

**COLLAGEN-CONTAINING NITROGEN–BORON FIRE-RETARDANT
COMPOSITION FOR NATURAL LEATHER**

Xakimova M.Sh.¹, PhD., ass. prof., **Islamova D.A.**¹, ass., **Rafiqov A.S.**¹, d.ch.s., prof.,
Kadirov Sh.U.², ass.

¹Tashkent Institute of Textile and Light Industry, Tashkent, Uzbekistan

²Jizzakh Polytechnic Institute, Jizzakh, Uzbekistan

Abstract: Most substances used for the final finishing of natural leather significantly increase its flammability. However, for the use of leather materials in the automotive, furniture, and light industries, it is important to impart flame-retardant properties to them. Due to the toxicity of traditional halogen-containing flame retardants, particular interest is given to the use of halogen-free nitrogen-, boron-, and phosphorus-containing fire-retardant compositions. To address this issue, a composition based on collagen and polyacrylamide, characterized by a high nitrogen content, with the addition of boron-containing compounds, was used in this study. Samples of finished natural leather and suede splits were treated with this composition. The fire-retardant and morphological properties of the samples were investigated. The obtained results showed a reduction in the flame propagation rate of materials treated with the nitrogen–boron-containing composition. Surface structure analysis confirmed the formation of a film coating.

Keywords: fire-retardant composition, leather, flame retardant, collagen, boron, nitrogen.

I. INTRODUCTION

Leather, due to its strength, elasticity, and aesthetic properties, is widely used in areas such as construction, automotive manufacturing, furniture production, and clothing [1]. The production of natural leather is associated with the generation of a large amount of by-products. On average, about 250 kg of untanned waste can be produced from one ton of raw hides during leather processing [2]. The use of these by-products as secondary raw materials represents a promising approach that can reduce the environmental burden on the leather industry and yield products with high added value. One possible method of utilization is collagen extraction [3,4,5,6].

Due to its high nitrogen content and strong reactivity, collagen can be used as a component of a nitrogen–boron-containing fire-retardant composition [7]. Many natural proteins, such as DNA, egg white, chitosan, and casein, have already been studied as eco-friendly and effective flame retardants for textile materials [8,9,10]. However, this type of flame retardant has not yet been considered for leather materials. To meet the fire safety requirements necessary for leather applications, the natural flame resistance of leather is insufficient [11].

In addition, fatliquoring agents, which provide leather with softness and elasticity, decompose upon heating with the release of heat and toxic vapors. This significantly reduces the material's fire resistance [1, 11]. To overcome this drawback, special fire-retardant finishing compositions are used at the final processing stage [1].

Nitrogen atoms in the structure of collagen can form molecular nitrogen and ammonia during combustion. The gases produced dilute the oxygen environment in the combustion zone, reducing the oxygen supply to the material and thereby slowing down pyrolysis and flame propagation processes [12, 13]. To enhance the barrier effect, collagen can be combined with boron-containing compounds. Upon thermal decomposition, these compounds form a glassy layer that acts as a protective barrier, limiting the penetration of oxygen and heat [14].

Unlike most flame retardants, which act as additives, collagen-based compositions can chemically bond with leather, forming a durable coating that provides long-lasting flame-retardant properties [15]. Thus, the use of collagen extracted from leather waste not only enables the development of environmentally friendly fire-retardant compositions but also promotes the principles of a circular economy aimed at the reuse of industrial resources.

II. EXPERIMENTAL PROCEDURE

The selection of components for the fire-retardant composition was carried out with the aim of increasing the thermal stability of leather materials while preserving their physical properties. Collagen and polyacrylamide solutions were used as nitrogen-containing components of the flame retardant. To obtain a collagen solution from raw hide trimmings, an alkaline extraction method described in [18] was applied. The preparation of the polyacrylamide solution involved dissolving 5 g of polymer granules in 495 g of water under constant stirring at a speed of 250 rpm. For this purpose, a digital overhead stirrer BGD 701–704 was used. The complete composition of the formulation is presented in Table 1.

Table 1. Chemical composition of the fire-retardant solution

Component	Amount
Collagen solution	200±5 mL
Polyacrylamide solution	200±5 mL
Urea	25±1 g
Boric acid	50±1 g
Water	Up to the total volume (1 L)

A sample of chrome-tanned leather (tanned split) was treated with the fire-retardant composition. Before impregnation, the leather material was cut into strips measuring 20 cm in length and 8 cm in width. The resulting samples were immersed in a bath with the flame retardant and periodically turned, allowing treatment to proceed for 6 hours. After 6 hours, the samples were placed in a drying oven for 3 minutes at 160 °C for thermal fixation. The leather strips were then further dried at room temperature for 8 hours.

To assess the fire resistance of the treated materials, the following indicators were determined: duration of afterflame, afterglow time after removal of the flame source, and the length of the charred area. These parameters characterize the material's ability to sustain combustion and reflect the effectiveness of the barrier layer formed during thermal exposure. The absence of afterflame and afterglow indicates that the leather does not support self-sustained burning and does not pose a significant hazard during brief contact with a flame. The length of the charred area, in turn, reflects the quality of the protective carbonized layer.

The measurements of these parameters were carried out using a Fabric Flame Retardant Tester. The leather sample was mounted vertically in the testing chamber. A controlled flame was applied to the surface of the material for 30 seconds, after which the afterflame and afterglow times were recorded. After cooling, the length of the charred zone was measured.

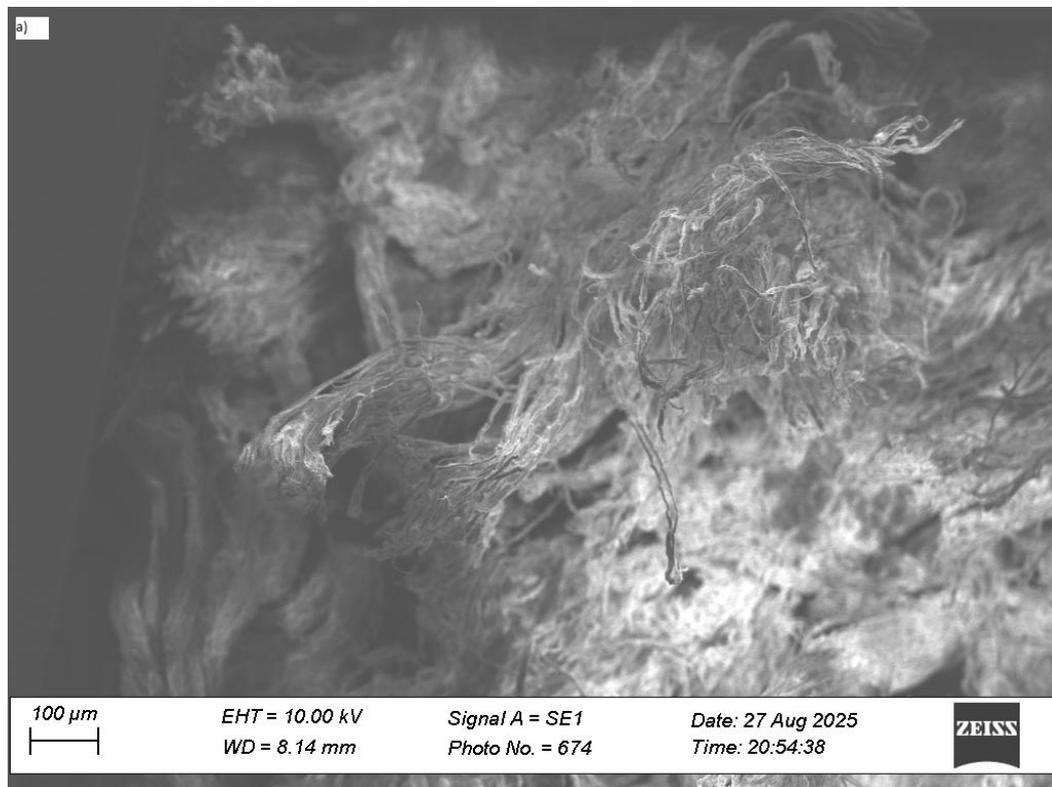
The obtained results were compared with the requirements of the GOST 11209–2014 standard, clause 7.21, according to which, for flame-retardant materials, the duration of afterflame and afterglow should not exceed 2 seconds, and the length of the charred area should be no more than one-third of the total sample length.

The experimental data on the fire-resistance indicators of the treated leather samples are presented in Table 2.

Table 2.
Fire-resistance indicators of leather samples

Sample	Thickness	Names of indicators		
		Afterflame duration, s	Afterglow duration, s	Charred area length, %
Untreated split	1.7±0.02	0	12±2	25±5
Treated split	1.8±0.04	0	0	14±2

Analysis of the experimental data showed that the fire resistance of the untreated split did not meet the standard requirements for afterglow duration, and the length of the charred area was nearly at a critical level. The treated split exhibited no signs of afterflame or afterglow, and the charred area length was less than 15%. This indicates that combustion ceased immediately after the flame was removed and confirms the material’s self-extinguishing capability. This difference is likely due to the microstructural features and morphology of the split before and after treatment. Figure 1 shows images of the split surface before and after treatment with the flame retardant.



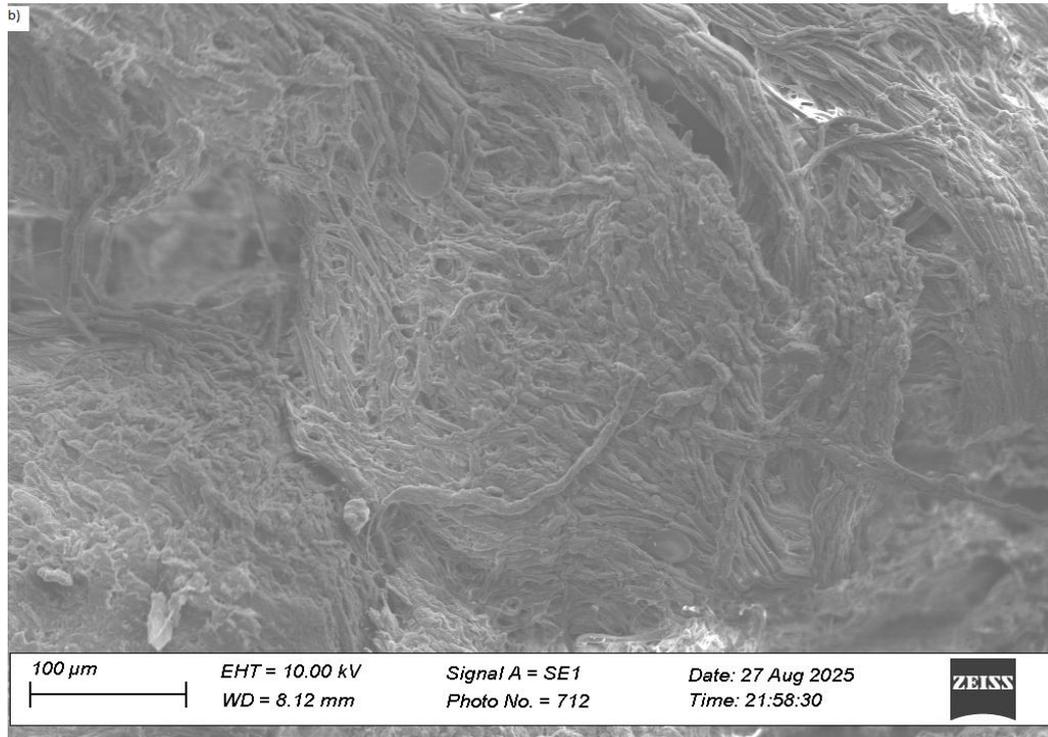


Fig. 1. Morphology and surface structure of the split: a) untreated with fire-retardant composition;
b) treated with fire-retardant composition

In the image of the untreated split, small fibers are scattered and unevenly arranged, with noticeable inter-fiber gaps and visible fiber ends. The material structure is loose and porous. In the treated sample, the structure is more cohesive and compact, with fibers lying closely together and bonded, and the inter-fiber spaces are smaller. The reduced porosity and uniform surface structure of the treated sample indicate the formation of a film coating. The densification and decreased porosity of the structure help limit oxygen access, thereby reducing flammability. These changes also positively affect the physical and mechanical properties. Elemental analysis of the material surfaces, shown in Figure 2, revealed significant differences between the treated and untreated splits.

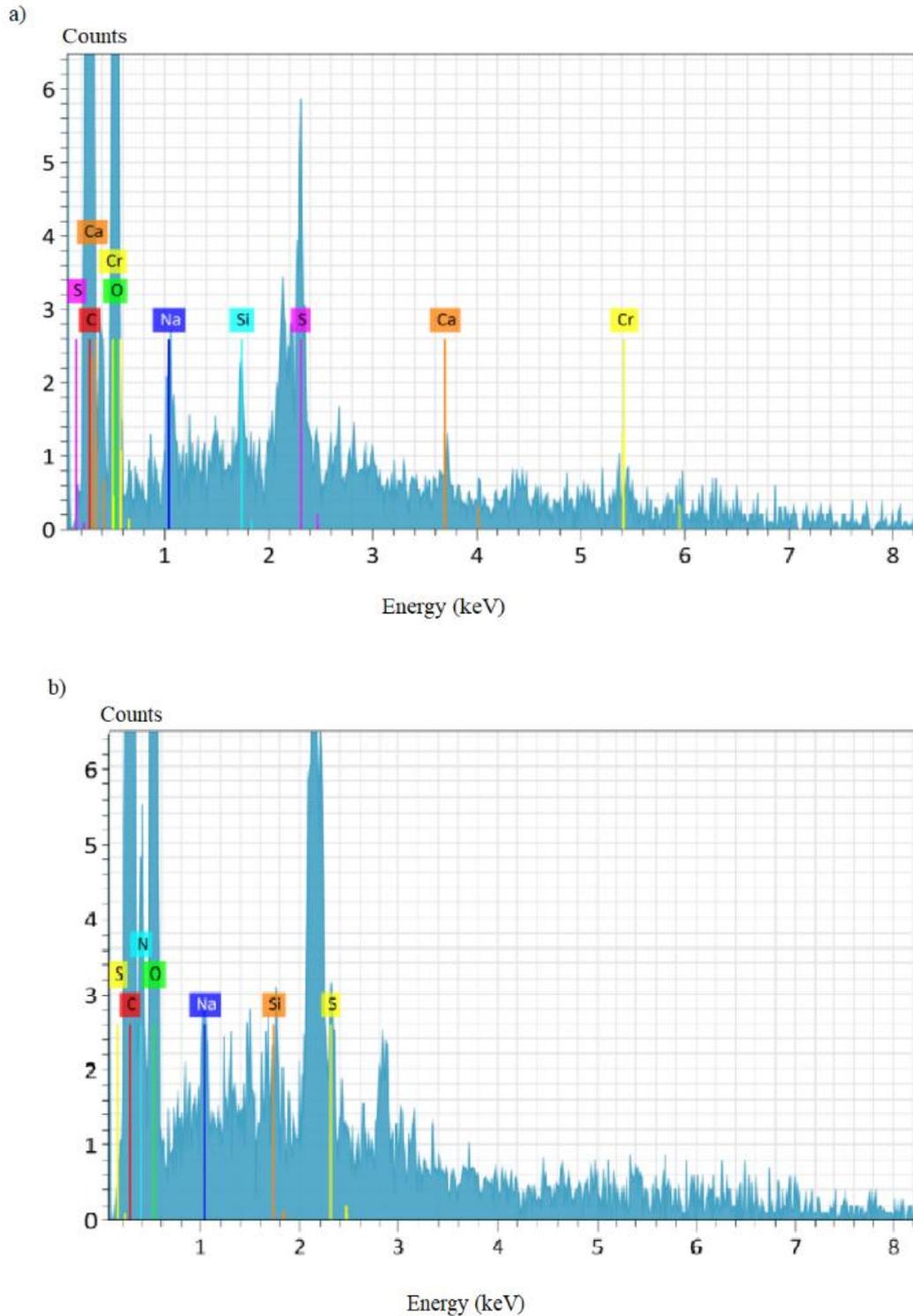


Fig. 2. EDX spectra of the split surface: a) treated with fire-retardant composition; b) untreated with fire-retardant composition

The EDX analysis shows that no nitrogen signal was detected on the surface of the split sample untreated with the flame retardant. Although nitrogen atoms are present in the leather structure, the surface of the sample is covered with a layer of fatliquoring and tanning agents, which isolate the protein structure from the outer surface. After impregnating the sample with a

solution containing collagen and polyacrylamide, the surface concentration of nitrogen increased sharply, resulting in a pronounced peak at 0.39 keV.

III. CONCLUSION

Treatment of leather with a nitrogen- and boron-containing composition based on collagen derived from leather waste and polyacrylamide resulted in the formation of a thin protective layer on the surface, as confirmed by the appearance of nitrogen in the EDX spectrum. The treated samples exhibited no afterflame or afterglow, and the length of the charred area did not exceed the standard limits. These results confirm the effectiveness of the developed composition and its environmental feasibility..

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