EVALUATION OF POLYMER RESINS AND FILMS FORMED BY LEATHER FINISHING

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***Abstract* - The final appearance and technical features of leather are determined by the finishing stages of leather processing, which comprise a range of operations and treatments. It is desirable to reduce or mitigate the existing defects in the original hide, to modify the surface properties of the leather and to improve leather properties under conditions of use. In the final stages of leather processing, many products are applied to form a protective coating. These coatings include resins such as polyacrylates, polyurethanes and casein. In this context, this work aims to describe aspects of the films formed with commercial polymeric resins used industrially in leather finishing. A methodology is proposed for characterizing the properties of polymeric film layers and their correlation with the material composition, through a parameter survey and physical tests.**

***Keywords*— Finishing, Resins, Polymers, Films, Leather.**

I. INTRODUCTION

Leather is a highly valued material. Leather goods are in great demand for their sophistication and inclusion in fashion trends, design and style. Leather is used in the manufacturing of items such as footwear, clothing, furniture, automotive upholstery and accessories, because of its natural features, diverse colors and textures.

New technologically innovative leather goods have being developed for comfort and elegance. Leather production technology is constantly evolving due to scientific research and chemical developments in the sector. The use of new techniques, for example the use of lasers in design (Santos *et al.*, 2011), allows one to obtain new products in a short time and with specific characteristics.

Brazil occupies a prominent position in the leather sector as the fourth largest producer of finished leather and largest exporter of cow hide heavy leather, having the second largest herd in the world (FAO, 2011). The industrial estate is composed of various leather factories for footwear, components, machinery and leather goods production.

Depending on the article produced, specifications and characteristics related to chemical resistance, physical-mechanical and chemical characteristics that are influenced by the associated technology and chemicals used are required for finished leather. Certain sectors, such as the automotive and furniture industries, have stricter controls regarding quality standards.

Leather finishing, comprising a set of treatment steps, is the final stage in the process of leather manufacturing in tanneries and fills the important role of ensuring the appropriate resistance properties in the final product are obtained. Finishing improves leather appearance, reduces surface defects and scratches and provides brightness, feel, color matching, color effects, tone, texture and various patterns, while still conserving or even restoring the natural look of the hide (Adzet *et al.*, 1985).

There are many finishing types, including transparent, matte, polished, sanded, embossed, etc. The most important factors in the finishing process are the characteristics of the leather to be prepared, chemical products employed and operating systems. The main steps in the finishing process are impregnation, bottom application, covers and tops, printings and polishes. The categories of chemicals products used are pigments, dyes, binders, auxiliaries and lacquers.

Polymers are materials of wide application that are employed in leather finishing and many other uses such as in packaging, adhesives, biomedical applications, automotive manufacturing and utensils, among others. Polymer based emulsions are widely used as coating materials for textiles, automotive paints, construction materials, leather, etc. Aqueous emulsion polymerization has environmental advantages and a simpler application procedure. However, in general, the water resistance and the mechanical properties of water based polymeric systems are inferior to solvent based polymeric systems. In contrast, silicate based polymer nanocomposites are an alternative for improving the properties of water based coatings (Yilmaz *et al.*, 2011). The search for materials based on components obtained from natural sources is of high importance. Natural composites have good mechanical properties and reduce the dependence of manufacturing on non-renewable material sources, thus bringing economic and environmental benefits (Barbosa Jr. *et al.*, 2010).

Many resins are employed in leather finishing to produce films or coating layers, as they serve to protect the leather from damage, increase its stability when in contact with moisture and give the desired appearance, covering, color, brightness, texture and other visual and surface characteristics.

In this context, this paper presents a literature review, a schedule for preparing films using polymeric resins used currently in the industry, and the evaluation of different resins in relation to the physical properties of the films. Studies of the coating layer properties of the finishing process usually involve the analysis of resins already applied on the leather material, and do not analyze the characteristics of the polymeric film itself. Scientific knowledge of film properties can improve leather quality and diversification and reduce material losses and failures. In the leather industry, custom formulations are usually used and are not disclosed.

II. REVIEW

A. Application of Finishing and Quality Control

Leather finishing is the application of various prepared chemical compositions for forming a film on the upper leather surface (grain side), followed by operations including drying, mechanical presses, polishes, and softening or breaking of the deposited film. These formulations, consisting of chemical mixtures (emulsions, dispersions, solutions) of resins in aqueous or organic solvents are performed through various mechanical application systems over the leather surface followed by drying. The drying step is used to evaporate solvents that were used for applying the finish. In curtain application systems, the preparation of leather finishing consists of an aerographic spray roller coat deposited in the form of a continuous sheet over the leather. In roll deposition systems, the preparation is transferred into a metal cylinder, printed, and then placed in direct contact with the leather. Figure 1 shows images of the equipments used in applying layers and pressing of leather finishing.

Quality control of leather finishing is made by the subjective observation of touch, smoothness, grain drop, cover and shine. Further assessment through physical-mechanical proofing and laboratory analysis are also conducted (Marx, 2008). Some of these analysis are: the determination of condensed volatile substances not fixed in the leather (fogging test), friction tests, tensile strength and elongation, resistance to solvents, light fastness, migration to PVC, and washing out.

B. Polymers Used in Leather Finishing

Polymers are macromolecules characterized by their size, chemical structure and intra and intermolecular interactions. They have chemical units linked covalently, repeated regularly along the chain, called mers. The mers number of the polymer is called the degree of polymerization.

Resins are substances consisting of waterborne particles of polymeric material of high molecular weight. As the basic substance for obtaining leather finishing films, resins (binder polymers) of different monomers are used, each one contributing in some way to the properties of the film.

Among the resins used in leather finishing, emphasis is given to casein, polyacrylates and polyurethanes. Polyurethanes are important due to many benefits including the resistance quality, adhesion and frame properties that are simple to modify. Polyacrylates have a good capacity for light fastness and are inexpensive. As a result, polyacrylates are the most frequently applied resins. In addition, casein, which is a natural protein binder, is also used and promotes a transparent, higher brightness, vitreous and more natural film appearance. Table 1 compares polyacrylates, polyurethanes and casein characteristics that are present in finished leather.

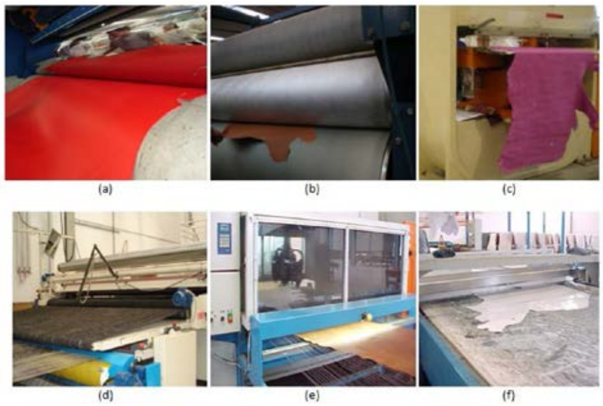

Fig. 1: Leather pressing: (a) rotary brightness press, (b) rotary gravure press, (c) hydraulic press; application of finishing products: (d) roller system application, (e) aerographic system, (f) curtain system.

Table 1: Acrylate polymers, polyurethanes, casein and their properties highlighted in leather finishing

Polyacrylates	Polyurethanes	Casein
Light fastness	Resistance to abrasion	Good adhesion
Flexibility coating	Tensile	Resistance to pressing and scratches
Filling more uniform	Resistance at low temperature	Resistance at high temperatures
Moldability of the coating under heat and pressure	Good flexibility	Natural appearance
Water resistant	Easy grip	Glossy finishing
Heat retention and gloss	Finishes are more resistant and durable	Advantages over synthetic polymers

Polyurethanes

Polyurethanes are produced from isocyanates and polyols, and result in durable finishes, more resilient than conventional finishes. The urethane resins are divided into two types: aromatic and aliphatic. The aromatics are characterized by their toughness, moderate flexibility, chemical resistance and abrasion resistance. However, the aromatics are not recommended for use in finishes that require light fastness. The aliphatic polyurethanes have good color retention and durability when exposed to the environment, high abrasion resistance, and high average chemical resistance (Amorin and Melillo, 1989).

The polyurethanes have good adherence to leather, are resistant to cold, have light fastness, and malleable properties. For long polymer chain lengths, polyurethanes exhibit high levels of flexion (Henkel, 1986). Polyurethane dispersions have gained popularity in leather finishing due to their remarkable abrasion resistance properties, good chemical resistance, tensile strength and low temperature flexibility. The polyurethanes have the disadvantage of a high cost, but this can be substantially reduced by using acrylic and vinyl comonomers. Combining a high adhesion capacity on substrates with vinyl-pyridine monomers, superior finishing properties can be obtained, including bacterial and fungal attack resistance and the need for less pigment (Sundar *et al.*, 2006).

Acrylic Resins

Acrylic resins (polyacrylates) are obtained by copolymerization of acrylic monomers, as acrylic and methacrylic acids. Acrylates are macromolecules that, depending on their chemical structure, result in film forming substances with characteristics of hardness, flexibility and resistance to chemical attack and degradation. As film forming materials, acrylates are particularly noted for hardness, flexibility, heat retention and gloss, good resistance to the action of solvents and weathering (Fazano, 1995). The properties of acrylates significantly improve leather performance (Pietrucha, 1981). Acrylates have a good light fastness, are economical and are therefore used more often.

With increasing environmental concerns and requirements of end materials, research has focused on water soluble materials, diversifying studies, such as the use of acrylic resins together with silicon oxide. A goal of this research is to reduce the use of emulsifiers and thus environmental pollution (Jing *et al*., 2008a). A further goal is the synthesis of a copolymer (butyl acrylate/acrylic acid) with improved water absorption for applying the finishing (Jing *et al*., 2008b). Furthermore, studies have been carried out to improve the rheological behavior of acrylate compounds and their application in leather finishing as a binder (Yilmaz *et al*., 2011).

Casein

Casein is a completely biodegradable natural thermosetting polymer that has film forming properties, including good adhesion and resistance to pressing, scratches and high temperatures. However, casein films have low elasticity and low water resistance, and so there are some restrictions involved in applying this material. Chemical modifications in the structure or casein bonds with other materials, including plasticizers, waxes, polymers, and nanoparticles, are used to improve the properties. Modified casein is widely used as a film binding component, and so it has a wide range of applications such as in papermaking, printing, coating, leather finishing, and other fields (Jianzhong *et al*., 2012).

The casein film, due to its pronounced transparency, gives a more natural appearance, and is mainly applied to high quality leather products, where it is desirable to maintain the natural look of the hide (Gratacos *et al.*, 1962). Finished leather using casein has a vitreous and a less plasticized appearance.

Other Polymers and Mixed Finishing

There are many other polymeric resins used industrially in leather such as vinyl, polybutadiene, nitrocellulose, acetobutyrate, and other hybrid resins. Efforts to improve leather finishing, especially in relation to their mechanical properties, have led to the establishment of a large variety of finishing techniques, which try to combine the advantages of traditional binders and folders based on casein or nitrocellulose with a polymeric dispersion binder.

Possibilities for increasing the advantages of various polymers, in combination with potential products, have led to further developments. Kozakiewicz (1996) has already utilized the advantages of polysiloxanes with polyurethanes in order to improve the finishing layers.

Other Products in Leather Finishing

Pigments are products consisting primarily of chromatic substances of various origins, classified into two main groups: organic and inorganic. Organic pigments impart high gloss and bright colors, but have little covering capacity and limited light fastness (Jianzhong *et al*., 2012). On the other hand, inorganic pigments, in general, have less liveliness, but achieve excellent coverage and light fastness.

The solvents used in the formulations must be sufficiently stable for the building of a good film when deposited on a leather surface and an evaporation ratio sufficiently fast to avoid producing defects (i.e. to achieve complete sheeting). Examples of commonly used solvents are: isopropanol, ethyl glycol, butyl glycol and ethanol. As an alternative to traditional finishing systems containing solvents, there are aqueous systems, which aim to reduce atmospheric emissions, satisfying high quality requirements. In addition, the method of application has a major role in reducing solvent emission. By the application of a chemical preparation with a roller machine (multipoint), it is necessary to use ¼ the amount of solvent relative to the amount used in spray applications (Will and Eckert, 1991). Auxiliary products are used to correct minor defects, modify features or give any desired property. These products are penetrators, and include thickeners, matting, crosslinkers, hydrophobic agents, and touch and release agents. Crosslinking agents react with polymeric material (Levy, 2008) and contribute to the high level of physical resistance of polymeric films (Hesselmans *et al*., 2009). Examples of crosslinking agents are aziridine, isocyanates, and carbodiimides, among others. Polyaziridine and polysilane are more effective as crosslinking agents for butadiene binders (Bacardit *et al*., 2010). Polyaziridine reacts with acrylic binders better than polyurethanes (Bacardit *et al*., 2008). Concerning matting agents in aqueous finishing, the best results are obtained through the use of silicic acids.

C. Procedure of Film Formation and Proposal of Film Testing

By drying the resin (aqueous or organic solvent dispersion) deposited on the surface of the leather by water evaporation, the various particles of polymer material are joined to each other, and form a film layer. The principle of polymerized film binder forming in leather finishing is explained as follows. When applying the chemical preparation or formulation (pigments, resins, auxiliaries and solvents) to deposit over the leather surface, a portion of the water or solvent of the dispersion is absorbed by the fibrous structure of the leather. The remaining portion evaporates, concentrating the medium. The binder dispersion precipitates the polymer to form a film. For pigmented films, one should take into account the size of the pigment particles, which influences the coverage properties and coloring power. Adzet (1988) calculated the volume concentration of pigment taking into account the volume ratio of the components that do not contribute to film formation (pigments + fillers + waxes) with the volume of all elements (pigments + fillers + waxes + binders).

The physical properties of the polymers are related to the power of the covalent bonds, the rigidity of the segments in the polymer chain and the strength of the intermolecular forces between the molecules. Besides the chemical nature of the monomers and the molecular weight of the polymers, another important factor that affects the properties of the material is its macromolecular structure. From a technological standpoint, polymeric materials must present satisfactory mechanical strength (Mano and Mendes, 1999).

The properties of the polymeric film determine the fundamental characteristics of the finishing. Properties such as transparency, color, flexibility, elasticity, stickiness, etc. are analyzed in the formed films as shown in Table 2.

To conduct a study of polymeric chemicals used in the industrial finishing step, a survey of parameters is designed to relate the composition of resins with the properties of the formed films. The films may or may not have additional pigments.

The methodology for the production of films requires the analysis and calculation of the solid content of the resin (ABNT 11062, 2004) and thermobalance method) and is based on the ABNT 11033 (2004; preparation of films) and technical indications (Henkel, 1986).

In the preparation of no pigmented films, it is proposed to fix the amount of total solids to10%, taking into account the percentage of solids of the resin used. For pigmented films, the ratio of resin to solids is proposed to be 2.5 : 1. In a Petri dish, moisture consisting of resin and water in the previously mentioned proportion is disposed and dried in an oven for 24 h at 60°C.

Examples of acrylic and polyurethane films are shown in Fig. 2. The acrylic films exhibit distinct characteristics: (a) is bright, transparent and without roughness, while (b) presents opacity, and less transparency with a soft touch. The polyurethane films also exhibit other characteristics: (c) is bright, translucent and not flexible, in (d) the aspect is opaque, matte, and with a soft touch.

The films are also analyzed by sensory criteria, physical tests and characterizations by fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC).

Table 2: Properties of the films and analysis

Property	Analysis
Hardness	Resistance to deformation under pressure of a rigid body
Extension to break	Percent increase in length until rupture of the film
Elasticity	Percentage increase recoverable, as the previous test, but without arriving at a break
Water absorption	Amount of water absorbed per unit area of the film at a given time
Fastness to solvents or other dissolution	Dissolution, destruction, or structural deformation of the film by immersion in the product that is specified
Light fastness	Resistance of the color film to light exposure, as assessed by comparison of the scale of blues

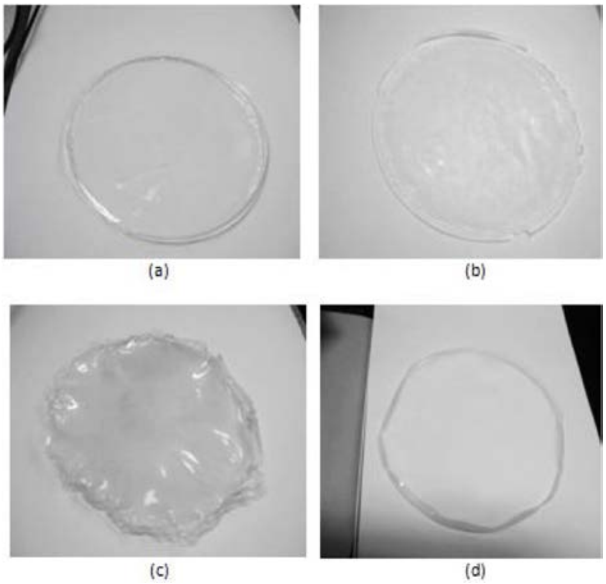

Fig. 2: Films formed after the drying of resins in the oven. (a) – (b) Acrylic films; (c) – (d) Polyurethane films.

III. CONCLUSIONS

The study of polymeric films is promising. As the specific characteristics of each resin become known, new technological improvements may be realized and provide superior properties in finished leather products. Moreover, it is possible to combine resins to achieve better results with respect to leather product requirements. The addition of auxiliaries, pigments and new combinations of agents will contribute to new possibilities for chemical products that improve required quality specifications and lead to innovations in the leather finishing sector.

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