A Mini Review
Role of Natural Binders in Leather Finishing- A Comparative Approach

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Abstract

Leather finishing has its own importance in leather making. A variety of chemicals are used in the finishing operation, to provide the aesthetic look of the leather products. The role of finishing chemicals such as pigments, dyes, plasticizers, wax emulsions, cross linkers, fillers, wetting, penetrating agents and binders have their own role to give finished look to the leather products. A binder plays significant role in the leather finishing. This review elaborated on the role of natural binders with respect to their properties, application and binding effects in leather finishing against synthetic binders. This review focuses on a greener approach to leather finishing.

Introduction

Leather is a natural material that has been used for versatile applications. The most common raw materials used for leather making, are domestic animals like cattle, goats, sheep, and to a lesser extent pig.[1] Multiple steps, such as pre-tanning, tanning, post tanning, and finishing are involved in leather processing.[2,3] The pre-tanning process consists of the removal of hair and flesh from the animal by trimming process, while tanning is an essential step which makes it stable and durable. The post tanning process involves the use of fat-liquoring, retanning agents and dyes for better appealing look of leather.[1,3] Leather finishing is the final step in the leather manufacturing process for the effective, natural, defect less, and regular appearance of leather.[4]

Role of finishing step

The finishing step of leather processing is the final and important step of leather making. The principle objective of leather finishing is to improve the aesthetics and surface properties of the leather by protecting the leather surface against dirt, stain, wetting problems, rubbing, scuffing, and flexing.[4,5] Leather finishing is an important phase to modify the leather surface, shade, gloss and physical strength.[5] The following practices and techniques are used for leather finishing.

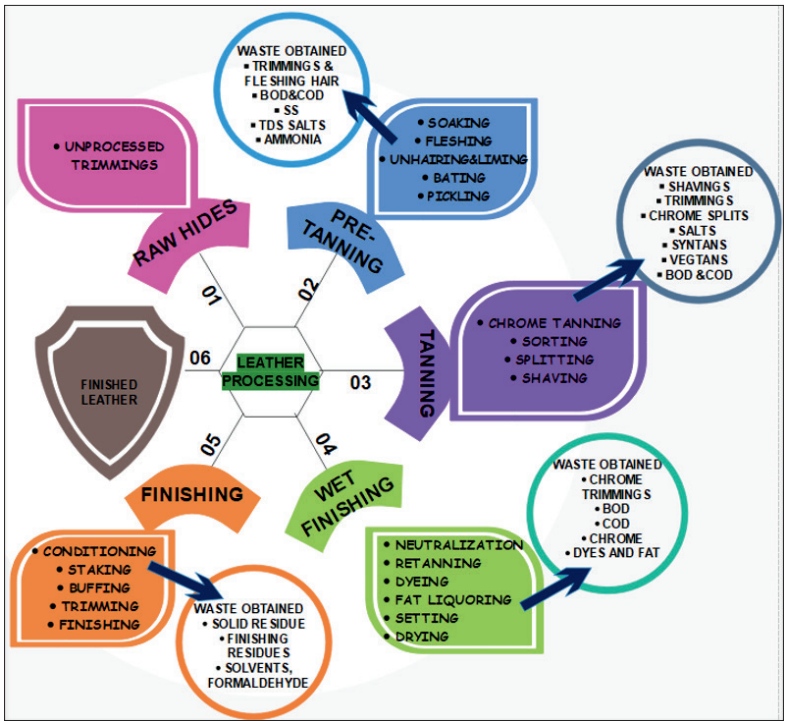

Figure 1. Processes involved in leather processing

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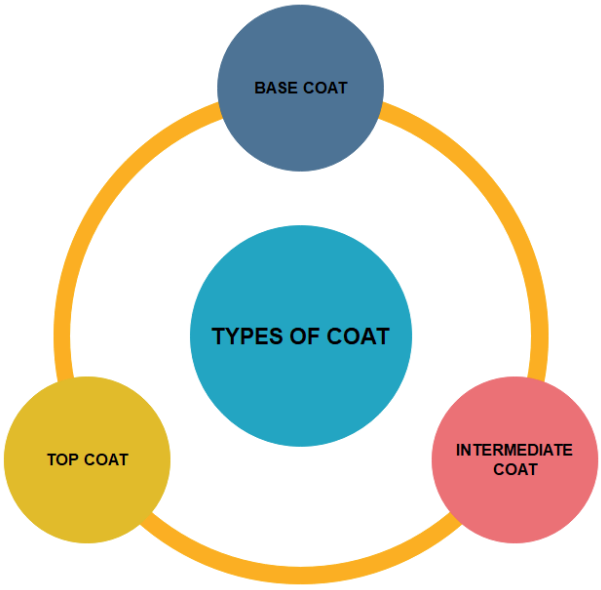

Figure 2. Different types of coating process in leather finishing

Different coats used in leather finishing

Leather finishing can be classified into three coats: base coat, intermediate coat and top coat

- Basecoat: It chemically modifies the surface property of the crust (post tanned) leathers to fix the finishing chemicals. The finishing formulation for base coat consists of solvents, resins and possibly pigments.[6,7]
- Intermediate coat: It majorly consists of binders for filling and enhancing the physical properties. It also acts as a carrier for pigments and dyes to be fixed on leather. In addition, depending on the choice of binders and fillers, the finishing properties can be controlled for the final application. Fillers in the finishing composition influence the uniform texture and levelling of dyes and pigments on the surface.[6,7]
- Topcoat: It is comprised of resins based on polyurethane and cellulose derivatives to protect the leather finish.[6,7]

Different types of finishing techniques used in leather finishing

Leather finishing is operated in many ways, which can produce finished leather with multifunctional properties depending upon the finishing chemicals employed. Following Table I and Figure 3 indicates the techniques used in leather finishing.

Different types of finishing chemicals consist of natural compounds

The application of versatile finishing chemicals on leather provides an aesthetic appearance with improved physical strength to the leather surface. Commonly used leather finishing chemicals are polymers, pigments, binders, wax, resin, dyes and auxiliaries. Various add-on properties such as anti-stickiness, resistance to abrasion, light/heat and water resistance can be implemented by the application of multiple finishing chemicals and processes.[8,9,10]

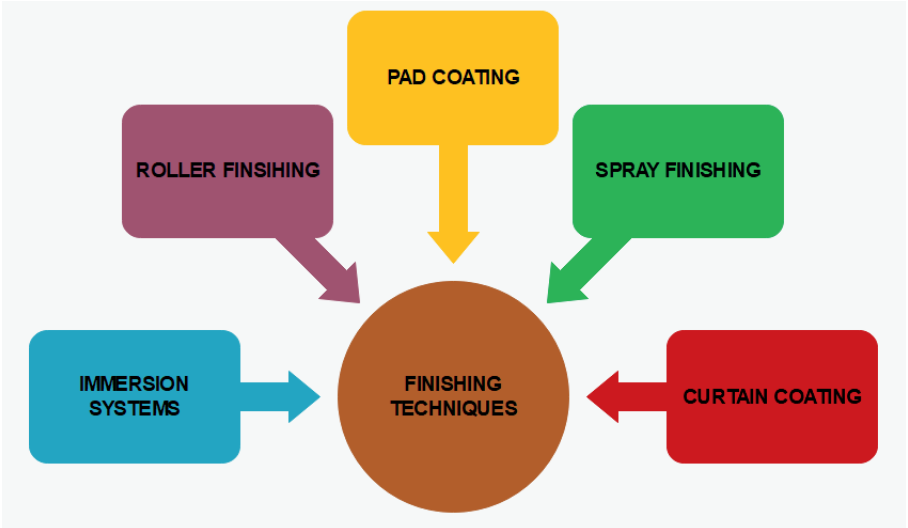

Figure 3. Different types of finishing Techniques for leather finishing

Table I

Represent the different types of leather finishing techniques

S. No	Techniques	Process	Reference
1	Pad coating	Pad coats are usually applied using a plush pad - a wooden board covered with a soft velvet-like cloth. It is done by hand and is, therefore, labor-intensive but it does ensure that the finish is worked well into the leather and evenly applied across the hide	6,7
2	Spray finishing	The most commonly used method. A finish, is supplied through a fine jet in the atomizing part of the spray gun.	6,7
3	Curtain coating	Curtain coating involves applying the finish to leather in the form of a liquid curtain of finish. Gap machines are particularly useful for applying heavy coats of finish, but their use in the industry is limited	6,7
4	Roller coating	In this technique, the finish is applied by passing the leather between two cylinders. Forward and reverse roller coating exists.	6,7
5	Immersion systems	Here crust leathers are passed through a dye solution as an alternative to traditional spray dyeing methods.	6,7

To provide color to the finished surface of the leather, pigment paste and dyes are applied. The pigment paste with natural compounds in the form of blending of oils is applied to enhance the resistance to ageing of coating.[11] The application of metal oxide with oil and wax emulsion also explored to increase the thermal stability.[12] The natural extract from Bixa orellana seeds can be used to finish the leather to improve fastness.[13] Wax emulsion from beeswax and biodegradable surfactants provide gloss, smoothness and touch to the leather surface.[12,37] The application of fillers in the form of nanocomposite latex were also tried and the resultant leather showed better mechanical and flame retardant properties.[14,15]

Since this review focuses on the use of natural compounds, specifically binders, in the leather finishing Table II represents the use of various finishing chemicals where such natural compounds are used.

Table II

Finishing materials consisting of natural compounds

Finishing materials	Natural compound used for finishing	Work	Details	Inference	Reference
Pigment pastes and plasticizers	Flax seed oil and poppy seed oil	Leather Finishing with New Pigment Paste	Pigment pastes in the form of Flax seed oil (brown color) and poppy seed oil (yellow color) as plasticizer	Plasticizers improved resistance to ageing of coating	11
	Castor oil	New Pigment Paste for Leather Finishing	New pigment paste composition made up of Black iron oxide, Polyacrylic binder, Ethoxylated lauric alcohol, castor oil and wax emulsion	Shows higher thermal stability	12
Dye	Extract from Bixa orellana seeds	Studies on the application of natural dye extract from Bixa orellana seeds for dyeing and finishing of leather	The extract from Bixa orellana seeds	Enhancement in color measurement and fastness properties	13
Wax emulsions	Beeswax, lanolin	Obtaining and Characterization of an Ecologic Wax Emulsions for Finishing Natural Leathers and Furs	The mixture obtained from the mixing of wax, lanoline and emulsifier triethanolamine monostearate	finishing films, a waxy feel and better resistance to scratches and water.	37
Fillers	Casein	Construction of hetero-structured fillers to significantly enhance the fire safety of bio-based nanocomposite coating	The spay of hetero-structured filler prepared by double hydroxide-reduced graphene oxide blended with waterborne casein-based nanocomposite latex	The mechanical properties of experimental leather were improved by 71.8% with increase in flame retardant property	14

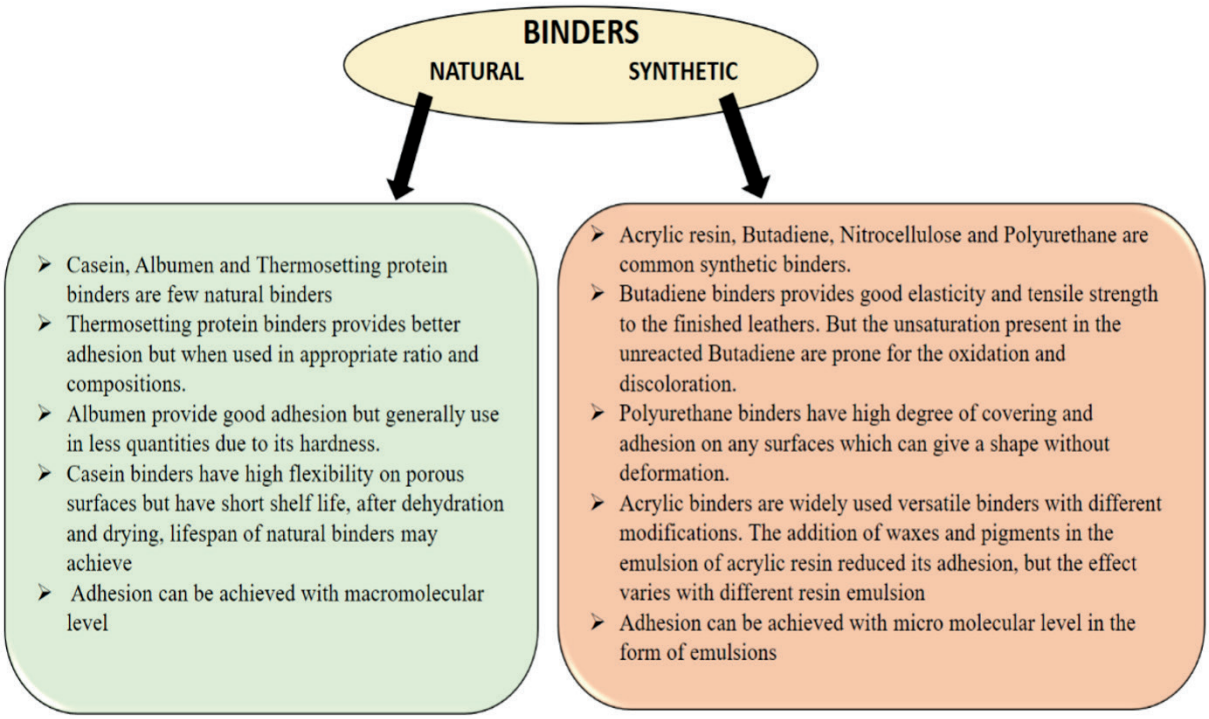

Figure 4. The comparative properties of natural and synthetic binders

Binders

Film-forming materials improve the properties of leather by holding the collagen fibers of leather together thereby creating a stronger leather structure. Binders are used for repairing the damages of the leather surface and to bind the pigments, their nanostructured derivatives and other finishing chemicals with leather.[16]

The role of Binder

The role of binders in leather finishing has its own importance. It forms a continuous film on the surface of the leather for the improvement of physical, stability and crack resistance. Leather finishing chemicals with additives and binders can hide leather surface defects.[16] Leather finishing describes the process for enhancing the physical and fastness properties such as resistance to abrasion, heat/light and water, and improving the surface coloring of leather. Commonly used binders for the leather industry are protein and resin-based binders. Generally, binders provide finish film with excellent properties like good flexibility, strong adhesion, light fastness, soft and elastic films.[16,17]

Types of binders used for leather finishing:

Natural binders

Protein-based binders contain casein, a natural protein, obtained from bovine milk which is biodegradable and non-toxic in nature and forms stable films with excellent adhesive force and strong heat resistance.[18,19] The formation of stable casein films is mainly due to its secondary protein structure and weak intermolecular interaction. Despite these properties, there are a few limitations for casein such as low flexibility, high water sensitivity, and susceptibility for the bacterial attack. To overcome these drawbacks casein, with its derivatives from biosynthetic polymers, inorganic nanoparticles, and plasticizers were explored.[15,19]

A biodegradable composite of caprolactam-modified casein and waterborne PU had been used for leather finishing. Experimental leathers were found to be superior in elongation at break (99.77%) and the fastness to wet rub 4/5 than control values 72.46% and 3 respectively.[20]

The chitosan- poly vinyl alcohol-based coating was explored as a thin transparent film on the leather surface. The prepared chitosan

product was applied on shoe lining leather, resulting in a low cost and environmentally friendly finished leather product with antimicrobial and antifungal properties.[21]

The application of gelatin, extracted from leather solid waste for leather finishing was explored. The chemically modified gelatin was blended with the commercial binders to produce a low-cost and eco-friendly film for leather finishing application.[22] The leather shaving scraps were also explored as protein binder for finishing application to set a better example of sustainability for the leather sector.[23]

Synthetic binders

Polymeric and resin-based binders are compatible and show versatile applications in leather finishing.[31] The combination of these synthetic binders with different polymers, nanoparticles, organic and inorganic composites is also a trend in leather finishing.[3] The commonly used synthetic binders used in leather finishing are acrylics, polyurethanes, butadiene and their derivatives. They are well known for their resistance to hydrolysis, hardness-softness, high blocking resistance, good adhesiveness, good film-forming properties, and are cost effective.[24,25]

Due to the capacity to form highly stable polymeric film, the polymeric binders are used to protect the leather from damage and provide desired properties such as better appearance, texture, color and surface feel.[8] Synthetic polymeric binders act as pigment carriers to form a homogeneous film on the leather surface. Blending biodegradable polymers with synthetic polymers to improve the biodegradability of leather has gained much interest recently.[16]

The application of acrylic-based resin binder and its effect on water vapor permeability of finished leather was also explored. The results indicated that the finished leather samples had good water vapor permeability 47.84 g/h m^2 and excellent wet rub fastness (3-4/5).[26]

The quality of flocked leathers coated with acrylic and polyurethane binders was tested and compared. Results proved that the polyurethane binder had better qualities and superior binding characteristics as compared to acrylic binders. The polyurethane binder shows better abrasion, fastness and durability characteristics than the solvent-based/ acrylic binders.[5]

The application of mixture of water-based polyurethane with silicon dioxide nanoparticles in leather finishing were tried. The experimental leather showed better water vapor permeability 0.3889 g/h m^2 than conventional leathers.[27]

The application of various blends in leather finishing has also been evaluated such as the cross-linking reaction between polyisocyanate with acrylic and polyurethane binders to improve the strength properties of finished leather.[38] Similarly, the crosslinking reactions of butadiene binders with different binders such as polyaziridine, polyisocyanate, epoxy compounds, polycarbodiimide, and polysilane improve the wet fastness properties.[28]

The application of silicon oxide nanoparticles modified acrylic resin as binder showed improved water and air permeability by 11.5% to 15.4%.[27,37]

The application of cellulose derivatives such as nitrocellulose and ethyl cellulose in the leather finishing has also been evaluated. These extracted cellulose derivatives from groundnut husk and sugarcane bagasse are used in leather finishing. The work indicates better upgrading of low-quality leathers, by the use of different concentrations of plasticizer and binders.[34]

The mixture of water-based acrylate/clay nanocomposites composed of terpolymer (butyl acrylate-methyl methacrylate-acrylamide) was explored as a base coat in leather finishing. The experimental leathers showed improvement in mechanical and thermal properties with better film-forming properties, elasticity and pigment binding efficiency than conventional binders.[29] Nanocoatings of acrylic resin are widely used in leather finishing because of their better penetration effect.[30] The protein binder mixed with PU finishing binder is also applied in leather finishing to achieve a natural binder effect with improved properties.[32]

The polymeric dispersion of polyurethane co-vinyl pyridine copolymer as a binder has its own importance in leather finishing. The presence of cationic charge in polymeric backbone provides good adhesion to the leather surface.[7] Polyvinyl alcohol blended with non-toxic chemicals, applied for leather finishing. Experimental leathers showed better wet and dry rub fastness, adhesion to finishing, tensile strength, elongation at break, and softness than control leathers.[43]

The following Table III provides details of the uses of natural and synthetic binders and the enhanced properties associated with experimental finished leather

Table III

List of binders for leather finishing

S. No	Title of paper	Binder used	Type of Binder	Property enhanced and application	Reference
1.	Evaluation and Application of Acrylic Based Binder for Leather Finishing	Acrylic-based resin binder	Synthetic	Finishing formulation containing a high amount of binder showed excellent rub fastness value (4-4/5) and water vapor permeability (47.84)	26
2	Enhancement of antimicrobial properties of shoe lining leather using chitosan in leather finishing	PVAc binder	Synthetic	The prepared chitosan with binder helped to minimize the microbial attack in shoe lining leather, employing a low-cost environmentally method to inhibit the bacterial and fungal attack on finished leather.	21
3.	A novel approach in leather finishing: Surface modification with flock fibers	Acrylic and polyurethane binders.	Synthetic	Polyurethane binders showed better results than the acrylic binders. PU binder can be a better replacement for solvent-based binders.	5
4	Preparation of polyurethane silicon oxide nanomaterials as a binder in leather finishing	Water-based polyurethane is used as a binder.	Synthetic	Improved mechanical properties with eco-friendly approach for leather finishing.	27
5	Use of water-based carbonyl-functional polymers on a cross-linker-free high performance leather finishing	Acrylic and polyurethane binders	Synthetic	The use of water-based acrylic polymers which contain a carbonyl-functional group shows high performance in upholstery leather without crosslinkers.	33
6	Study of Cross-linking Reactions on Butadiene Binders in Aqueous Finishing	Butadiene binders	Synthetic	The use of butadiene binders Improve wet fastness properties of finished leather. The applied butadiene binders improved the fastness properties (4/5) of finished leather.	28
7.	The acrylic resin leather coating agent modified by nano-sio$_2$	Acrylic resin binder	Synthetic	The application of SiO_2-acrylic resin in leather finishing showed an increase in air and water permeability.	37
8.	Extraction of cellulose from renewable resources and its application in leather finishing	Cellulose binder	Synthetic	This study provided better approach towards waste to best concept by utilization of cellulose to impart the fullness of finished leather.	34
9.	Preparation of stable acrylate/ montmorillonite nanocomposite latex via *in situ* batch emulsion polymerization: Effect of clay types	Acrylate binders	Synthetic	The application of water-based acrylate/clay nanocomposite provide better thermal properties to experimental leathers.	29
10	Aqueous dispersions of polyurethane–polyvinyl pyridine cationomers and their application as binder in base coat for leather finishing	PU binders	Synthetic	The performance of Aqueous dispersions of polyurethane–polyvinyl pyridine cationomers as binder exhibited good adhesion properties to the leather surface.	7
11	Preparation and evaluation of non-toxic top coatings for leather to minimize pollutants in leather finishing process	PVA binder	Synthetic	The effect of non-toxic top coatings of PVA binder brought eco-friendly approach for leather finishing.	43

S. No	Title of paper	Binder used	Type of Binder	Property enhanced and application	Reference
12	Application and evaluation of the performance of poly (vinyl alcohol) and its blend with nitrocellulose in leather top coating.	Nitrocellulose	Synthetic	The presence of surface-active agents on the derived binder showed smooth and continuous film with better dry and wet fastness properties.	35
13.	Preparation of acrylic silicon dioxide nanoparticles as a binder for leather finishing	Acrylic binders	Synthetic	The blending of acrylic compounds with silicon dioxide nanoparticles provides good flexibility, strong adhesion, light fastness, soft and elastic films to the leather surface	30
14	Blend composites of caprolactam-modified casein and waterborne polyurethane for film-forming binder: Miscibility, morphology, and properties	Biodegradable caprolactam-modified casein and waterborne polyurethane binder	Natural	Finished leather samples showed an increase in elongation at break from 72.46% to 99.77% and wet rub fastness from 3-4/5.	20
15	Application of Extracted and Modified Gelatin from the Leather Solid Waste in Commercial Finishing Agents	Modified gelatin	Natural	The binders blended with modified gelatin showed better biodegradability than commercially available binders.	22
16.	Effect of Finishing Auxiliaries on Permeability of Leathers	Protein and PU finishing binder	Natural and Synthetic	Leather coated with protein binder shows minimal permeability reduction, as compared with acrylic and polyurethane binders.	24
16.	Hydrolysis of leather shavings waste for protein binder	Protein binder	Natural	Protein binder obtained from leather shaving scraps explored for the alternate of synthetic binder and with sustainability approach.	23
18.	The use of protein binder from shaving waste for leather finishing: Judging from the physical, chemical, and morphological properties of lizard skin leather	Protein binder	Natural	The application of protein binder obtained from shaving waste showed better physical strength properties.	32

Environmental concern

Generally, leather finishing associates with application of natural compounds, synthetic chemicals and their derivatives such as polyamide–imide, polyethersulfone, polysulfone, polyphenylenesulfone, polyphenylenesulfide, polyimide, polyaryletherketones, polyetherimide and polyurethanes. The lack of purification and treatment of unused finished chemicals creates a negative impact on the aquatic environment which leads to the problems associated with high BOD, COD, TDS. The longer impact of these chemicals may develop possibilities of side reactions such as chlorination, amidation, oxidation and sulfonation due to presence of active groups in their structure.39 The polyurethane and its derivatives are preferred synthetic binders for leather finishing. Being a combustible material, they liberate high concentration of hydrogen cyanide, carbon dioxide, carbon monoxide and various oxides of nitrogen which contributes high to the carbon footprint of the leather industry.[40] Some of the solvents used in finishing with binders can liberate volatile organic compounds which are also toxic to the human health and the environment.[41] Chronic exposures to these chemicals may cause several diseases especially skin and lung cancer. The solvent free or water-based formulations and application of these binders may decrease the carbon footprint judicially.[42]

The application of natural binder alone or with the blending of synthetic binder may contribute to a smaller environmental footprint for leather finishing. Moreover, the influence of application of above blending depends upon the origin of the natural binder as well as surroundings of the chosen environment.[22]

Conclusion

The review focused on the detailed properties and importance of use of natural binders in leather finishing. The details of finishing processes and chemicals used are also discussed here. The uses of natural binders and its derivatives may overcome the dependency of uses of synthetic binders and contribute towards more sustainability and smaller carbon footprint. The eco-friendly and biodegradable binders may be considered for the leather finishing.

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