%	20.95	73.85	126.65	1.43	4/5	3/4	4

CONCLUSIONS

This study is supported by Sakarya University Scientific Research Projects Coordination Unit. Project Number: 2016-01-02-001. In leather manufacture; to produce an effective flame retardant leather is so important for some leather types. The oxygen index of the fire-retardant leather with 24% TBP increased significantly to a value of 30.5 %. The TGA results indicate that the TBP fire-retardant material can effectively inhibit the leather burning and reduce its mass loss, therefore effectively improve leather thermal stability and flame-retardant effect. Although physical properties of leathers decreased by increasing TBP rates; all values of fastness are found in recommendations standard values of UNIDO. In this way the research proved that TBP can be confidently used in order to obtain flame retardant leather. However 16% and 24% values obtained from all tests are so similar and in commercial leather product it is not necessary to rise amount of TBP chemical. It can be said that the ideal usage dosage of TBP for flame retardant leather is around 16%.

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REFERENCES

[1] A.I. Renzi, C. Carfagna, P. Persico, “Thermoregulated natural leather using phase change materials: An example of bioinspiration”, Applied Thermal Engineering, vol. 30, pp. 1369-1376, 2010.

[2]. B.R. Duan, Q.J. Wang, “Influence of Flame Retardant on Leather Fatliquoring and Fire Resistance”, International Conference on Emerging Materials and Mechanics Applications, pp.748-752, 2012.

[3]. Y. Jiang, J. Li, B. Li, H. Liu, Z. Li, L. Li, “Study on a novel multifunctional nanocomposite as flame retardant of leather”, Polymer Degradation and Stability, vol. 115, pp. 110-116, 2015.

[4]. B. Li, J., Li, L. Li, Y. Jiang and Z. Li, “Synthesis and Application of a Novel Functional Material as Leather Flame Retardant”, Journal- American Leather Chemists Association, vol. 14, pp. 239-245, 2014.

[5]. B. Schartel, “Phosphorus-based Flame Retardancy Mechanisms—Old Hat or a Starting Point for Future Development?”, Materials, vol. 3, pp. 4710-4745, 2010.

[6]. E. Schmitt, “Flame retardants Phosphorus-based flame retardants for thermoplastics”, Plastics Additives and Compounding, vol. 9, no. 3, pp. 26–30, 2007.

[7]. ASTM D 2863-77, “Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)”, 2006.

[8]. EN ISO 2419, “Leather Physical and mechanical tests Sample preparation and conditioning”, International Organization for Standardization, 2012.

[9]. EN ISO 2418, “Leather Chemical, physical and mechanical and fastness tests Sampling location”, International Organization for Standardization, 2002.

[10]. EN ISO 11640, “Leather Tests for colour fastness Colour fastness to cycles of to-and-fro rubbing”, International Organization for Standardization, 2012.

[11]. EN ISO 105-A02, “Textiles Tests for colour fastness Part A02: Grey scale for assessing change in colour”, International Organization for Standardization, 1993.

[12]. EN ISO 105-A03, “Textiles -- Tests for colour fastness -- Part A03: Grey scale for assessing staining”, International Organization for Standardization, 1993.

[13]. EN ISO 2589, “Leather - Physical and mechanical tests - Determination of thickness”, International Organization for Standardization 2016.

[14]. EN ISO 3376, “Leather – Physical and mechanical tests - Determination of tensile strength and percentage extention”, International Organization for Standardization, 2002.

[15]. EN ISO 3377-2, “Leather -- Physical and mechanical tests -- Determination of tear load -- Part 2: Double edge tear”, International Organization for Standardization, 2002.

[16]. Q. Zhanga, J., Gua, G. Chena, T. Xinga, “Durable flame retardant finish for silk fabric using boron hybrid silica sol”, Applied Surface Science, vol. 387, pp. 446–453, 2016.

[17]. W. Zhang, T-L. Xİng, Q-H. Zhang, G-Q. Chen, “Thermal Properties of Wool Fabric Treated By Phosphorus-Doped Silica Sols Through Sol-Gel Method”, Thermal Science, vo. 18, no. 5, pp. 1603-1605, 2014.

[18]. Shodhganga website, Flammability of Textile, 2017, Available: www.shodhganga.inflibnet.ac.in, [Accessed: 24-JULY-2017].

[19]. Natureworks website, Fiber and Fabric Properties,2017, Available: www.natureworksllc.com, [Accessed: 24-JULY-2017].

[20]. F. Cheng, L. Jıang, W. Chen, C.C. Gaıdau, L. Mıu, “Influence of Retanning Materials with Different Roperties on The Flammability of Leather”, 4th International Conference on

Advanced Materials and Systems, p.179-186, 2012.

[21]. A. Bacardit1, M.D. Borràs, J. Soler, V. Herrero, J. Jorge, L. Ollé, “Behavior of leather as a protective heat barrier and fire resistant material”, Journal- American Leather Chemists Association, vol. 105, pp. 51-61, 2010.

[22]. B. Lyu, J. Gao, J. Ma, D. Gao, H. Wang, X. Han, “Nanocomposite based on erucic acid modified montmorillonite/sulfited rapeseed oil: Preparation and application in leather”, Applied Clay Science, vol. 121–122, pp. 36–45, 2016.

[23]. L. Yang, Y. Liu, Y. Wu, D. Lanli, L. Wei, M. Chunping, L. Li, “Thermal degradation kinetics and flame retardancy of hide treated with montmorillonite-amino resin nano-composite”, Journal- Society of Leather Technologists and Chemists, vol. 94, no. 1, pp. 9-14, 2010.

[24]. L. Yang, L. Liu, C. Ma, Y. Wu, W. Liu, C. Zhang, F. Wang and L. Li, “Kinetics of Non-Isothermal Decomposition and Flame Retardancy of Goatskin Fiber Treated with Melamine-Based Flame Retardant”, Fibers and Polymers, vol. 17, no. 7, pp. 1018-1024, 2016.

[25]. W. Xu, J. Li, F. Liu, Y. Jiang, Z. Li, L. Li, “Study on the thermal decomposition kinetics and flammability performance of a flame-retardant leather”, Journal of Thermal Analysis and Calorimetry, vol. 128, pp. 1107–1116, 2017.

[26]. Y. Gong, W.Y.. Chen, J.P. Chen, H.B. Gu, “Influence of finishing on the flammability of leather”, Journal Of The Society Of Leather Technologists And Chemists, vol. 91, no. 5, pp. 208-211, 2007.

[27]. R. Artzi, S.S. Daube, H. Cohen, R. Naaman, “Adsorption of Organic Phosphate as a Means To Bind Biological Molecules to Gas Surfaces”, Langmuir, vol. 19, pp. 7392-7398, 2003.

[28]. S. Shuangxi, S. Kaiqi, L. Ya, J. Lan, M. Chun’an, “Mechanism of Chrome-free Tanning with Tetra-hydroxymethyl Phosphonium Chloride”, Chinese Journal of Chemical Engineering, vol. 16, no. 3, pp. 446-450, 2008.

[29]. A.N. Pudovik, “Atlas of IR spectra of organophosphorus compounds. (Interpreted Spectrograms)”, Moscow/London: Nauka Publishers/Kluwer Publishers; 1990. p. 5.

[30]. F. Ahmed, R. Dewani, M.K.. Pervez, S.J. Mahboob, S.A. Soomro, “Non-destructive FT-IR analysis of mono azo dyes”, Bulgarian Chemical Communications, vol. 48, no. 1, pp. 71-77, 2016.

[31]. UNIDO, “Acceptable Quality Standards in the Leather and Footwear Industry”, United Nations Industrial Development Organization, Vienna, 1996