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Consolidation Materials Used in Strengthening Weak Historic Leather: A Review of the Most Important Traditional and Modern Materials

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Abstract:

This research focuses on materials used to consolidate fragile historical and archaeological leathers. The study examines both traditional materials, such as guar gum and casein, and modern alternatives, including nano-hydroxyapatite, hydroxypropyl-β-cyclodextrin, polyacrylamide, poly (MMA-HEMA), silicone oil, halloysite nanotubes (HNTs), and collagen nanoparticles. The primary objective is to evaluate the effectiveness of these materials in restoring the physical and chemical properties of deteriorated historical leathers, thereby contributing to their stabilization and structural reinforcement. A range of previous studies was reviewed and analyzed to provide a comprehensive comparison between traditional and modern consolidants. The results highlighted the individual advantages of each material, as well as the potential benefits of combining certain materials to enhance treatment outcomes.

Keywords:

Nanomaterial's; Guar Gum; Consolidation; Leathers; Polymer

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مواد التقوية المستخدمة في تقوية الجلود التاريخية الضعيفة: مراجعة لأهم المواد التقليدية والحديثة

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الملخص

يهدف هذه البحث إلي إلقاء الضوء علي بعض المواد التي استخدمت كمواد تقوية للجلود التاريخية والأثرية الضعيفة، حيث نتناول المواد التقليدية مثل صمغ الغوار والكازين، وكذل كبعض المواد الحديثة مثل الهيدروكسي أباتيت النانوية، هيدروكسي بروبيل-β-سيكلوديكسترين، البولي أكريلاميد والبولي (MMA-HEMA)، أنابيب الهالوسيت النانوية (HNTs)، بالإضافة إلي جسيمات الكولاجين النانوية، يهدف هذا البحث في الأساس إلي تقييم كفاءة تلك المواد من حيث القدرة علي استعادة بعض من الخصائص الفيزيائية الكيميائية للجلود التاريخية المعرضة للتدهور والتلف للمساهمة في احداث عملية الاستقرار والتدعيم للجلد التالف، تم مراجعة العديد من الدراسات السابقة وتحليل نتائجها وذلك لتكوين مقارنة شاملة بين المواد التقليدية والحديثة، وأظهرت النتائج التي توصلت اليها الدراسة إلي مميزات كل مادة مستخدمة علي حدة مع إمكانية دمج بعض تلك المواد لتحقيق تأثير أفضل للمادة المستخدمة في المعالجة.

الكلمات الدالة

المواد النانوية؛ صمغ الغوار؛ التقوية؛ الجلود؛ بوليمر.

1. Introduction:

Historical leathers are significant cultural heritage materials (Fan et al., 2024), but they are complex due to the various manufacturing techniques employed—particularly the tanning materials used—and their heterogeneous, layered composition (Miu et al., 2020). However, these materials are highly vulnerable to degradation caused by factors such as temperature fluctuations, humidity, light exposure, acidic or alkaline solutions, microorganisms, and air pollutants (Zang et al., 2022). Leather can deteriorate in multiple ways, including molecular denaturation at high temperatures, microbial degradation of collagen and tannins, and hydrolysis in acidic or alkaline environments (Chen et al., 2024).

Given the historical and cultural significance of leather artifacts, it is crucial to preserve and protect them from environmental conditions and chemical reactions that contribute to their deterioration (Chen et al., 2024). Environmental and biological factors can expose the collagen and tanning agents in leather to oxidation, hydrolysis, and acid degradation over time. These processes break the bonds between collagen molecules, compromising the structural integrity of the leather and potentially resulting in the complete loss of the artifact as deterioration progresses (Zhang et al., 2021). Therefore, the use of consolidation materials has become essential for restoring the physical, mechanical, and chemical properties of deteriorated leather.

This research paper provides a comprehensive review of the most prominent materials used in the consolidation of historical leathers, highlighting the key features of each material. It covers a range of consolidants, from traditional substances such as casein and guar gum to modern nanomaterials like nano-hydroxyapatite and halloysite nanotubes. By analyzing previous studies, the research presents a comparative analytical assessment of the effectiveness of these materials, identifying the factors that influence the success of the consolidation and preservation process.

Recently, researchers have begun exploring new materials and treatment methods to preserve leather artifacts by restoring their physical and chemical properties. Consolidation is regarded as an essential and necessary intervention in the preservation of archaeological materials (Abdel-Maksoud et al., 2022), as it primarily aims to enhance the chemical and physical stability of the artifact. This is typically achieved through application methods such as spraying, immersion, or brushing (Kučerová, 2012). Consolidation is also employed to halt the deterioration of fragile leather using natural and synthetic materials, including resins and polymers (Abdel-Karim, 2019). To be considered suitable for consolidation, a material must meet specific criteria that ensure its effectiveness without causing adverse effects on the artifact, such as:

- Enhancing the mechanical properties of the leather.
- Inhibiting further deterioration caused by environmental or biological factors.
- Remaining chemically stable without reacting with the leather or its surrounding environment.
- Preserving the original color and appearance of the leather.

- Being reversible, allowing for its removal without damaging the original material (Hassan, 2004).

2. Materials used in the treatment and consolidation of weak historical leathers:

It is essential to apply appropriate maintenance methods to limit the deterioration of artifacts and prolong their lifespan. The restoration and consolidation of historical leather artifacts have long posed challenges for conservators, as leather objects preserved in libraries and museums are often exposed to unsuitable environmental conditions, including fluctuations in temperature, relative humidity, and varying light levels (Abdel Maksoud & Elamin, 2013). Additionally, heat-induced deterioration is a major factor contributing to the degradation of leather artifacts, as high temperatures can cause burning or render the leather brittle and weak (Polka, 2019).

Air pollution is another significant factor contributing to the deterioration of leather artifacts. The low pH values commonly found in historical leather lead to brittleness, weakening, and the loss of the granular layer, often resulting in surface powdering (Lama et al., 2015). As this problem persists without a definitive and satisfactory solution to counteract the degradation of leather, numerous theories and materials have been explored to address it. Among the most important traditional natural and synthetic materials used for the consolidation of deteriorated historical leathers are:

2.1. Casein

Casein, a protein derived from milk (Korany, 2011) (Fig. 1), becomes water-soluble when combined with an alkaline substance. It is known for its strong adhesive properties, making it suitable for use as an adhesive or consolidant. Its application became widespread in the early 20th century. Casein is typically prepared by heating skim milk to 35 °C and gradually adding hydrochloric acid until the solution reaches a pH of 4.6. The mixture is then allowed to settle and washed thoroughly to remove any remaining traces of hydrochloric acid, resulting in the formation of casein as precipitates in water. A strong alkaline substance is then added to the precipitate to create a colloidal solution. When casein is prepared from the dry sodium salts of milk protein (sodium caseinate) and mixed with calcium hydroxide, it gradually transforms into water-insoluble calcium caseinate upon contact with water. This compound eventually solidifies as the water evaporates (Maher, 2019).

Casein consists of approximately 94% protein and 6% low-molecular-weight compounds, primarily colloidal calcium phosphate. It comprises four main phosphoproteins: αS1-casein, αS2-casein, β-casein, and κ-casein. In medical applications, casein is used either as acid casein, which has low water solubility, or as sodium caseinate, which dissolves readily in water except near its isoelectric point.

Caseinates are proline-rich proteins with an open molecular structure. The presence of proline residues disrupts the formation of regular α-helices and β-sheets, contributing to casein's unique conformation. Due to the absence of disulfide bridges, casein exhibits thermal stability. However, its open structure, resulting from the high proline content, also makes it more susceptible to proteolytic cleavage (Elzoghby, 2011). As noted by Maher (2019), one of the disadvantages of using casein as a reinforcing agent is its inflexibility. Upon drying, it tends to harden, which can lead to a reduction in the mechanical properties of the treated material.

Figure 1. Illustrative image of casein. Adapted from https://www.hrs-heatexchangers.com/food/hrs-heat-exchangers-dairy-processing/whey-casein-lactose-products/, accessed on 19 January 2025 at 12:00 PM.

2.2. Guar Gum:

Guar gum is a natural polysaccharide derived from the drought-resistant seeds of *Cyamopsis tetragonoloba*, a member of the Leguminosae family. It primarily consists of high-molecular-weight polysaccharides known as galactomannans. Guar gum is cultivated in several countries, including India, Pakistan, Brazil, Australia, and South Africa (Kawamura, 2008).

Commercial samples of guar gum typically contain 4–12% moisture, 2–6% acid-soluble ash, and 2–6% protein. Like other polysaccharides, its biological properties are primarily influenced by its behavior in aqueous media. Guar gum dissolves in polar solvents, forming strong hydrogen bonds (Fig. 2), whereas in weakly polar solvents, it forms only weak hydrogen bonds. One of the most significant properties of guar gum is its viscosity, as it dissolves rapidly in cold water to produce a highly viscous solution. The viscosity of guar gum is influenced by several factors, including temperature, concentration, pH, and ionic strength (Abd El-Fatah, 2021).

In addition, it has been shown that when used as a consolidant, guar gum can withstand high temperatures; however, increasing its concentration leads to a reduction in color brightness. It also contributes to enhancing the mechanical properties of treated samples, including tensile strength and elongation rate (Abd El-Fatah, 2021).

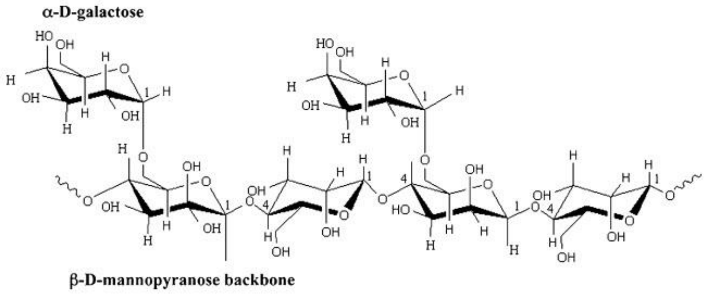

Figure 2. Molecular structure of guar gum. Adopted from Mudgil, D. et al., 2014.

2.3. Nano-Hydroxyapatite and Polyethylene Glycol:

Historical leather artifacts are highly prone to deterioration due to their fragile structure and sensitivity to environmental fluctuations, such as changes in temperature and relative humidity, as studied by Langroudi and Mirmontahai (2013). In their research, nano-hydroxyapatite (HA), with the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ (Mohd Pu'ad et al., 2019), and polyethylene glycol (PEG 4000) were used as consolidation materials for weakened leather samples. Hydroxyapatite interacts with collagen tissues, with its mineral particles promoting the unification of biological structures by bonding with collagen. Polyethylene glycol, commonly used as a humectant, helps maintain the leather's moisture content and, unlike some other substances, does not contribute to the degradation or weakening of collagen fibers (Langroudi & Mirmontahai, 2013).

The results demonstrated that this method is effective and beneficial for strengthening leather, as tensile tests indicated enhanced mobility of collagen fibers and reduced internal friction.

2.4. Hydroxypropyl -β - Cyclodextrin:

Hydroxypropyl β-cyclodextrin is a bio-derived compound obtained from cyclodextrin, with the chemical formula $C_{63}H_{112}O_{42}$. It is commonly used in the medical and food industries. This polymer possesses excellent properties that make it suitable for the consolidation and reinforcement of deteriorated vegetable-tanned leathers. When applied, it helps protect leather from brittleness, improves chemical stability, and enhances mechanical properties.

Hydroxypropyl β-cyclodextrin is a cone-shaped oligosaccharide modified with hydroxypropyl groups (Fig. 3). It has a hydrophilic outer surface and a hydrophobic inner cavity. This unique structure contributes to its high melting point of 278 °C, which enhances the thermal stability of leather and provides resistance to temperature fluctuations in controlled environments such as museums and libraries.

Results have shown that treating vegetable-tanned leathers with hydroxypropyl β-cyclodextrin improves their mechanical properties. This enhancement is attributed to the interaction between cyclodextrin molecules and the leather fibers. The hydroxypropyl groups present in cyclodextrin enable the formation of hydrogen bonds with the collagen fibers, thereby enhancing both the adhesive and cohesive properties of the material. As a result, the treated leather exhibits higher tensile strength and elongation compared to untreated aged leather samples (Abdel-Maksoud et al., 2024).

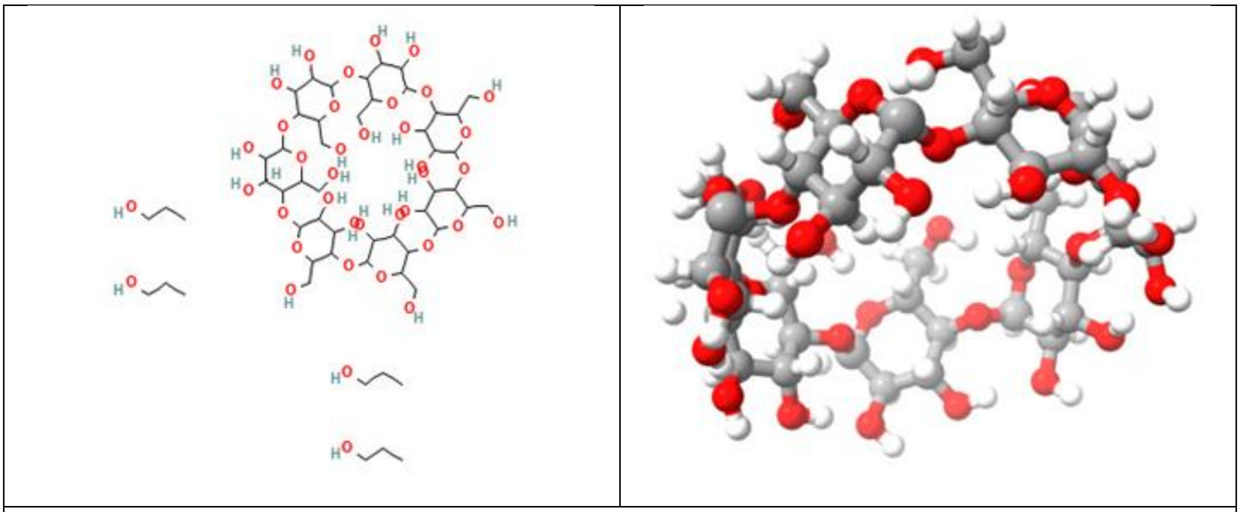

Figure 3. Chemical structure and morphology of the compound hydroxypropyl-β-cyclodextrin. Adopted from https://pubchem.ncbi.nlm.nih.gov/compound/2-Hydroxypropyl-beta-cyclodextrin, accessed on 19 January 2025 at 9:00 PM.

2.5. Polyacrylamide and Poly (MMA-HEMA):

Polyacrylamide (PAM) is a swellable polymer derived from the acrylamide monomer, with a glass transition temperature of approximately 130 °C. The commercially important form, known as 2-propenamide, has the chemical formula $[-CH_2CH(CONH_2)-]$. Polyacrylamide is a non-ionic, water-soluble biopolymer, making it suitable for a wide range of applications across various industries. It can be synthesized either as a simple linear chain or as a cross-linked structure. The cross-linked form is particularly notable for its ability to absorb and retain large quantities of water, as the amide groups form strong hydrogen bonds with water molecules.

Polymers composed of polymethyl methacrylate/hydroxyethyl methacrylate (MMA-HEMA) exhibit excellent chemical stability due to their three-dimensional polymer networks. This structural feature makes them highly valuable for a wide range of applications (Abdel Maksoud et al., 2024).

2.6. Halloysite Nanotubes (HNTs):

Undoubtedly, leather deterioration is an inevitable consequence of interactions between environmental factors and physical wear caused by preservation methods, handling, or use. As a result, archival materials such as manuscripts, leathers, and parchments are exposed to significant risks. The consolidation of deteriorated leather has garnered considerable attention; however, the materials and methods employed in leather preservation can pose various risks—particularly due to the inherent sensitivity and instability of collagen (Dignard & Mason, n.d.).

In recent years, the exploration of nanoparticles for preserving artistic and historical objects has gained increasing attention. In 2016, chemical gels loaded with nano-cleaning agents were applied to remove surface dirt and dust from historical leather. A 2018 study investigated the use of nano-collagen in the restoration and treatment of the leather cover of an 18th-century book (Bicchieri et al., 2018). Additionally, Cavallaro et al. (2015) employed an acetone-based emulsion containing high-density nanotubes and polymers to treat waterlogged archaeological wood.

Halloysite is a natural nanoclay that has attracted considerable scientific and industrial interest due to its abundance and biocompatibility. Chemically, it is composed of layered aluminum silicates with the formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ and features a hollow tubular structure typically less than a micron in diameter and 1–3 microns in length. Studies have shown that halloysite nanotubes (HNTs) are uniformly distributed within the polymer matrix, contributing to enhanced tensile strength (Fig. 4). In addition, HNTs improve the thermal stability of the polymer by trapping deteriorated components within their internal cavities. Research has also concluded that HNTs partially restore the structural integrity of collagen, attributing this effect to the improved thermal stability of the collagen–tannin matrix (Badea et al., 2019).

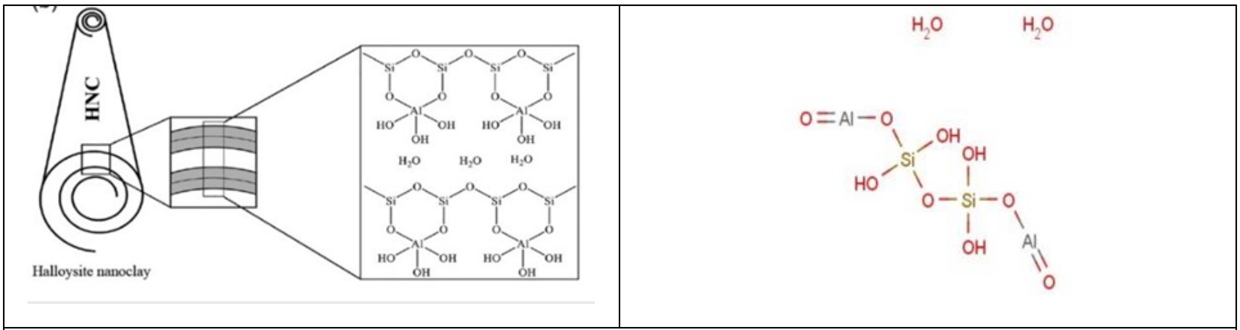

Figure 4. Halloysite nanotubes. Adopted from Nguyen et al., 2018.

2.7. Collagen Nanoparticles:

Collagen is one of the primary structural proteins involved in tissue formation, consisting of triple polypeptide chains known as α-chains. Bicchieri et al. (2018) evaluated the application of collagen nanoparticles (Collagen NPs) for the reinforcement and consolidation of leather book covers (Fig. 5). The study yielded highly promising results, demonstrating that collagen nanoparticles enhanced the mechanical properties of the treated leather samples. In addition, the treatment showed favorable outcomes regarding minimal color change and contributed to an increase in the leather's shrinkage temperature (Bicchieri et al., 2018).

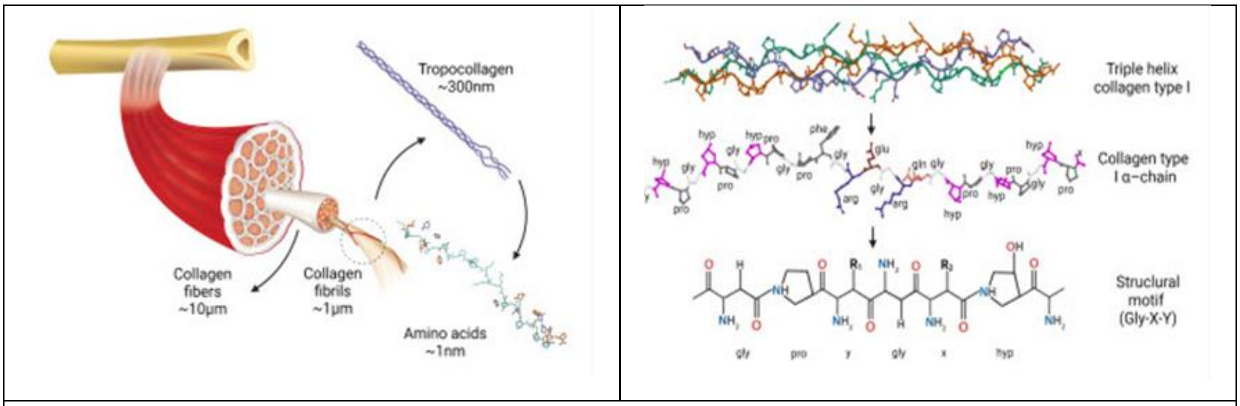

Figure 5. Skin collagen, triple peptide chains, and the chemical structure of skin collagen. Adopted from Amira et al., 2022.

3. Conclusion:

This review has presented an overview of several materials that have been used and proven effective in the treatment and consolidation of historical leathers. It highlighted traditional natural materials such as guar gum and casein, as well as modern nanomaterials, including nano-hydroxyapatite, halloysite nanotubes, and collagen nanoparticles. Additionally, the review examined synthetic polymers such as hydroxypropyl-β-cyclodextrin, polyacrylamide, and poly (MMA-HEMA). All of these materials have been evaluated in terms of their condition and effectiveness in consolidating weakened and deteriorated leathers. However, further testing and analysis are essential to confirm their long-term performance and to provide a comprehensive understanding of their suitability for the conservation of historical leather artifacts.

References:

1- Abdel Fattah. N., (2021). Evaluation of Some Treatment Materials and Methods Used in the Conservation of Decorative Leather Artworks Applied to a Selected Model, PhD, Faculty of Archaeology, Cairo University. (Translated from Arabic)

2- Abdel-Karim. M., (2019). The use of Re-Tainning Materials for the Treatment of Vegetable Tanned Leather: Article Review, Faculty of Arts, Sohag University, Vol.2.

3- Abdel-Maksoud, G., & Elamin, A. (2013). The investigation and conservation of a gazelle mummy from the Late Period in ancient Egypt. Mediterranean Archaeology and Archaeometry.

4- Abdel-Maksoud, G., et al. (2022). Evaluation of a Mixture of Castor Oil and Polyvinylpyrrolidone for the Lubrication of Dry Vegetable Tanned Leather Artifacts, Journal- Society of Leather Technologists and Chemists, Vol. 106.

5- Abdel-Maksoud, G., et al. (2024). Evaluation of the efficiency of polyacrylamide and poly (MMA-HEMA) for the consolidation of vegetable-tanned leather artifacts. *Pigment & Resin Technology, 53*.

6- Abdel-Maksoud, G., et al. (2024). Evaluation of the performance of hydroxypropyl-β-cyclodextrin for the consolidation of vegetable-tanned leather artifacts. Heritage Science, 12.

7- Badea, E., et al. (2019). The effect of halloysite nanotubes dispersions on vegetable-tanned leather thermal stability. *Heritage Science, 7*.

8- Bicchieri, M., et al. (2018). The solution to an unresolved problem: Newly synthesised nano collagen for the preservation of leather. *Journal of Cultural Heritage, 33*.

9- Cavallaro, G., et al. (2015). Thermal and dynamic mechanical properties of beeswax-halloysite nanocomposites for consolidating waterlogged archaeological woods. *Polymer Degradation and Stability, 120*.

10- Chen. Q., et al., (2024). Influences of high temperature and humidity on vegetable-tanned leather, Journal of Cultural Heritage, Vol. 68

11- Dignard, C., & Mason, J. Caring for leather, skin and fur. Part of CCI's preventive conservation guidelines for collections online resource. Retrieved from https://www.canada.ca/en/conservationinstitute/services/preventiveconservation/guidelines-collections/caring-leather-skinfur .html

12- Elzoghby, A. (2011). Casein-based formulations as promising controlled release drug delivery systems. Journal of Controlled Release, 153.

13- Fan. J., et al., (2024) "Green synthesis of silver-titanium dioxide nanoparticles using chestnut extract for the preservation of leather artifacts", Journal of Cultural Heritage, Vol. 69

14- Hassan. R. R., (2004). An Experimental Study on the Consolidation Materials for Vegetable-Tanned Leathers with Application on Selected Archaeological Models (Master's Thesis), Faculty of Archaeology, Cairo University. (Translated from Arabic)

15- Kawamura. Y. (2008). "GUAR GUM" Chemical and Technical Assessment

16- Korany, M. S. (2011). Study of the Effect of Oil Media and Binders on the Deterioration of the Oil Paintings and Methods of Treatment and Conservation Applied on a Chosen Example (MA Thesis, Faculty of Archaeology, Cairo University).

17- Kučerová, I. (2012). Methods to measure the penetration of consolidant solutions into 'dry' wood. *Journal of Cultural Heritage*, *13*.

18- Lama, A., et al. (2015). A new formulation for the treatment of acid-deterioration (red rot) in historic leathers.

19- Langroudi, A., & Mirmontahai, A. (2013). Hydroxyapatite nanoparticles and polyethylene glycol treatment of historical leather: Mechanical properties. Journal of the American Leather Chemists Association, 108.

20- Maher. A., (2019). Treatment and Preservation of Paper Documents: An Experimental Study to Evaluate the Efficiency of Some Modern Materials and Methods Applied to a

Selected Model (Master's Thesis), Faculty of Archaeology, South Valley University, Qena. (Translated from Arabic)

21- Miu. L., et al., (2020). Chemical and physico-mechanical characterizations of leather for Restoration Conference: The 8th International Conference on Advanced Materials and Systems.

22- Mohd Pu'ad. N., et al. (2019). Syntheses of hydroxyapatite from natural sources, Heliyon, Vol. 5.

23- Polka, M. (2019). Leather thermal and environmental parameters in fire conditions. Sustainability Journal.

24- Zang. M., et al (2022). Biodeterioration of collagen-based cultural relics: A review, Fungal Biology Reviews, Vol. 39.

25- Zhang, Y., et al. (2021). SEM, FTIR and DSC investigation of collagen hydrolysate treated degraded leather. *Journal of Cultural Heritage, 48*.