The Flame Retardant Effect Of Tributyl Phosphate On The Leathers

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Abstract: The production of flame retardant leather is important for some leather types as motorcyclist jackets, flight or automotive upholstery leathers. For this reason, in this research it is aimed to produce flame retardant leather and effect of flame retardant on leathers treated with Tributyl Phosphate (TBP) were investigated. Tributyl phosphate (TBP) chemical solutions were applied to the leathers at differing rates that are; 0%, 7%, 14% and 21% by padding finishing technique and after the flame retardant application, the leathers were finished with traditional finishing recipe. Flame retardant property of leathers were researched by vertical (ISO 6941:2007) and horizontal (ISO 3795: 1989) fire resistance tests. Also leathers were characterized by TG+DTG and SEM. The results showed that TBP treated leathers have good flame retardant properties and can enhance effectively the fire retardancy of leathers.

Index Terms: Leather, Fire, Flame Retardant, Tributyl Phosphate

1. INTRODUCTION

Leather which is widely used in every part of our life, is more different material than textile because of its organic nature. Although textile industry has realized many applications like antimicrobial, waterproof, antistatic, flame retardancy, non-flammable, etc., some of these applications have been used in the leather industry by different methods. However, flame retardant or non-flammable leather production still have not 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 and harmful organic compounds.1,2 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.3,4 Flame retardants are one of the most important additives for the materials to improve their fire resistance. Briefly, they can be 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 and no molten dripping during fire. 5,6,7,8 Phosphorus based flame retardant chemicals are one of these categories and there are many written work about the effects of flame retardants in literature. Some of them are ammonium polyphosphate, melamine phosphate, monomeric cyclic phosphonate, phosphorylated pentaerythritol, oligomeric phosphatephosphonate, tributyl phosphate (TBP), triphenyl phosphonate (TPP), triphenylphosphine oxide (TPPO), triallyl phosphate (TAP) and triallyl phosphoric triamide (TPT). When flame retardancy mechanisms of phosphorus based flame retardants is examined; they start to pyrolysis during the combustion and their decomposition products may react into volatile or solid products. Especially carbon is replaced by phosphor and this change leads to reduced heat release of burning compound. 9,10,11 TBP is one of these retardants (Figure 1.) and it is known as very effective on flame retardant textile products. However, there is not any work in literature about flame retardant effect of TBP on leather products and flame retardant effect of TBP on the finished leathers is researched in this paper.

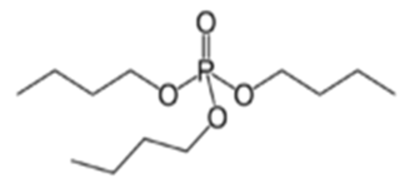

Figure 1. *Chemical Formulation of TBP*

2. MATERIAL AND METHODS

2.1. Materials

Black color cattle leathers which did not had finishing process, 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 (Sarchemb.v.) aspolyurethanebinder,Saracryl 588 (Sarchemb.v.) as acrylic binder,Sarfill 8537 (Sarchemb.v.) as filler, Sarkol K Black (Sarchemb.v.) as black Pigment,Sarwaks 8147 (Sarchemb.v.) as wax, Selladerm Black (TFL Company) asanilin dye, Sartop 118 (Sarchemb.v.) as protein binder, Melio EW 348B (Clariantb.v.) ashydrolacque, Melio WF 5226 (Clariantb.v.) as feeling agent.

2.2 Method

Leather samples were cut into 3 pieces sized 170 x 560 mm for vertical flammability test and into 5 pieces sized 95 x 350 mm for horizontal flammability test. First, Tributyl Phosphate-2-Propanol (TBP-IPA) mixtures were prepared at different concentrations for the flame retardant application. (0%, 7%, 14%, 21%). 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 1.

TABLE 1: *FINISHING RECIPE OF TBP APPLIED LEATHERS*

Chemical	Rate (gram)	Finishing Application
Polyurethane Binder	100	1)2x Spray
Acrylic Binder	100	Press (70 atm, 90 oC,1sn)
Filler	35	1 x Spray
Protein Binder	50	Press (70 atm, 90 oC,1sn)
Black Pigment	80	
Wax	75	
Anilin Dye	20	
Water	450	
Hydrolaque	100	2)1 x Spray
Feeling Agent	10	Press (70 atm, 90oC, 1 sn)
Water	150	

2.3 Measurements

The flammability measurements of leathers were evaluated by vertical (ISO 6941:2007) and horizontal (ISO 3795: 1989) fire resistance tests. For the vertical flammability test, samples are placed in a rectangular frame in a vertical position. 12,13 Conditions of test environment were conditioned at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 4%. Vertical flammability test was performed at 21 oC temperature and 57% relative humidity. Butane gas was used for the test. Leather samples were exposed for 10 at 40 mm flame height and contacted with flame situated perpendicularly to the sample surface or directly below the sample edge. For the horizontal flammability test, samples are placed in a U-shaped frame in a horizontal position. Conditions of test environment were conditioned at 23 ± 2 °C and 50 ± 5% relative humidity. Horizontal flammability test was carried out at 22 °C temperature and 56% relative humidity environment and also methane gas was used. Leather samples were exposed to fire for 15 seconds at a 38 mm flame height. Thermogravimetry/differential thermal analysis (TG/DTA) of flame retardant leathers (0%, 7%, 14% and 21%) 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. The samples were placed on a scanning electron microscope (Zeiss EVO LS 10) 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 a Perkin-Elmer Spectrum 100 device with ATR equipment. For this purpose, the leather samples were scanned with IR spectrums at a wavelength of 4000-400 cm-1 and the results were evaluated in the FTIR Spectrum Software (Perkin Elmer) and compared with the spectrums in the literature.

3. RESULTS AND DISCUSSION

3.1 Vertical Flammability Test of Leathers

0%, 7%, 14% and 21% vertical flammability test results were given Table 2. According to results, vertical flammability of 0% TBP treated leather show 0 second flame expansion time, 15-75 s flame combustion time and approximately 12-46 s flameless combustion time when the flame is edge situated. However vertical flammability of 7%, 14% and 21% TBP treated leathers are observed non-ignitable materials (combustion time: 0 mm/min). This result is attributed that TBP possibly cross-linked nitrogen containing resins or ammonium containing chemicals which is found in leather fibers and the ignition of leather is prevented by this nitrogen and phosphoric acid interaction.11 Also 0% TBP treated group is ignited, but flame in leather is going out before the first point of the measurement. This is related with natural structure of leather and similar result obtained in a work which is compared flammability between natural leather and artificial PU leather. It showed that flammability of natural leather without flame retardant has got more durable than artificial PU leather due to be effect of fat-liquoring chemicals and tanning agents.14,15 Interesting phenomena is 7%, 14% and 21% TBP treated leathers showed no ignition in vertical flammability test like horizontal flammability test although TBP chemical is applied on surface of leathers. This is related to TBP has reached into leather fibres by IPA, being used as penetrator in leather industry, and so phosphate in this chemical transfer its retardant effect inside leather samples. In this way TBP chemical is not only showed effect in horizontal flammability test but also influenced in vertical flammability test results.16

TABLE 2: *VERTICAL FLAMMABILITY TEST RESULTS OF LEATHERS*

Group	Flame Expansion Time (s)	Ignition	Flame CombustionTime (s)	Flameless Combustion Time (s)
0-1	0	Non Ignition		
0-2	0*	Ignition	15	46 min 45 s
0-3	0*	Ignition	75	12 min 10 s
7-1	0	Non Ignition		
7-2	0	Non Ignition		
7-3	0	Non Ignition		
14-1	0	Non Ignition		
14-2	0	Non Ignition		
14-3	0	Non Ignition		
21-1	0	Non Ignition		
21-2	0	Non Ignition		
21-3	0	Non Ignition		

3.2 Horizontal Flammability Test of Leathers

0%, 7%, 14% and 21% horizontal flammability test results were given Table 3. results obtained by using ISO 3795:1989 method which is important due conduct surface measurements of flammability on leathers. According to results, that are obtained from 0% TBP treated leathers with sample numbers 3,4 and 5 that are burned and ignited as smoldering but flame went out before the first point of the measurement. For this reason, flame expansion time of that group of samples is zero. However, leathers with sample number 1 and number 2 showed that flammability degree are 1.0-1.9 mm/min respectively, 5-16 mm length of sample burned and 54 s to 1005 s combustion time. These different results can be related with non-homogenous structure of natural leather.14,17 But also 0* result of leathers with sample numbers 3,4 and 5 may be related to the fact that natural leather has more difficult flaming property than other materials. However, after TBP application leathers showed effective results in horizontal flammability test. 7% and 14% TBP treated leathers burned out before the first point of the measurement and also flame expansion times are zero without number 2 of 14% TBP treated leather. Difference of number 2 than other samples is related as standard deviation to be application mistake during the TBP implementation on surface of leather. Interesting phenomenon is non-ignition at 21% TBP treated leather samples. Also 21% TBP rate in leathers provide more flame retardancy effect than 7% and 14% TBP treated leathers. In this way TBP can effectively reduce the combustion properties of leather and increase its non-flammability.

TABLE 3: *HORIZONTAL FLAMMABILITY TEST RESULTS OF LEATHERS*

Group	1	2	3	4	5
0 %	Flammability Degree: 1.0 mm/min Length of Sample Burnt: 16 mm Combustion Time: 1005 s	Flammability Degree: 1.9 mm/min Length of Sample Burnt: 5 mm Combustion Time: 54 s	0*	0*	0*
7%	0*	0*	0*	0*	0*
14%	0*	Flammability Degree: 2.3 mm/min Length of Sample Burnt: 130 mm Combustion Time: 3417 s	0*	0*	0*
21%	0	0	0	0	0

3.3 Thermal Degradation of Leathers

Figure 2 shows TG, DTG and DTA curves by graphical illustration untreated and TBP treated leather samples under air at a heating rate of 20 oC and at Table 4, 0%, 7%, 14% and 21% TBP treated leathers are given mass loss of TBP treated leathers at initial, middle and final stages.

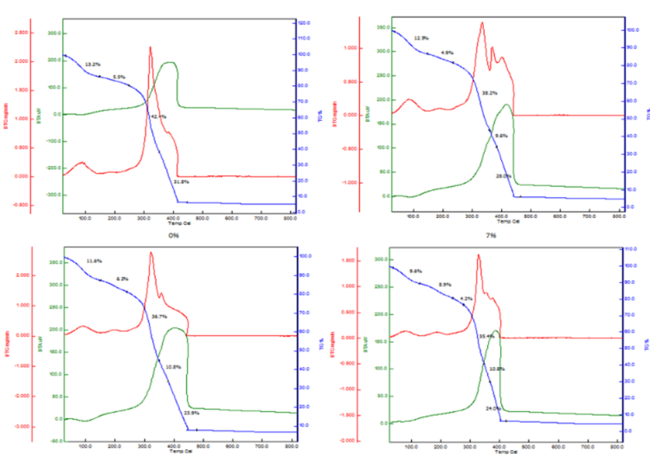

Figure 2. *Results of Thermal degradation on TBP Treated Leathers*

According to results, DTA analysis at about 350 °C has an exothermic peak as a wide curve in all groups, this decomposition may occur because of the oxidation of trivalent chromium as stated in Kozlowski et al. research.14 The thermogram data of the leather samples indicate that the actual decomposition of leather starts around 300-400 oC depending on the rate of TBP. Before the decomposition temperature, there is a slight weight loss due to loss of water in leather samples. 7%, 14% and 21% TBP treated leathers have gradually decomposition while 0% TBP treated leather samples decomposed large part of them with one sharp curve between 300-400 oC and this show that samples have slower combustion rate at the actual decomposition area after TBP application on leather samples.8,9,10,11 However, the percentage of mass loss at initial stage of decomposition is also important to carry out flame retardancy effect of leather. Mass loss of leathers at the initial stage is reduced depending on increasing TBP rates in Table 4. This attributes that TBP can interact with nitrogen containing resin tannins or other leather chemicals that are containing ammonium. In this way the results indicate that thermal stability of leather can be improved by synergic effect of nitrogen and TBP.

TABLE 4: *MASS LOSS OF TBP TREATED LEATHERS AT INITIAL, MIDDLE AND FINAL STAGES*

Group	Mass Loss at Initial Stage (35-150 oC)	Mass Loss at Middle Stage (150-350 oC)	Mass Loss at Last Stage (350-800 oC)
0%	13.2 %	47.9 %	37.3 %
7%	12.5 %	43.1 %	37.5 %
14%	11.6 %	42.9 %	36.6 %
21%	9.6 %	48.5 %	3 %

3.4 ATR-FTIR Analysis of Leathers

ATR-FTIR spectrum for finished leathers control group and 7%,14% and 21% treated with TBP are given in Figure 3. Leather consisting of Type-1 collagen based protein was designated as peptide groups. In this way ATR-FTIR results has got some characteristic peaks of leather which are 1731 cm-1, 1644 cm-1, 1630 cm-1 Amide I group (vibration of C=O C-N group), 1463 cm-1, 1448 cm-1 and 1536 cm-1 Amide II group (a mixture of N-H, C-N, C-C), 1234 cm-1 Amide III group (complex structures due to protein denaturation). 3064 cm-1 and 2917 cm-1, Amide B group (consists of asymmetric CH_2 groups).

Figure 3. *ATR-FTIR Spectra of TBP Treated Finished Leathers*

The peaks at 3000-3600 cm-1 represent to OH stretch and hence the peaks of 3750 cm-1 and 3693 cm-1 in ATR-FTIR has been associated with 2-propanol (IPA). There is homogeneity between samples inclusive of 0% group because IPA was used on all leather groups.11,19 699 cm-1and 667 cm-1 peaks in the spectrum are attributed to trivalent chromium which is used in tanning process. 1093 cm-1 is related to be P=O stretching vibration. The peak at 911 cm-1 could be attributed to either P-OH stretching or P-OC stretching. 1155 cm-1 peak could be attributed to P-O/P=N stretching frequency. Also peak at 1020 cm-1 could be attributed to PO2 symmetric stretching.8,20,21

3.5. Surface morphology of Leathers

SEM images 100 µm and 20 µm magnifications of TBP treated leathers after finishing application is given in Figure 4, Figure 5, Figure 6 and Figure 7. These images show that in 0%, 7% and 14% TBP applied leather samples have not observed significantly changing and the deformations on the surfaces of the leathers are similarly same. So TBP showed that it does not cause damage problems in these application rates for the leathers. However, 21% TBP applied leather surfaces in SEM images shows that small section was influenced due to be high rate of 21 %TBP chemical.

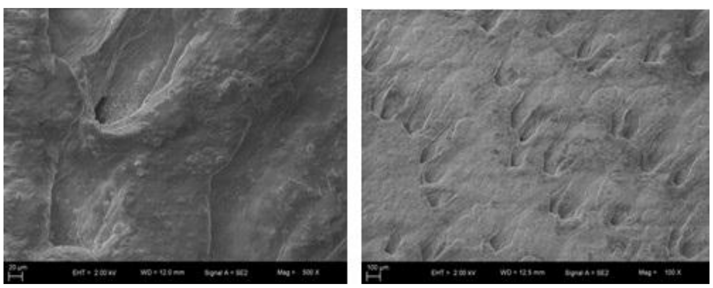

Figure 4. *SEM image of 0% Leather Samples in 20 µmand 100 µm Magnification*

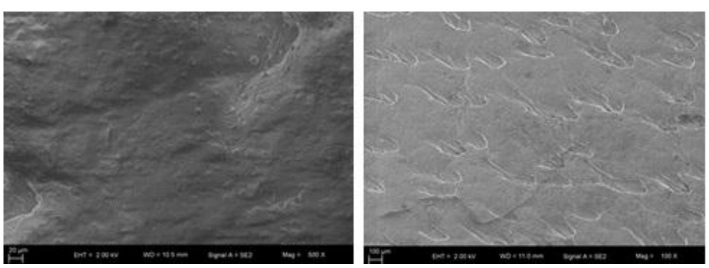

Figure 5. *SEM image of 7% Leather Samples in 20 µm and 100 µm Magnification*

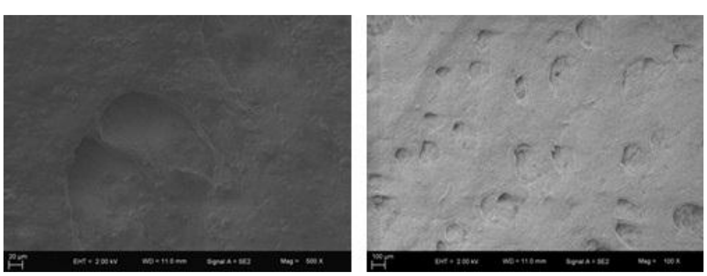

Figure 6. *SEM image of 14% Leather Samples in 20 µm and 100 µm Magnification*

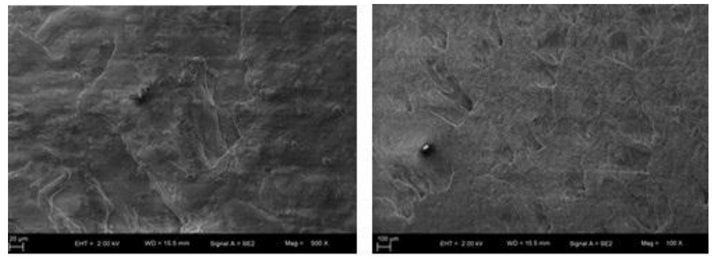

Figure 7. *SEM image of 21 % Leather Samples in 20 µm and 100 µm Magnification*

4.

5. CONCLUSIONS

In this work, the flame retardant effect of TBP in surface of leathers were studied. Increased TBP rates of treated leather samples indicated the effective flame retardant property in vertical and horizontal flammability tests. Especially in vertical flammability test results; 7%, 14% and 21% TBP treated leathers are observed non-ignitable materials and this is related to P-N synergism phenomena. TBP chemical possibly bounded with nitrogen containing resins or ammonium containing chemicals which are used in leather manufacture and so nitrogen and phosphoric acid interaction prevented flammability of leather. According to all results we advise that TBP can be applied to leather products before finishing and TBP can be researched with different chemicals in further studies in order to increase of its effect.

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