THE USE OF RE-TAINNING MATERIALS FOR THE TREATMENT OF VEGETABLE TANNED LEATHER: ARTICLE REVIEW

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Different leather artifacts in museums and libraries are exposed to different deterioration factors such as variation in humidity and temperature, Light Irradiation, Mechanical damage and biological factors like microorganisms and insects. According to these factors, leather artifacts loss their mechanical properties, and became weak. This study aims to make a survey on the re-tanning materials used for the treatment of vegetable tanned leather artifacts, explain the advantages and disadvantages of these materials and methods of their evaluations will be detected.

KEYWORDS: vegetable-tanned leather, collagen, deterioration, Re-tanning materials, Mineral materials, Conservation.

Introduction:

The vegetable-tanned Archeological leather is considered one of the sensitive materials. Collagen is considered the basic ingredient of the Archeological Leather, which is being affected by the surrounded environmental conditions, such as fluctuation between temperature and relative humidity. The improper handling of the bookbinding may lead to the

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deterioration of the surface of leather, such as cracks, spreading the salts on the surface of the leather. Sometimes the loss occurs in some parts of the bookbinding, increasing the acidity resulted from hydrolysis process. The oxidation and the hydrolysis of the leather are breaking the links in the materials of tanning in the leather; sometimes the collagen itself is broken. There are also some causes of hydrolysis of the historical leather such as the spread of air pollution gases such as sulfur dioxide (SO_2), where sulfur dioxide (SO_2) is converted into sulfur oxides (SO_3), and sulfur oxides(SO_3) are absorbed on the surface of the leather and interact with the materials of tanning on the surface of the leather to create sulfuric acid H_2SO_4 in the existence of the humidity, so H_3O comes as result of that interact. This leads to the breakdown of the amino bonds found in the chemical composition of collagen. (Kite and Thomson, 2006) & (Sebestyen et al., 2015). All the previous forms of deterioration encourage scientists and researchers to focus on the conservation processes to solve these problems. The re-tanning materials are considered one of the most important materials that are using for the treatment some of these forms of deterioration.

The process of re-tanning is one of the important stages in the operation of the leather manufacture to get some of the required qualities such as fullness. This process may be useful as a restoration stage of vegetable tanned leather and Fill Missing parties of the tanning layer of the historical leather. The interact is happening between material of tanning through the active groups found in the substance of re-tanning such as CN, $CONH_2$, COOH, with peptide link in protein. These materials improve the connection of collagen fibers by forming hydrogen bonds with collagen fibers. They also improves the resistance of the leather for the water and temperature and improving the mechanical characteristics of the leather. (Naviglio, et al., 2005).

Re-tanning used also to improve some properties of leather such as physical properties: grain Firmness and leather filling .Type of re-tanning materials: vegetable tannins (Tara and Mimosa), metal re-tanning, syntans, various types of resins and some polymer. Using re-tanning agent consist of the poly hydroxyl phenol gives leather some properties such as antioxidant showing and good temperature fastness. (Musa et al., 2014).

Re-tanning agents:

The re-tanning materials can be divided into metal re-tanning materials and organic materials depending on nature of the material (Jankauskauskaite et al., 2012).

Metal re-tanning materials:

It can be also divided into metal and semi metal materials, but it was advised that metals materials can't be used for the conservation of vegetable tanned leather, due to the deformation process of collagen, change of color and reduction of the shrinkage temperature such as: Aluminum salts, Chromium salts, Zirconium salts, Vanadium quadrilateral oxide (VO_2), Iron oxide Nano Particles (Fe_3O_4), Silver Nano Particles (AgNPs), Silicone dioxide (SiO_2), Zinc Oxide (ZnO) , Titanium Oxide (TiO_2), Sodium montmorillonite (NaMMT) and Manganese salts nanoparticle (Mn_2o_3) **(**Jankauskauskaite et al., 2012).

Aluminum salts can be used as a treatment material such as tri format aluminum ($C_3H_3AlO_6$), aluminum chloride ($AlCl_3$) and aluminum sulphate $(Al_2(SO_4)_3$ These materials have some advantages such as improving the mechanical properties, stability of color change and increasing the pH value of the treated leather (Blmra, 1984); Duki et al., (2013)

Haroun et al., (2009) tested aluminum sulphate as re-tanning materials and the results Confirmed that the material improved the tensile strength, elongation at break, tear strength and also high Shrinkage temperature achieved by materials and leather

became soft after the treatment, Mechanical properties of leather also improved due to the increased formation of cross-links between active groups of re-tanning agents and functional groups of protein. The presence of aluminum at combination of leather systems increased the hydrothermal stability of the resultant leathers.

Ohlidalove et al., (2017) did conduct a study about the presence of transition metals such as ions and copper at historical leather. They cause accelerated ageing of samples leather to simulation historical leather. Structural changes in leather were examined by using SEM and SDS-PAGE .Changes in mechanical properties for exposure to the accelerated ageing samples were determined by Young's modulus of elasticity (tensile strength and elongation at break were Decreased) . pH values for samples leather decreased and reached 2.6. The Presence of cations of transition metals decrease the shrinkage temperature. Damage of historical leather such as: loss of firmness, fragility and even powdering happens mostly due to oxidation and acidic hydrolysis. Cations of transition metals catalyst oxidation and presence oxygen at atmosphere can cause acid hydrolysis.

In the presence of condensed tannins in leathers, they decrease the infection of leather with oxidation and acidic hydrolysis due to as tannins work to form semi Quinone radical arising hydrolysable tannins which are more resistant to oxidation than leathers which were that treated by condensed tannins.

Re-tanning process material is also considered one of the most important materials used during tanning process, beside its use as a conservation material to resist the harmful surrounding environmental conditions .Some criteria and requirements should be apply when selecting Re-tanning materials such as reversibility .This is due to that the conservator use, sometimes some materials which they proof good efficiency during treatment, but they got bad results with natural or artificial ageing process. According to this, the conservator can remove

these materials without damage for historical artifacts. (Van Soest et al.,1984)& (Dienst, 1985).

The re-tanning materials dissolved in organic solvent are better than the materials dissolved in water, especially if vegetable tanned leather exposed to oxidation and hydrolysis processes. (Haines, 1977) & (Kite and Thomson, 2006).

Organic materials:

These materials are divided into syntans, resins and polymers.

Syntans

These materials can be divided it as role it at re-tanning stage (pre-tanning syntans_ replacement syntans _auxiliary syntans _ re-tanning syntans).We can use it as pre-tanning with glutardialdehyde, as re-tanning materials to filling and softening leather, as auxiliaries during fat liquoring and replacements when combination with vegetable extracts.

Some syntans materials are forming from condensation products of aromatic compounds like phenol, naphthalene sulphonic acid with formaldehyde or urea. Syntans are better soluble in water than vegetable Tannins, because their molecules are smaller, so syntans achieve well penetrate at leather matrix compared with vegetable tannins due to syntans have small molecules. Jankauskauskaite et al., (2012).

Resins

Resin is an organic material that has a high polymerization ability, and a transparent appearance that helps to use it as a restoration material and achieve the desirable result for leather reservation and it can be divided into:

- Thermoplastic Resins
- Thermosetting Resins
- Cold setting Resins

The re-tanning can be achieved by various categories of substances such as acrylic resins, dicyandiamidic resins and melaminic resins.

When using resins as restoration materials you have to be careful because some materials are resulting from the condensation of Formaldehyde and Melamine which used as re-tanning agents; Despite the development of mechanical and physical properties their still some disadvantages, it is a non-reversible material so we can avoid the using it as restoration material .Naviglio, et al., (2005)

Polymers:

Most polymers used at re-tanning stage, which we can use as restoration materials, are co-polymer from acrylic acid and its Derivatives, which spread out when using it.

Leather became flexible and its features depend on the Sub-installation of polymer

While leather vegetable tanned contains active groups such as NH_3 or COOH or OH that cause strong reaction and correlation between materials used and leather Naviglion et al., (2005).

Many small polymers cause the formation of links between materials and leather and improve penetration materials at leather during restore it. physical and mechanical properties of leather are improved such as Fullness ,tensile and elongation materials penetrate into the structure of leather and make good links with collagen that protect leather from deterioration factors(Suparno,2005) ,

The role of Nano materials in the re-tanning process:

It was noticed that Nano materials have become vital in the conservation field. Nano materials are used in Re-tanning stage and gave good results such as resistance against microorganisms and ultraviolet radiation. One of these materials is a silver Nano particle which is characterized by catalytic activity, thermal conductivity, high electrical, anti-

microbiology and small size which gave it the ability for penetration through fibre structures.
It can be added that the nature of vegetable tanned leather play an important role for the efficiency of Nano materials used as a re-tanning materials. The vegetable tanned leather contains Homogeneous film for polyphenolic, which facilitates penetration and formation link with polymer substrates present at vegetable tanned leather. (Olivares et al., 2014)

The application materials by Immersion or brush depending on Archaeological material status and natural materials when use it as restoration materials such as colloidal silver solution, which works to improve leather Characteristics and prefer addition of Polyhyoxiurethunes with silver solution (Ma et al., 2014)

Nawaz et al., (2011) used zinc oxide(ZnO) at Nano particle size for re-tanning stage of vegetable tanned leather materials. This material gives good resistance against microbial deterioration. This material gave leather an improvement in some properties such as solidity, and also keep original Features such as color of leather after the application process.
Ma et al., (2014) studies about using Nano composite-based green tanning process (Polymer/Zno Nano composite- silicon dioxide (SiO_2) and applied it in tanning and re-tanning process during suede leather making. They investigated and examined leather after application and after application of chrome and chrome mix with Nano particles by scanning electron microscopy and atomic force microscopy and found that there is good distribution of Nano particles and improved mechanical properties, softness, and biodegradability of leather. These improvements may due to carboxyl groups in the nano composites which reacted with amino groups of collagen, special hydroxyl groups on the ZnO surface form hydrogen

bonds with the amino groups or carboxyl groups on collagen structure. It also improves the hydrothermal stability of leather. They found that best results obtained when particles size are 60:150 nm. The effectiveness of silicon dioxide improves gradually with increasing the concentration of Nano silicon. It also give improve penetration inside the fiber structure.

Olivares et al., (2014) focused on the using of sodium montmorillonite (Na+Mt) added with size Nano particle and with different rates with specific conditions during re-tanning process for the treatment of leather.

Examining leather by scanning electron microscopy showed Nano particles dispersed into structure for leather. the thermal stability of leather improved due to presence of clay mineral, it also Increase shrinkage temperature .some Mechanical properties such as tensile , tear strength improved by applied NA+Mt with different rates and mechanical properties improved due to effect clay mineral platelets and reacted with leather structure.

sodium montmorillonite is not preferred to use with water as a solvent for the treatment of leather during the process of re-tanning, but it is used with water during the manufacture of leather

Pan et al., (2017) used silica Nano particles in the polymer matrix to improve resistance to aging, mechanical properties, and resistance environmental conditions. This material is recommended to be used as a re-tanning agent for the treatment of leather artefacts.

The Nano –size silica can use it with organic or inorganic composite materials such as: Methacryloxy (propyl) trimethoxysilane, dimethyl diallyl ammoniumchloride poly (meth acrylic acid) and show unique physical and chemical properties during react with polymer.

The spherical Nano size-silica (SiO_2) are combined with the collagen fibres- the treated leather- through chemical bonds, which is reflected on the physical, mechanical and thermal

properties of the leather. The internal structure of the leather is improved due to the linkage of the leather structure with the nanoparticles, increases the leather resistance to heat, increases shrinkage temperature and leather resistance to tensile strength and elongation. .

The use of spherical Nano size-silica with poly methyl acrylic acid as re-tanning materials gives better results than the use of Nano silica only. There is group that works to increase bonding with collagen fibres and the formation of hydrogen or chemical links increases the leather's resistance to tensile strength and elongation compared to the use of nanoparticles of silica, such as (NH_2), carboxyl (COOH) and hydroxyl (OH) .

The silica nanoparticles begin to dissipate at 600 °C, so it help to improve the resistance of the leather to high-temperature, The physical and mechanical properties of leather treated with PMAA-SiO_2(poly Meth acrylic acid with silica) were the strongest compared with different modifiers for SiO_2 due to the excellent dispensability of PMAA-SiO_2 and it works to increase interaction between polymer PMAA_ modified silica Nano particles as well as chemical bond formation between collagen fibres and PMAA- SiO_2 Nano composite .

Factors affected re-tanning stage:

Types of materials used, pH value, Time of treatment, the previous history of the leather material is also important, the temperature of the re-tanning bath, time of application and method of application Martials (Haroun, 2009).

- Types of re-tanning materials: The effectiveness of re-tanning material on treated leather differs by difference of the material itself as mentioned above in the division of re-tanning material
- Time of treatment: Function of treatment time effect of fluorescence intensity, the fluorescence intensity reached the lowest value when the treatment process was carried out for 6 h, which indicated that most liquor used during treatment had penetrated the leather and combined with collagen fibres until

this time. The reactive time increased after two hours, the parts of liquor without bonding with collagen had come back in the drum under the mechanical force at the time, so the optimal treatment time is about 6 h. Pan et al .,(2017).

- PH value: The pH value was obtained as the average between 2 measurements, the samples for leather is finely tuned to adjust the pH from 3.6 up to 4.5, which is considered to be an optimal value for leather archeology. Baglioni et al.,(2016)
- the previous history of the leather material: Identification of animal leather used for leather & Identification of tanning materials and also Identification of Previous restoration work if found, to avoid unwanted reactions between re-tanning materials used with previous restoration materials found the treated leather, so it caused damage for leather.
- Method of application Martials: The methods of application of re-tanning materials vary on the treated leather, including by spraying, by immersion or using a brush and depends on the condition of the treated leather. (Kite and Thomson, 2006)

Some examinations and analysis used for the evaluation of re-tanning materials:

- **Scanning electron microscopy (SEM)**

The examination by Scanning electron microscopy (SEM) is one of the most examinations used in the field of restoration and conservation of the archaeological leather. It may be used for identifying the leather fibers and determining the leather kind by examining the morphology of the leather surface. Also we can determine the effectiveness of the used materials during treatment through documenting the leather status before and after adding the material. Olivares and others have used SEM to determine the efficiency of Nano particles of materials used during the treatment with size of μm to 400 nm100. It can be also observed the best spread and permeability of the materials with JEOL Model JSM-T20 SEM. A morphological study was

carried out for leather in comparison with re-tanned leather. SEM of the grain surface (X50) and the cross-section of the (X1000) of the leather with and without retained materials were carried out to show the effect of the prepared materials on the grain and fiber bundles as re-tanning agents. (Nashy.et.al., 2010) & (Olivares et al., 2014).

Also it has been determined elements in the leather, as well determining deformation of surface leather and missing parts of original tanning materials and elements composing leather by SEM and EDAX (Abdel-Maksoud,2011)

- **IR analysis:**
  The re-tanning materials were examined by IR analysis to determine the functional groups Identification of active matter of leather after added re-tanning agents. .(Naviglio, et al., 2005).
- **Thermal analysis:**
  There are many thermal analyses that can be used as experimental study of the ageing leather, as TGA analysis (Thermo gravimetric analysis). This analysis depends on recording the resulted changes for weight sample. Through it, shrinkage temperature can be found; besides, shrinkage temperature can be also determined by some devices like Theis shrinkage tester.
  Musa and other performed thermal analysis for ageing leather samples after adding re-tanning materials through TGA by Q500 analyzer machine. (Musa et al., 2014).
  Nashy and other performed thermal gravimetric analysis for the leather samples by using Shimadzu TGA-50 apparatus to estimate the weight loss of the leather samples as a function of temperature. (Nashy.et.al., 2010)
  There is another method by using Dynamic mechanical thermal analyzer: Rheometric Scienti®c DMTA Mk3) sample of

Leather was clamped in tensile mode under a small static applied force , and monitor the change in its displacement as it passed through the shrinkage temperature. Information could therefore be obtained on the percentage shrinkage and the temperature range over which it occurred. (Haron.et.al., 2012)

- **determination of tanning material by High Performance Liquid Chromatography (HPLC):**
  The determination of the tannin type used with the leather was determined by the comparison of the retention times and UV spectra between several tanning materials and tannin material extracted from leather and it can be utilization to expect reaction between tanning leather and materials used at treatment before applied it. (Abdel-Maksoud,2011)

- **Mechanical analyses:**
  The identification of the mechanical characteristics of the most important mechanical tests of the leather of the archaeological to determine the efficiency of the treatment material to improve the mechanical properties of the treated leather during the experimental studies of the materials of the leather samples similar to the case of treated leather, because the mechanical tests are a test of the samples of samples used in the same test so cannot expose the leather to those tests. Leather samples are exposed to the same conditions of the leather, such as thermal aging. The test is then carried out and the samples are prepared for testing at 23 ° C and relative humidity 65% for two days, then the samples are cut horizontally and vertically, and the thickness and width of the samples are measured**,** the area of cross section of each specimen was calculated, then the samples put at the tensile machine, the machine was run until the specimen was broken and the highest load reached was taken as the breaking load. (Nashy.et.al., 2010).
  Tensile strength=Maximum breaking load/Cross sectional area.

Elongation: The initial free length between the clamps before and after the final free length at the instant of break.

Elongation%=Final free length-Initial free length / Initial free length.

Tear strength: The samples were cut as a rectangle 50 mm long and 25 mm wide and put it at Template machine, the machine was run until the specimen was torn apart and the highest load reached during tearing was recorded as the tearing load. (Haron.et.al., 2012)

- **Porosity measurements:**

Sample Leathers from different areas were cut into pieces with 20 mm diameter and its thickness was measured. For porosity measures, samples leather in dry condition were subjected to flow of nitrogen gas then the same leathers were subjected for wetting with Cal wick liquid (surface tension = 15.9 dynes cm−1) and again leathers were subjected to the flow of above mentioned gas. For all the leathers, changes in the flow rate in dry and wet condition were measured as a function of pressure, and the pore size and its distribution was calculated by. $\mathbf{D = \gamma \cos\theta / P}$. (Velmurugan.et.al., 2017)

- **Color Measurements:**

Color is an important characteristic of archaeological materials and colour changes must be measured in order to preserve the authenticity and shape of the archaeological leather by Color measurements of the treated leather samples in comparison with untreated one, The CIELAB (L*a*b*) coordinates and the k/s values could measure using Ultra Scan PRO Spectrophotometer with D65 illuminant at 10o standard observer. (Nashy.et.al., 2010)

- **Softness :**

Determine softness and hardness for bookbinding is an important test at experimental study for bookbinding in order to keep original characteristics for leather treatment, softness determine by softness test: by pressing down to arm the machine lower down and sample leather clamp in the tester, the

deflection load plunger is measured and document with difference value for change surface leather in mm. (Haron.et.al., 2012).

Conclusion:

Leather can be treated with different materials during work manufacturing to improve protein chemistry, shrinkage temperature, tanning interferences, and other matters to prevent leather from deterioration factors in the future. Where severe although deterioration of leather can occur through chemical processes hydrolysis and oxidation.

Using re-tanning materials as treatment process and their selective depending on nature of both leather and re-tanning materials. Furthermore, it referred to value Re-tanning stage during leather manufacturing where old not use this stage and after 1850 widely used mineral salts as re-tanning agents such as aluminum sulphate or chloride and chrome to improve shrinkage temperature and properties of leather. but due to the disadvantage of these materials for leather future and the effect of using chrome which harm the environment. It is preferred avoid using it as restoration materials and even it is if available during manufacturing leather we can exchange it with selective organic materials.

Table (1) Survey for the most materials used in the process of re-tanning of vegetable tanned leather.

Aluminum salts
Aluminum tri-formate with chemical formula $C_3H_3AlO_6$ gives best results compared to other aluminum salts but the pH of the leather also increased after using. Jankauskauskaite et al., 2012 & Haroun et al., (2009) & Duki et al., (2013).
Chromium oxide
Chromium oxide is an inorganic chemical compound with the formula Cr_2O_3 and has shaped according to the method of preparation either bright green crystals and harsh or in the form of green powder is not

crystalline. It has disadvantages such as harmful to the environment despite obtaining desirable qualities of the leather such as improving its mechanical properties **(**Jankauskauskaite et al., 2012)& Zhang,et al,(2017).

Zirconium salts

Zirconium propionate with chemical formula Zr $(CH_3CH_2COO)_4$ is soluble in isopropanol, ethanol, and ethyl acetate but not soluble in water. It gives leather certain properties such as softness of the texture but increases pH and changes the color of the treated leather then becomes whiter. **(**Jankauskauskaite et al., 2012).

4-Vanadium quadrilateral oxide

Vanadium quadrilateral oxide is a chemical compound with the formula VO_2 or V_2O_4, which is in the form of black crystalline powder. It cannot be used in the treatment of Archaeology leather, due to colorful changes for leather treatment. . Jankauskauskaite et al., (2012)& Ohlidalove et al., (2017)

5-Iron oxide

Iron oxide is a chemical compound with the formula FeO. It is in the form of a crystalline black powder, and it also defects the color of the leather treated. Ohlidalove et al., (2017)

6- Silver Nano Particles

Silver Nano Particles has chemical symbol AgNPs. AgNPs are characterized by catalytic activity, thermal conductivity, high electrical, antimicrobial damage, as antifungal substances, and they give better results when used with Polyhyoxiurethunes. Ma et al., (2014)

7-Silicon dioxide SiO_2 Nano particles.

It works to increase the resistance of the treated leather to the strength of tensile and elongation, as well as increase leather resistance to high temperature. Ma et al., (2014) & Pan et al., (2017).

8-Zinc Oxide ZnO

It is characterized to thermal stability. Moreover, resistant to bacterial growth of the leather and improves the mechanical properties as well as tensile strength and elongation. Ma et al., (2014)

9-Titanium Oxide TiO_2 nanoparticles

Titanium oxide is characterized as water-insoluble and increases the resistance of the treated leather to external factors such as high temperature and humidity, as well as resistant to microbiological damage. Zengin, et al,(2012)& Ma et al., (2014).

10-Sodium montmorillonite (Na+Mt)

It gives good results when used in nanometer size. Also, It is best to use

organic solvent and not to use water so as not to affect the leather. Subsequently, leather is characterized by resistance to high temperature. Olivares et al., (2014)

11-Silver doped hydroxyapatite

It has the chemical formula (Ag-HA) and is applied by spraying. As a result, the treatment of leather by it, leather is characterized by resistance to bacterial growth. Ma et al., (2014) & Pan et al., (2017).

12-Manganese nanoparticle

Manganese nanoparticle has chemical symbol MnO or Mn_2O_3 which increases the degree of heat shrinkage of the leather significantly. Ma et al., (2014).

13- A mixture of chromium sulphate with phosphonium sulphate

It has chemical Symbol (THPS) $[(CH_2OH)\ 4P]\ 2SO_4$ It increases the degree of heat shrinkage of treated leather and is not harmful to the environment compared to chromium. López Muñoz, et al, (2011)& Zhang,et al,(2017).

14-Amino acid was mixed with silica and tetramethylammonium hydroxide TMAH

It works to complete the missing parts of the treated leather as well as improves its mechanical properties by forming collagen bonds with collagen. Shi, et al (2012) & Pan et al., (2017).

15-Newly synthesized Nano collagen

Newly synthesized Nano collagen maintains the physical properties of the treated leather as its color does not change, increases the degree of heat shrinkage and improves the mechanical properties of leather such as tensile strength and elongation. Bicchieria,et al,(2018).

16- Acrylic resins in nano size

Acrylic resins in nano size are widely used in Archaeology of leather because in this case leather is characterized by properties such as improving the physical and mechanical its properties. Moreover, acrylic resin contains active groups such as COOH or OH that increase the cohesion of the treated leather with the treatment material. Ma et al., (2014)& Chuan et al, (2009)

17- Ploy methyl acrylates Colloidal Silver Solution (CSS) with Polyhyoxiurethunes

Ploy methyl acrylates has chemical formula n $(C_4H_6O_2)$ which widely used as treatment of Archaeology leather because it is characterized by its characteristics. Also, characterized by drought after the formation of a solid transparent glossy membrane, and can be used as a material of

retaining of leather with the addition of acrylamide acid or acrylamide. It can be applied by spraying or immersion. The treated leather is characterized by resistance to ambient conditions such as high temperature or relative humidity, as well as resistance to microbiological damage. Chuan et al, (2009)& Nashy.et.al., 2010) & Pan et al., (2017).
18-Poly Meth acrylic acid with silica PMAA- with SiO2
The use of nanoparticles of silicon oxide with acidic poly meth acrylic improves the mechanical properties of the treated leather compared to using each of them to such extent as tensile strength or elongation. Pan et al., (2017)
19- Ploy methyl acrylates
Ploy methyl acrylates has chemical formula n ($C_4H_6O_2$) which widely used as treatment of Archaeology leather because it is characterized by its characteristics. Also, characterized by drought after the formation of a solid transparent glossy membrane, and can be used as a material of retaining of leather with the addition of acrylamide acid or acrylamide. Nashy.et.al., (2010)
20-Extraction of Oil and Phenolic
Oil and phenolic can be extracted from the roots of some plants such as Avocado Seed, helps to increase collagen cohesion so it can be used in cases of spreading cracks and fractures of the treated leather. Also, it increases the mechanical properties of the treated leather such as tensile strength and elongation. (Suparno , 2005)
21-Nano chitosan
Nano chitosan contains amino groups that increase the strength of cohesion with treated collagen fibers, which improves the mechanical properties of the leather such as tensile strength and elongation. Velmurugan et al ., (2017)

References:

1. Abdel-Maksoud,G., "Analytical techniques used for the evaluation of a 19th century quranic manuscript conditions " *Measurement* , **44**,pp:1606-1617, **(2011).**
2. Ali, S.B., Haroun, H.E., Musa,A.S., "Haraz Bark Powder Extract for Manufacture of Nappa Upper Leather as Alternative Re-tanning Agent", *Journal of forest products & industries*, , **2(5)**, pp:25-29,**(2013)**.

3. Antoniou,J., Liu,F., Majeed,H., Qi,J., Yokoyama,W., Zhong,F., "Physicochemical and morphological properties of size-controlled chitosan–tripolyphosphate nanoparticles" *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **465**, pp137:146, **(2015)**.
4. Baglioni, M., Bartoletti, A., Bozec, L., Chelazzi, D., Giorgi, R., Odlyha, M., Pianorsi, D., Poggi, G., Baglioni, P., "Nanomaterials for the cleaning and pH adjustment of vegetable tanned leather" *Applied Physics*, **122**, pp114:122, **(2016)**.
5. Boopathy, R., Karthikeyan,S., Mandal,A.B., "Characterisation and recovery of sodium chloride from salt-laden solid waste generated from leather industry", *Clean Techn Environ Policy*, **15**, pp:587-600, **(2013)**.
6. Budrugeac, P., Cucos, A, Miu,L, "Use of thermal analysis methods to assess the damage in the bookbindings of some religious books from XVIII century, stored in Romanian libraries", *J Therm Anal Calorim,* **116**, pp:439-450,**(2013)**.
7. Budrugeac,P., Cucos,L., Miu,L., "The use of thermal analysis methods for authentication and conservation state determination of historical and/or cultural objects manufactured from leather", *J therm anal calorim*, **104**, PP:439-450,**(2011)**.

8. Bicchieria,M., Valentini,F., Pascalicchio,F., Riccard,M.L, Colaizzif,P., Del Re,C., Talamo,M., "The solution to an unresolved problem: newly synthesised nanocollagen for the preservation of leather. " *Journal of Cultural Heritage*,**33,**pp:1:9,**(2018).**

9. Chuan, W.X., Tao,Q.T., Fang, R.L., Ming, S.,Ting, Z.Y., Yan, F.J.," Preparation of Fat liquoring- re-tanning agent with a reinforcing effect by free-soap micro emulsion copolymerization", *International Union of Leather Technologists &Chemists Societies* 30th, **400**, pp:1-6, **(2009)**.

10. Crudui,M., Deselnicu,V., MeteMutlu ,M., Gulumser,G., Bitlisli,B.O., Basaran,B., Zengin ,A.C.A, "New Tanning Agents Based on Titanium and Zirconium" Proceedings of the 3rd Advanced Materials and Systems Conference ICAMS, pp: 27-32, **(2010)**
11. .DeBrito, A.L.F., Prasad,S., Muniz, A.C.S., "Re-tanning of goat leather using aldehyde after utilization of trivalent chromium salts", *Journal of the American Leather Chemists Association*, **97**, pp:1-18, **(2002)**.
12. Dienst,E.V., "Some Remarks on the Conservation of Wet Archaeological Leather" *Studies in Conservation*, **30**, pp. 86-92**,(1985).**
13. Duki,A., Antunes,A.p.m., Covington,A.P., Strachan, J.G., " The stability of metal-tanned and semi-metal tanned collagen" , *International Union of Leather Technologists and Chemists Societies* , volume: Fundamental Research in Leather Technologies Cite this publication ,Istanbul/Turkey, pp:1-10**, (2013)**.
14. Falcão,L., Eduarda,M., Araújo,M., "Tannins characterisation in new and historic vegetable tanned leathers fibres by spot tests" *Journal of Cultural Heritage*, **12**, pp149:156**,(2011)**.
15. Fuck, W.F., Gutterres, M., Marcilio,N.R., Bodingnon,S., " The influence of chromium supplied by tanning and wet finishing processes on the formation of Cr(VI) in leather" *Brazilian Journal of chemical Engineering*, **28**, pp:221-228**,(2011)**.
16. Grasel,F.D.S., Ferrão,M.F., Wolf,C.R., "Ultraviolet spectroscopy and chemometrics for the identification of vegetable tannins" *Industrial Crops and Products*, **91**, pp279:285**,(2016)**.
17. Haines,M.,B., "Deterioration in leather book bindings-our present state of knowledge" *The British Library Journal*, **3**, pp: 59-70**,(1977)**.
18. Haines,M.,B., "The conservation of leather bookbindings" *Studies in Conservation*,**29**,pp:50:54,**(1984)**.
19. Haron, M.A., Khirstova,P., Gasmelseed,G.A., Covington,A., "Potential of vegetable tanning materials and basic aluminum

sulphate in Sudanese leather industry (part II)" ,*SuranareeJ.Sci.Techno*., **19**, pp: 31-41**,(2012)**.

20. Haroun,M., Palmina, K.,Gusrshi, A., Covington, D., "Potential of vegetable tanning materials and basic aluminum sulphate in Sudanese leather industry" Journal of Engineering Science and Technology, **4**, pp: 20 – 31**,(2009)**.
21. Hassan,R.R.A., "A preliminary study on using linseed oil emulsion in dressing archaeological leather " *Journal of Cultural Heritage*, **21**, pp:786:795**,(2016)**.
22. Http://www.basf.com/leather. (2009).Pocket Book for the Leather Technologist, Fourth edition BASF Aktiengesellschaft, 67056 Ludwigshafen, Germany, pp: 17-18.
23. Ibrahim, A. A.; Youssef, M. S. A.; Nashy, E. H. A.: Using of hyperbranched poly (amidoamine) as pretanning agent for leather, *International Journal of Journal of Polymer Science*, **5**, 690-695, **(2013)**
24. Jankauskaite,V., Jiyembetov,I., Gulbiniene, A., Sirvaityte,J., Beleska,K., Urbelis,V., "Comparable Evaluation of Leather Waterproofing Behavior upon Hide Quality. I. Influence of Re-tanning and Fat Liquoring Agents on Leather Structure and Properties", *Materials science*, **18**, pp: 150-157**, (2012)**.
25. Jiang,Y., Li,J., Li,B., Liu,H., Li,Z., Li,L., " Study on a novel multifunctional nanocomposite as flame retardant of leather" *Polymer Degradation and Stability*, **115**, pp110:116**, (2015)**.
26. Kathpalia, Y.P., Conservation and restoration of archive materials, Paris, pp:37-39**, (1973)**.
27. Kite,M., Thomson.R., Conservation of leather and related materials, Oxford, pp:30.86.231.239**, (2006)**.
28. López Muñoz ,BE., Rivera Robles, R., Iturbe García ,JL., Olguín Gutiérrez, MT. , " Adsorption of basic chromium sulfate used in the tannery industries by calcined hydrotalcite. " *Journal of Mexican Chemical*. ,**55**, pp:137:141, **(2011).**

29. Li,J., Yan, L.,Shi, B.,Zhang, J., "A Novel Approach to Clean Tanning Technology", ,Journal of Chemistry and Chemical Engineering ,**65**, pp:1203-1212,**(2013).**
30. Lofrano,G., Meric,S., Zengin,G.E and Orhon, "Chemical and biological treatment technologies for leather tannery chemicals and wastewaters: A review", *Science of the Total Environment* , **461**,pp:265-281**,(2013)**.
31. Ludwick L., A comparative study on surface treatments in conservation of dry leather with focus on silicone oil, BA/Sc thesis, Department of Conservation, University of Gothenburg, Goteborg, Sweden, **(2012).**
32. Lyu,B., Gao,J., Ma,J., Gao,D., Wang,H ., Han,X., "Nanocomposite based on erucic acid modified montmorillonite/sulfited rapeseed oil: Preparation and application in leather " *Applied Clay Science*, **121**, pp36:45**,(2016)**.
33. Ma,H., Zhou,J., Hua,L., Cheng,F., Zhou,L ., Qiao,X., "Chromium recovery from tannery sludge by bioleaching and its reuse in tanning process" *Journal of Cleaner Production*, **142**, pp2752:2760**, (2017)**.
34. Ma,J., Lv,X., Gao,D., Li,Y., Lv,B., Zhang,J., "Nanocomposite-based green tanning process of suede leather to enhance chromium uptake" *Journal of Cleaner Production*, **172**,pp:120-126**, (2014)**.
35. Musa,A.E., Gasmelseed, G.A., " Development of Eco-friendly Combination Tanning System for the Manufacture of Upper Leathers", *International Journal of Advance Industrial Engineering*, **1**, pp:9-15**, (2013)**.
36. Musa,A.E., Gasmelseed,G.A, "Application of Acacia nilotica spp nilotica Pods (Garad)Powder as Alternative Vegetable Re-tanning Material" , *Journal of forest products & industries*, **3**, pp: 112-117**, (2014)**.
37. Nashy, El-S. H. A., Hussein, A. I., Essa, M. M. "Re-tanning Agents for Chrome Tanned Leather Based on Emulsion Nano-

particles of Styrene/Butyl Acrylate Copolymers" *New York Science Journal*, **3**, pp: 13 – 21**, (2010)**.

38. Characterization of Tannery Chemicals: Re-tanning Agents. E-book: http://www.aaqtic.org.ar/congresos/istanbul2006/Visual%20 Displays, pp:1-20**, (2011)**.
39. Nianhua,D., Shuping,J., Rui, Z.,Weihua,D., Zengjian,M., "Optimize of Re-tanning Plate of Stimulate-glaze Goatleather Upper Leather "*International Union of Leather Technologists & Chemists Societies congress* , **73**.pp:1-6**, (2009)**.
40. Ohlídalová,M., Kucerová,I., Brezová,V., Cílová,.Z., "Influence of metal cations on leather degradation" *Journal of Cultural Heritage*, **24**, pp86:92**, (2017)**.
41. Olivares,G.S., Solis,A.S, Calderas,F., Torres,L.M., Manero,O., Di Blasio,A., Alongi,J., "Sodium montmorillonite effect on the morphology, thermal, flame retardant and mechanical properties of semi-finished leather" *Applied Clay Science*,**108**, pp:254-260**, (2014)**.
42. Onem,E., Gulumser,G., Renner,M., Yesil-Celiktas,O., " High pressure vegetable tanning of sheep leather s using supercritical carbon dioxide" *The Journal of Supercritical Fluids*, **104**, pp259:264**, (2015)**.
43. Pan,H., Long Li,G., Qi Liu,R., Xia Wang,S., Dong Wang,X., "Preparation, characterization and application of dispersible and spherical Nano-SiO2@Copolymer nanocomposite in leather tanning" *Applied Surface Science*,**426**, pp: 376:385**, (2017)**.
44. Pruneanu,M., Maier,S. , Niculescu, O., Vitan,F., Deselnicu,V., " Obtaining and Characterization of a Benzenesulfonate Melamine Formaldehyde Resin, with Applications in Leather and Fur Industry", *Revista de Chimie -Bucharest Original Edition*, **62**, pp:60-63**, (2011)**.
45. Saleem,R.,Adnan, A., Hanif, M., Saleem, M.,Lee, K.H., Qureshi, F.A. "Synthesis and application of sulfonated adipic dihydrazide formaldehyde-based resins under different molar

ratios as effective leather re-tanning agents", *Iranian Polymer Journal*, **23**, pp:69-78**, (2013)**.

46. Sebestyen, Z., Czegeny, Z., Badea, E., Carsote, C., Sendrea, C., Barta-Rajnai, E., et al. "Thermal Characterization of New, Artificially Aged and Historical Leather and Parchment." *Journal of Analytical and Applied Pyrolysis*, **115**, pp: 419-427**, (2015)**.
47. Sangeetha,S., Fathima, N.N., Sreeram, K.J., Rao, J.R.,Nair,B.U., "Stimuli Responsive leathers using smart re-tanning agents", *Journal of the American Leather Chemists Association* ,**107**, pp:196-204**, (2012)**.
48. Shi,B., Li,J., Wang,Y.N., Liao, X., Zhang, W., He, Q., Cao ,M., "A Novel wet white technology based on an amphoteric organic tanning agent", *Asia International Conference of Leather Science and Technology Congress, At Taipei*, pp:1-8**, (2012)**.
49. Suparno O., Phenolic reactions for leather tanning and dyeing. Ph.D. Thesis. University of Leicester, pp:34.45.46.132.180.181.182, **(2005).**
50. Teng, B., Jian,X., Gao,Y., Chen,W., "Comparison of polyflavonoids in bayberry tanning effluent and commercial bayberry tannin: prerequisite information for vegetable tanning effluent recycling*" Journal of Cleaner Production*, **116**, , pp:972:979. **(2016)**.
51. Valeika, V., Širvaitytė, J., Beleška, K., "Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather Materials Science, *Materials Science,* **16**, pp:330 – 336**, (2010)**.
52. Van Soest,H.A.B., Stambolov,T., Hallebeek,P.B., "Conservation of Leather " *Studies in Conservation*, **29**, pp. 21-31**,(1984)** .
53. Velmurugan.P., Ganeshan.V., Nishter.N.F., Jonnalagadda.R.R., "Encapsulation of orange and lavender essential oils in chitosan nanospherical particles and its application in leather

for aroma enrichment" *Surfaces and Interfaces*, **9**, pp124:132**, (2017)**.

54. White,L.G., Passivation Polymer Bulking Versus Sucrose Impregnation: A Cross-Methodological Approach to the Conservation of Leather, *A Senior Scholars Thesis, Department of Maritime Studies, Texas A&M University*, pp:8-20**, (2008)**.
55. Wu,C., Zeng, Y., Liao, X, Zhang,W., Shi,B., "Effect of Re-tanning Agents on Dry Heat Resistance of Leather s," *Journal of the American Leather Chemists Association*, **108**, pp:294-299, **(2013)**.
56. Zengin, A.C.A., Crudu, M., Maier, S.S., Deselnicu, V., Albu, L., Gulumser, G., Bitlisl,B.O., Basaran, B., Mutlo,M.M., "Eco-leather: Chromium-free Leather Production Using Titanium, Oligomeric Melamine-Formaldehyde Resin, and Resorcinol Tanning Agents and the Properties of the Resulting Leathers", *Ekoloji*, **21**, pp:17-25**, (2012)**.
57. Zhang,J., Han,Z., Teng,B., Chen,W., "Biodeterioration process of chromium tanned leather with Penicillium sp " *International Bio deterioration & Biodegradation*, **116**, pp104:111**, (2017)**.
58. Zhang,X., Yang,W., Chen,W., Cornelia,C.C., "Application of Fragrance Re-tanning Agent "*International Union of Leather Technologists & Chemists Societies 30th*, IULTCS Secretariat, China, pp:1-6**, (2009)**.