Effect of Finishing Auxiliaries on Permeability of Leathers

by
M. Sathish, Z. Mohammad Jamal Azhar, N. Nishad Fathima and J. Raghava Rao*
Chemical Laboratory, Central Leather Research Institute, Council of Scientific & Industrial Research,
Adyar, Chennai- 600 020, India

Abstract

The unique fibrous arrangement and architectural marvel of collagen in skin matrix are the basis for various physical properties of leather. Air permeability is one of the unique features of skin, which makes the leather matrix superior to synthetic materials. In leather manufacturing finishing process determines the air permeability of the final leather. Therefore, knowledge of the impact of different finishing auxiliaries on the permeability of leather may helpful in selecting an appropriate finishing system for a particular type of leather. In this work, an attempt has been made to analyze the effect of various auxiliaries used in protein, acrylic and polyurethane (PU) based finish coatings on the air permeability of leather. Capillary flow porometer was used to monitor the air permeability (Flow rate cc/sec) at different pressures (psi). The results show that the effect of wax/filler/slip and dye solution on air permeability reduction is low when compared to pigment and binder. In protein and PU finishes, the binder alone and season (combination of all finishing auxiliaries like pigment, binder, and other auxiliaries) has a strong influence on permeability reduction whereas in case of an acrylic based finish, the pigment and binder plays an important role in permeability reduction. Leather coated solely with protein binder shows minimal permeability reduction than compared to leather coated with acrylic or polyurethane binders, whereas in season, acrylic based finishing has a lower permeability profile than that of protein and PU. In that case the permeability profile of protein and PU season coated leathers is almost similar.

Introduction

The architectural marvel of collagen makes the natural hides/skins matrix superior to other synthetic matrices.[1-3] The penta-fibrillar assembly of collagen monomers aggregates to form fibrils, which are 2 to 20 microns in diameter. These fibrils aggregate to form fiber, which are 20 to 40 microns.[4-5] Then, the fibers are internally woven to produce hides/skins matrix. The unique fibrous arrangement makes the hides/skins matrix porous. The nature of pore sizes various from micro (< 2 nm), meso (2-50 nm) to macro (> 50 nm). The presence of various types of pores gives hides/skins matrix the ability to permeate the air, which provides more comfortable properties than synthetic materials. The employment of various physico-chemical processes and operations in leather manufacturing alters the air permeability nature of hides/skins matrix. The removal of non-leather making materials such as hair follicles, sebaceous gland and fat as well as separation of fiber bundles during the pre-tanning processes enlarges the void space and surface area of hides/skins matrix which increases the air permeability rate.[6-7] But, the subsequent tanning and post-tanning processes fill the void spaces which in turn reduces the air permeability.[8,9] In finishing, several surface coating agents are applied to improve the aesthetic value of the final leathers, which also reduce the air permeability. The permeability of the matrix is directly proportional to the porosity. Several attempts have been made to study the porous nature of hides/skins matrix using different instrumental methods.[10-17]

Zettlemoyer and co-workers estimated the internal surface area of un-tanned hide and formaldehyde tanned leather using water and nitrogen adsorption technique.[11] Later on Kanagy studied the macro-pores in leather using mercury intrusion porosimeter at absolute pressure ranging from 5 to 3000 psi.[12,13] The effect of shrinkage on surface area and porous nature of tanned and un-tanned leather was studied by Fathima and co-workers.[14] The changes in pore structure of skin during leather processing and the effect of cross-linking agents on pore structure of skin matrix have been investigated.[15,16] Grill and co-workers analyzed the variations in porous nature and water vapor permeability of the skin by using mercury intrusion porosimeter, nitrogen adsorption and water- vapor adsorption isotherm, after it had been subjected to various treatment processes such as dehydration, pickling, cross-linking with chromium and vegetable tannins.[17] Recently, Murali and co-workers studied the porous nature of goat and sheep wet-blue leathers at different regions such as butt, belly etc.[18]

Understanding the effect of various finishing auxiliaries on permeability of the final leather has not yet been reported. Generally, the chemical composition of the same class of finishing auxiliaries is not same. Also, each chemical company has binders with varying composition and/or solid

*Corresponding author e-mail: jrrao@clri.res.in; clrichem@mailcity.com; Fax: +91 44 24911589; Tel: +91 44 24411630
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content (e.g.. protein binder- 15%, acrylic binder- 30% and PU binder-30%). This is the first attempt to study the influence of conventional types of finishing on the permeability of leathers in spite of the inherent variations in different finishing systems.

MATERIALS AND METHODS

Goat upper leather was conventionally processed and used as starting material for permeability measurements. Samples having a diameter of 2.5 mm were taken from the official sampling position and conditioned for 24 hrs. at 25°C & 65% RH. The conditioned samples were subjected to permeability measurement prior to finishing in order to select samples of uniform permeability. Such selected samples (of dia. 2.5 mm) were then placed on top of crust leathers (3 square feet) and subjected to different types of finishing operations, where spray coat technique was used to transfer the finishing auxiliaries on the leather surface (4 cross coats of each auxiliaries and combination of all), as tabulated in Table I. After finishing, the conditioned samples were again subjected to permeability measurement.

Permeability Measurements

PMI capillary flow porometer was used to measure the air permeability and the block diagram of the same is shown in Figure 1.[19] In this technique, the conditioned sample were held between two "O" rings and the compressed air applied on the grain surface and allowed to pass out through flesh side. The pressure of the applied gas varies from 0-60 psi. The capillary flow porometer monitored the pressure (psi) and its corresponding flow rate (cc/sec). Pressure vs flow rate has been plotted to get permeability profile of each sample.

Measurement of Film Thickness

The film forming nature of the each finishing auxiliaries are not uniform. So, it is important to measure the thickness of the film formed by various finishing auxiliaries on the leather surface. Scanning electron microscopy technique was used to measure thickness of the film.

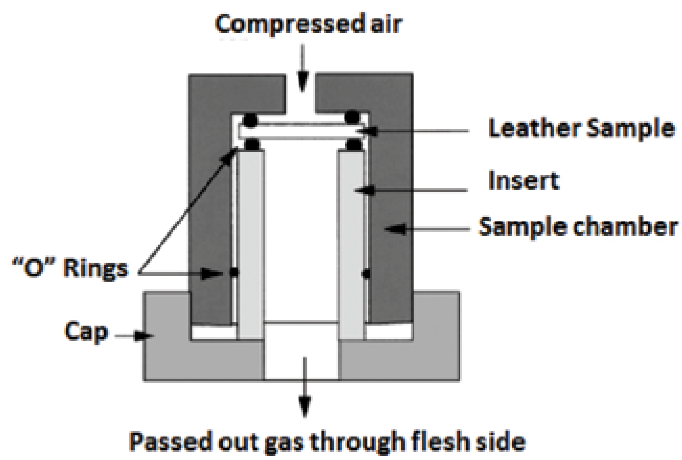

Figure 1. Block diagram of capillary flow porometer.

TABLE I
Process recipe for different finishing operations.

Finishing Auxiliaries	Protein Season (Parts)	Resin Season (Parts)	PU Season (Parts)
Wax/Filler/Slip	50	50	50
Dye solution	100	-	100
Binder	150	150	150
Pigment	-	100	100
Water	700	700	600
Water: Fixing agent*	1:1	1:1	-

*Glutaraldehyde for protein finish and lacquer (Nitrocellulose) for resin finish
Protein binder: Casein based product
Resin binder: Acrylic based product
PU binder: Polyurethane based product
Season: Combination of all finishing auxiliaries
Note: 4 cross-coats (4 times hand sprayed on leather surface) were applied.

RESULTS AND DISCUSSION

Selection of Uniformly Permeable Samples

The irregular pattern of the macromolecular structure of collagen makes the skin matrix heterogenic and the heterogeneity is further increased during the leather processing. The fiber density, packing arrangement of fiber, angle of weave, pore sizes and porosity of crust leather vary from region to region, which in turn affect the uniform permeability of the leather sample. It is necessary to have uniformly permeable crust leather samples, to compare the effect of different finishing auxiliaries on air permeability. Therefore, 50 crust leather samples (without any coating) have been taken from official sampling position and subjected to air permeability measurement where the gas pressure varied form 0-60 psi. The permeability profile of every sample has been plotted and the same is represented in Figure 2.

It is evident from Figure 2 that the permeability profile of samples is widely distributed, but some of the samples are having uniform permeability profiles. The uniformly permeable samples have been identified from Figure and subjected to further finishing experiment.

Protein Finishing

Five uniformly permeable samples were selected and subjected to protein finishing as tabulated in Table I. Two types of coating experiment were carried out like 1) individual coating (Separate spray coating of each protein finish auxiliaries), and 2) season coating (spray coating of combination of all protein finish auxiliaries). In case of individual coating, each auxiliary has been dispersed in water required for season coating and 4 cross coat sprayed on the crust leathers. For example, 50 parts of wax/filler/slip alone dispersed in 700 parts of water and sprayed on crust leathers. Similarly, 100 parts of dye solution and 150 parts of medium soft protein binder have been dispersed separately in 700 parts of water and sprayed. In case of season coating, 50 parts of wax/filler/slip, 100 parts of dye solution, 150 parts of medium soft protein binder were dispersed in 700 parts of water and sprayed. The trials were designed in such a way that the concentration of each auxiliary in individual coating as well as season coating is similar. The coated samples were dried and conditioned for 24 hrs. for permeability measurements. The permeability profile of each sample has been plotted and shown in Figure 3a. It is evident from Figure 3a that the effect of wax/filler/slip and fixing agent on air permeability is low when compared to other auxiliaries. It may be due to coating of low solid content on the surface as well as formation of discontinuous film. Dye solution has a considerable effect on air permeability reduction when compared to wax/filler/slip and fixing agent. Dye molecules applied on the surface are smaller in size; therefore the applied pressure may force the dye molecules to penetrate into the voids, which hinder air permeation.

It is also evident from Figure 3a that coating of protein binder significantly reduces the air permeability but which is lower than season coating. The effect of individual finishing auxiliaries as well as the season on reduction in air permeability has been quantified by using Equation-1 and the graph has been shown in Figure 3b.

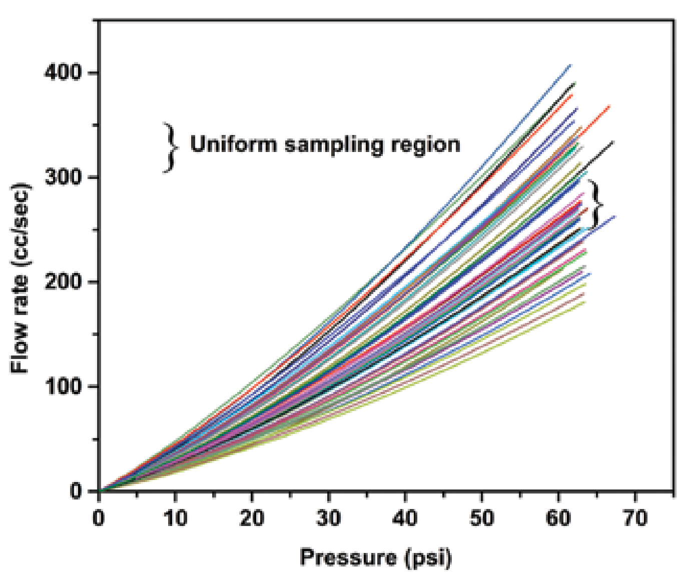

Figure 2. Selection of uniformly permeable samples.

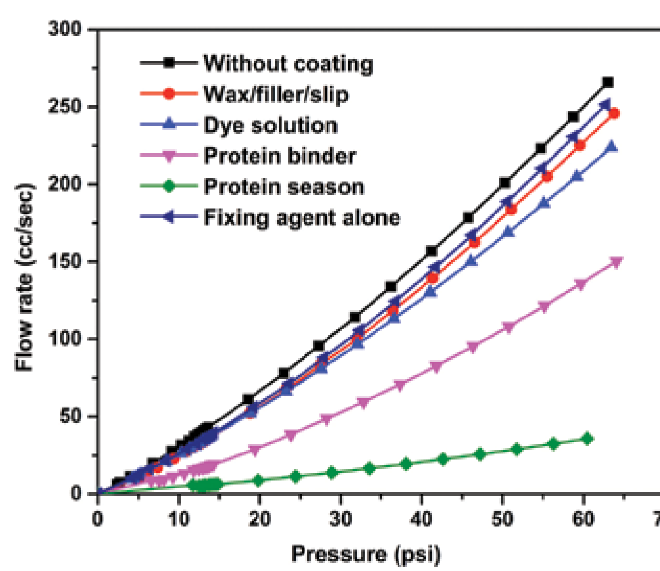

Figure 3a. Effect of protein finish auxiliaries on permeability profile.

$$APR = \frac{FR_{BC} - FR_{AC}}{FR_{BC}} * 100 \quad (1)$$

Where,

APR: Air permeability reduction in percentage
FR_{BC}: Flow rate (cc/sec) before coating at 60 psi
FR_{AC}: Flow rate (cc/sec) after coating at 60 psi

It is evident from Figure 3b that around 7% reduction and 9% reduction has been observed for wax/filler/slip and fixing agent respectively, whereas 18% reduction in air permeability of crust leather has been observed for dye solution coating. 45% reduction in binder coating and 85% reduction has been observed for season coating. From the above results it can be concluded that season coating has more effect on permeability reduction followed by binder, and the effect of other auxiliaries is minimal. The thickness of the each protein finish auxiliaries and the combination of all auxiliaries spray coated on the leather surface was measured and shown Figure 4. It has been observed from Figure 4 that the thickness of wax/filler/slip coated surface is 2.4 microns whereas dye solution is 3.6 microns and protein binder is 7.4 microns. The combination of all protein auxiliaries (protein season) was formed thicker film of 16 microns as compared to finishing auxiliaries.

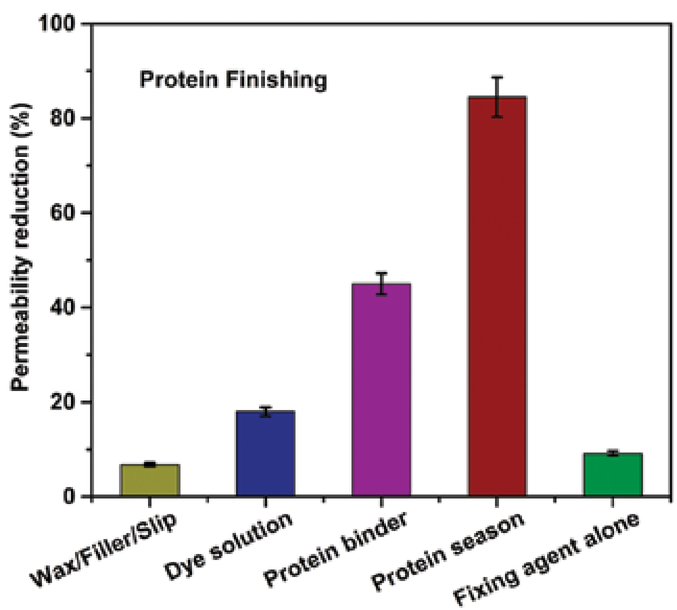

Figure 3b. Percentage reduction of permeability at constant pressure (60 psi) in protein finish.

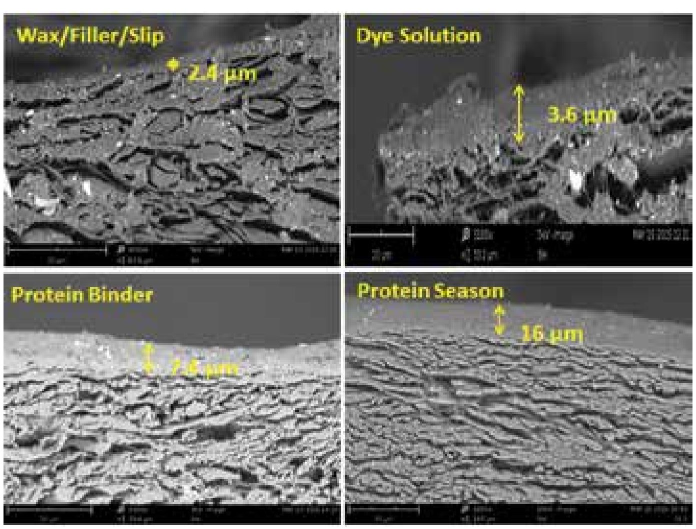

Figure 4. Film thickness of protein finish auxiliaries.

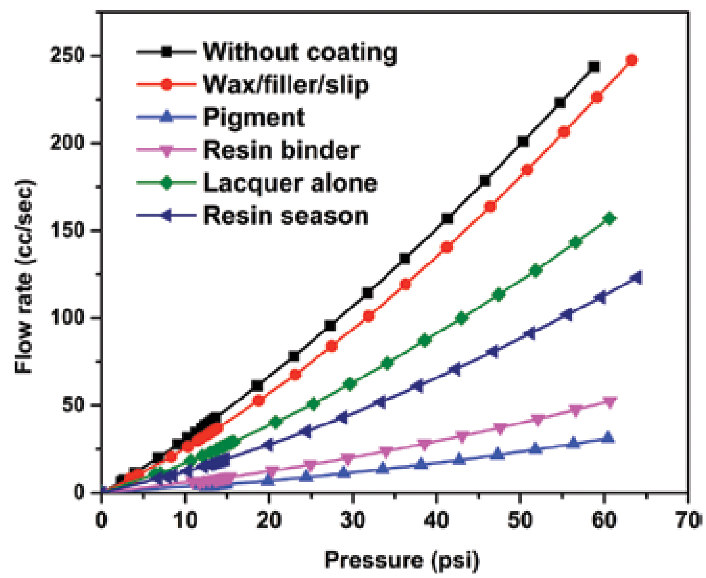

Figure 5a. Effect of resin finish auxiliaries on permeability profile.

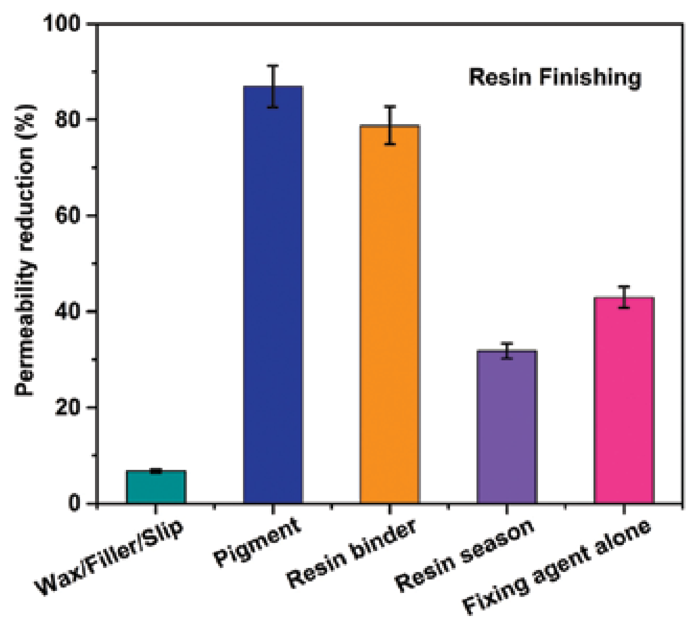

Figure 5b. Percentage reduction of permeability at constant pressure (60 psi) in resin finish.

Resin Finishing

In resin finishing, 50 parts of wax/filler/slip, 150 parts of medium soft resin binder and 100 parts of pigment have been dispersed separately in 700 parts of water and sprayed on uniformly permeable crust leather samples. The resin season has been prepared by dispersing all the above mentioned auxiliaries in 700 parts of water and sprayed on crust sample. 1 parts of lacquer dispersed in 1 parts of water and sprayed on crust leather as well as season coated samples. All the samples have been subjected to air permeability measurement after drying and conditioning. The permeability profile and percentage reduction in air permeability (calculated by using equ-1) have been pictorially represented in Figure 5a and Figure 5b respectively.

It has been observed from Figure 5a that wax/filler/slip coated sample has highest permeability profile than other auxiliaries or in other words it has lowest reduction in air permeability which is around 7% (Figure 5b). It is also evident from Figure 5a that pigment has lowest permeability profile, which contributes around 87% reduction in air permeability of crust leather, whereas resin binder alone contributes around 78% reduction. In resin finish, season coated leather has lowest air permeability reduction (32%) than solely coated pigment and binder sample. It may be due to direct contact of pigment particle on the crust leather surface, whereas in case of season, pigment molecules are embedded into the binder, which reduces the contact area between the leather and pigment. This might be one of the reasons for lower permeability reduction. Fixing agent also has considerable reduction (50%) in air permeability.

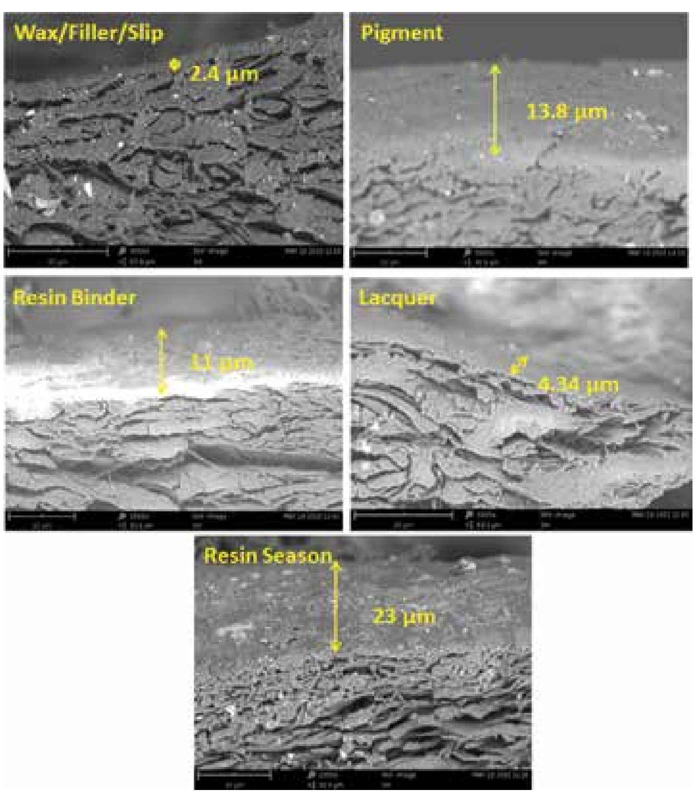

Figure 6. Film thickness of resin finish auxiliaries.

The thickness of the each resin finish auxiliaries and the combination of all auxiliaries spray coated on the leather surface was measured and shown Figure 6. It has been observed from Figure 6 that the thickness of wax/filler/slip-coated surface is 2.4 microns whereas pigment is 13.8 microns and resin binder as well as lacquer (Nitrocellulose based fixing agent) form 11 and 4.34 microns respectively. The combinations of all resin finish auxiliaries (resin season) formed thicker film (23 microns) than other finishing auxiliaries this is also higher than protein season layer. It might be due to the presence of pigment particle in resin finish system.

PU Finishing

In PU finishing 50 parts of wax/filler/slip, 100 parts of dye solution, 150 parts of medium soft binder, and 100 parts of pigment have dispersed separately in 600 parts of water and sprayed on crust leathers. The PU season has been prepared dispersing all the auxiliaries in 700 parts of water and sprayed on uniformly permeable sample. The permeability profile and percentage reduction in air permeability have been shown in Figure 7a and 7b respectively.

It has been observed from Figure 7b that the wax/filler/slip and dye solution coated sample has highest permeability profile and its percentage reduction is only about 14% and 25% respectively. It has also been observed that pigment and PU binder coated leather have almost similar permeability

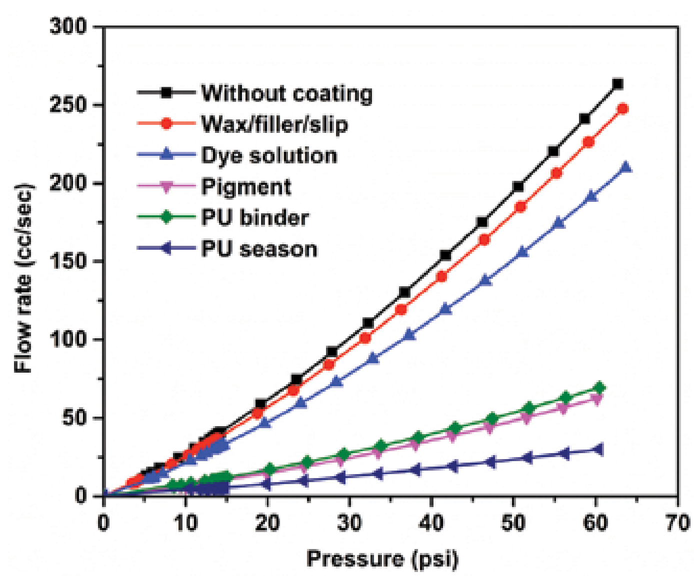

Figure 7a. Effect of PU finish auxiliaries on permeability profile of leathers.

profiles and percentage reduction is around 72% and 76% respectively. As like protein season, PU also has highest effect on permeability reduction, which is around 87%.

The thickness of each of the PU finish auxiliaries and the combination of all auxiliaries spray coated on the leather surface was measured and shown Figure 8. It has been

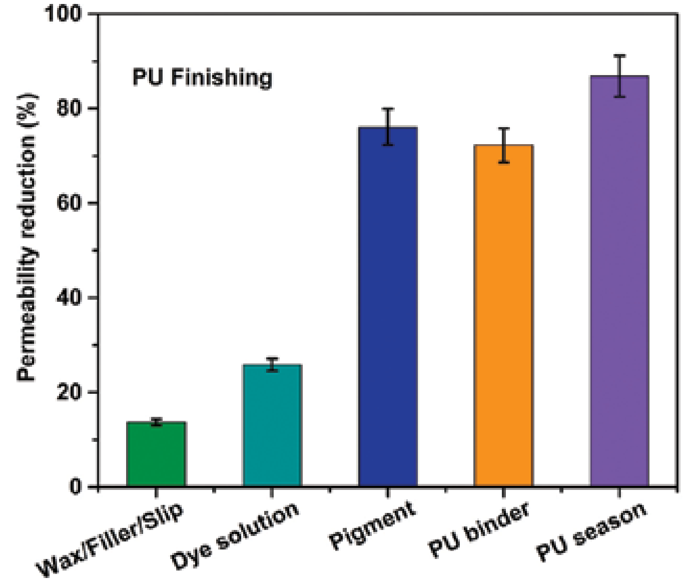

Figure 7b. Percentage reduction of permeability at constant pressure (60 psi) in PU finish.

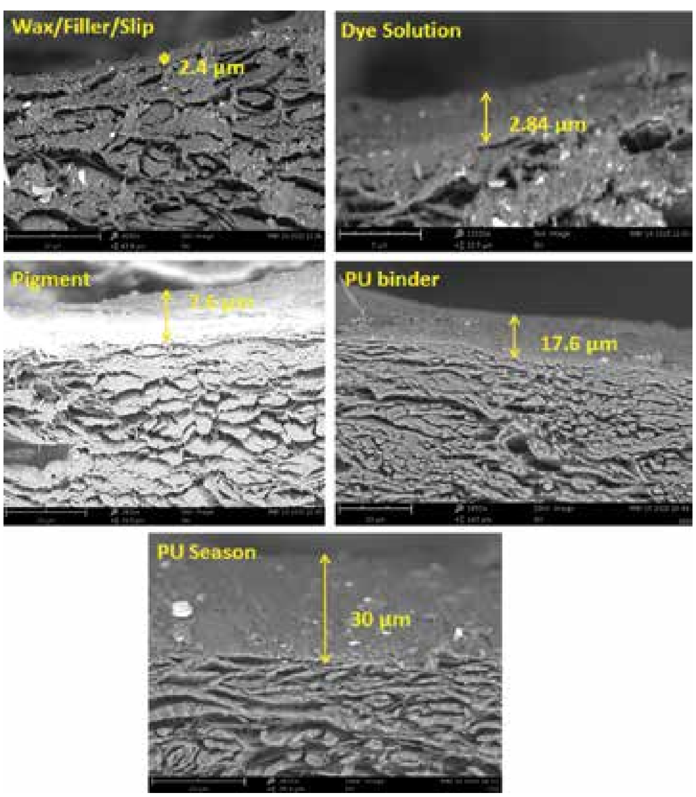

Figure 8. Film thickness of PU finish auxiliaries.

observed from Figure 8 that the thickness of wax/filler/slip coated surface is 2.4 microns whereas dye solution is 2.84 microns and pigment as well as PU binder form 7.6 and 17.6 microns respectively. The combination of all PU finish auxiliaries (PU season) was formed thicker film (30 microns) than other finishing auxiliaries, which is also thicker than protein season and resin season layer.

Protein vs Resin vs PU finishing

It is also important to compare all finishing system to conclude which system has largest effect on air permeability reduction. Figure 9 shows permeability profiles of protein, resin, and PU binder alone-coated leather samples.

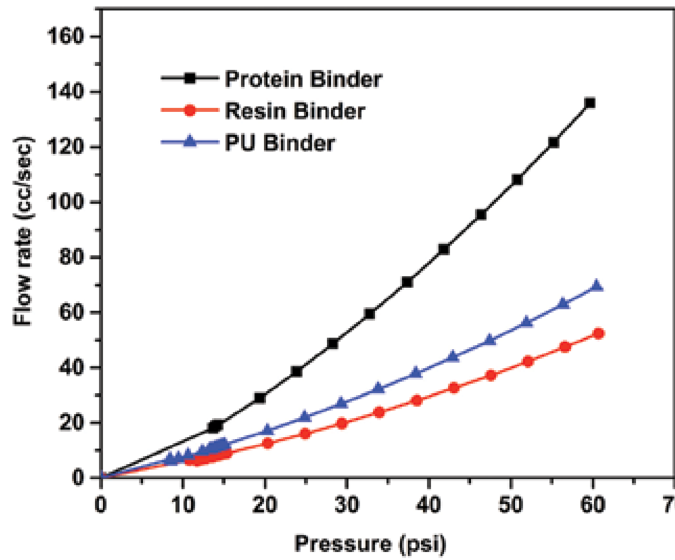

Figure 9. Comparison of protein, resin, and PU binder coated leathers.

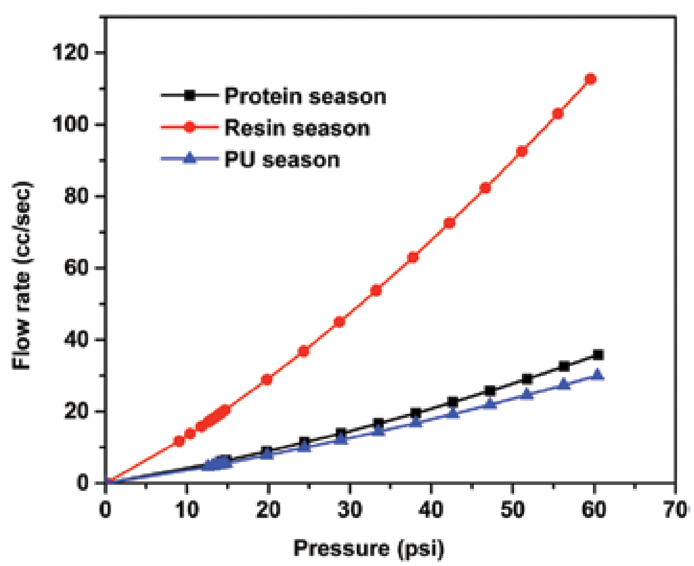

Figure 10. Comparison of protein, resin, and PU season coated leathers.

It is evident from Figure 9 that permeability profile of protein binder coated leather sample has lowest permeability reduction (45%) than resin and PU. It may be due to formation of a discontinuous film on the leather surface. When comparing the PU and resin binder, resin-coated leather has largest permeability reduction (APR: 78%) than PU binder coated leather (APR: 72%). But, the permeability profiles of season-coated leather are different from binder-coated leathers, which has been shown in Figure 10. It has been observed from Figure 10 that resin season coated leather has highest permeability profile (APR: 32%) than protein and PU. It may be due to decrease in direct contact area of pigment and binder on leather surface, which make the surface more permeable than others. But, the permeability profile of protein and PU coated leather samples are almost similar and its air permeability reduction is around 85% and 86% respectively.

Conclusions

The results of this study conclude that every auxiliary used for finishing operations influences the air permeability of final leathers. Lower effect has been observed for wax/filler/slip coated leathers, than other auxiliaries. In protein and PU finish, binder and season have strong influence on permeability reduction whereas in case of resin finish, pigment and binder play an important role in permeability reduction. When comparing the protein, resin and PU binder coated alone samples; protein has less effect on permeability reduction than resin and PU, whereas in season, resin finishing has less effect on permeability reduction than others. Permeability profile of protein and PU season coated leathers was almost similar.

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