Effect of Pigment-Acrylic Binder Ratio on the Surface and Physical Properties of Resin Finished Leather

by

Suriya Madhan,[a] Mishamo Wakaso,[b] Sathya Ramalingam[a] and Swarna V Kanth[a*]

[a]*CSIR-Central Leather Research Institute*, Adyar, Chennai- 600020, India.

[b]*Leather Industry Development Institute*, Ethiopia.

Abstract

The current study attempts to investigate the surface phenomenon and physical characteristics of leather finished with brown pigment and different types of acrylic binders. Using the contact angle measurements of three different liquids on the above finished leathers and films, the surface energy and work of adhesion were evaluated. The pigment to acrylic binder ratio (PABR) for best adhesion of finish film on the leather surface was optimized using the contact angle goniometer. Different types of acrylic binder films were coated and their surface behaviour was studied. The crust leather was coated with different types of pigment-acrylic binder (Very Soft, Soft and Medium Soft) finish formulations. The contact angle of both the acrylic films and the PABR finished leathers were measured against Water, Dimethyl sulfoxide (DMSO) and Hexadecane (HD). According to the study's results, the surface properties of finished leather were directly related to the degree of wetting. The PABR was found to be effective at 1:3 for very soft binder, 1:2.5 for soft, 1:2 for medium soft binders due to higher contact angle and lower surface energy values (γsv). At 1:3 and 1:2.5, the contact angle of very soft and soft binder leather was 82.62° and 83.45° and for medium soft binder it was 82.67° at 1:2 ratio. The surface energy values of optimized PABR of very soft binder (1:3) was 28.29 (mN/M), soft binder (1:2.5) was 27.50 (mN/m) and medium soft binder (1:2) was 29.27 (mN/m). The optimized PABR work of adhesion values of very soft binder, soft binder and medium soft binder was 82.15 (mJm^{-2}), 81.11 (mJm^{-2}), 82.09 (mJm^{-2}). In order to correlate the observed surface properties with leather finish properties, finished leathers were tested for finish adhesion, vamp flexing value, water vapour permeability, wet and dry rub fastness. According to the water vapour permeability, soft and medium binder showed good permeation due to the uncovering of nanopores. But the adhesion, grain crack resistance and grain smoothness were higher in the case of the soft binder. Overall leather properties divulges that the pigment to binder ratio and the type of binder plays an important role in surface properties of the finished leather. This study enables us to determine the optimal PABR for effective finish properties to meet the required leather standards for various usage, as well as better utilisation of finishing chemicals.

Introduction

Leather finishing is an essential process in leather production as it possesses a significant impact on the final appearance and performance of the leather product.[1] The finishing process not only gives a finished and aesthetic look, but also protects and adds value to it.[2] The finishing process increases the surface properties and resistance to mechanical stress such as bending, scuff resistance, wet and dry rub fastness by coating with acrylic, polyurethane (PU), butadiene, and other additives. The finishing process improves the quality of leather by minimising surface imperfections.[3] The finishing materials, methods and procedures might vary the texture, appearance, gloss and surface of the finished leather products. The constituents of leather finishing are pigments, dyes, acrylic binders, PU, protein binders, wax, emulsions, fillers etc. in the base coat with lacquer and lacquer emulsion at the top coat. Silicone and wax emulsions are also used as feel modifiers. Many acrylics, PU, and butadiene resin binders are used in the leather finishing process to generate films that improve the leather's resistance to moisture as well as its look and surface characteristics. These binders are macromolecular compounds with film-forming capability that holds the substrate together i.e., pigment and other chemicals used in leather finishing.[4] The pigment quality depends upon the degree of dispersion and particle size. Inorganic and organic pigments are used.[5] The covering power of organic pigments is less than that of inorganic pigments.[6] Pigment Volume Concentration (PVC) is the ratio of pigment volume divided by the sum of pigment and binder volume. Pigment Volume Concentration = Pigment volume / (Pigment + Binder volume). Excessive use of binder affects the adhesion, flexibility, and aesthetic look of leather and also enhances the cost of the finishing process.

Surface properties of the finished leather will vary based on the nature of the crust leather, mechanical operations and finishing auxiliaries. The surface related parameters of finished leathers were characterized based on the surface energy, work of adhesion and wettability on different solvents. Surface charge of the leather was strongly influenced by the penetration and fixation of chemicals in leather.[7] The resin binders (acrylic/PU/butadiene) significantly contribute to the charge of the finished film. The charge of the final leather acquiring a positive or negative charge depends on the quality

*Corresponding author email: swarna@clri.res.in

Manuscript received July 19, 2023, accepted for publication September 24, 2023.

Table I

Characteristics of the binder chosen for finishing application

Binder	Glass transition temperature (Tg, °C)	Mean Diameter (nm)	Solid contents %
Very soft acrylic binder	-34	96.1 ± 4	20-25
Soft acrylic binder	-30	101.7 ± 3	24-30
Medium soft acrylic binder	-27	120.3 ± 2	28-36

and quantity of the type of acrylic binders used.[8] Acrylic binders used for finishing are usually amphoteric. The water solubilising group of carboxyl, when reacted to the surface converts into an anion. The reliability of the finishing chemicals influences the physical performance of the finishes. The surface charge, surface tension and liquid–solid contact angle influences the wetting, penetration and spreading.[9-10] Water vapor permeability is the ability of moisture to penetrate through it. The adhesive strength and rub fastness are affected by a good finish.[11] It is one of the most essential physical properties of leather, which might lower permeability by adding binders. The finishing materials and process were chosen based on the leather's condition, the type of finish to be made, and the desired quality of the waterproof finished leather.[12-13]

In the present paper, different finishing formulations were prepared by varying the ratio of pigment and binder concentrations. Different finish films and finished leathers were prepared from various finish formulations. The study correlates the film forming properties of the finish formulations. Through the work, the optimum pigment to binder ratio was determined, which helps in the utilization of the exact amount of chemicals in the finishing process to qualify for the standards specified for varied leathers. It helps us to understand the surface morphology of leather finished using different pigment to binder combinations.

Materials and Method

Materials

In order to produce the dyed crust leather for the finishing process, the post tanning operations of wet blue leather from goat skins were carried out by using the conventional post tanning process. Similar grades of leather were used in the experiments.

Different finishing chemicals used in the finishing formulations were purchased from Stahl India, a leather chemical manufacturing company. The finishing chemicals used for the current study are acrylic based resin binders (very soft, medium soft, soft), pigment, wax emulsion, protein binder, filler and water. According to the T_g (Glass transition temperature), binders are classified as very soft, medium soft, and soft for experimental work. According to Winter et al., the lower the T_g value, the softer the polymer.[14] The T_g of the very soft binder was found to be -34°C, while the T_g of the medium soft binder was -27°C.

Method

Finish Formulation Preparation

Different finishing formulations were prepared by keeping the pigment and other auxiliaries constant and varying the concentrations of Very soft (VS), Soft and Medium soft (MS) binder as given in Table II.

Table II

Finish Formulations Prepared at a Varied Concentration of different Acrylic Binder

Finishing Chemicals	Quantity (ml)					
Pigment	100	100	100	100	100	100
Resin binder@	50	100	150	200	250	300
Filler wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Water	790	740	690	640	590	540
Total	1000	1000	1000	1000	1000	1000

The above finish season was applied on the dyed crust leathers with roller coater equipment for control and respective experimental leathers. 4 coats were given for all the samples with an intermediate hydraulic press using a plain plate. The unlacquered leathers were taken for measurement.

@ – Soft, medium soft and very soft binders were used.

Finished Upper Leather Preparation

Thirty pieces of Goat shoe upper black dyed crust leather in the range of 4-5 Sq. ft. were used to study the effect of pigment to binder ratio in the finishing process. The thickness of the crust was uniformly maintained at 1 mm. The finish formulations as given in Table II were used for the finishing process. Leathers with varied formulations of Pigment-Binders were denoted as 'F'. The formulation codes based on the quantity and nature of the binder were named as

FVS1 (25ml); FVS2(50ml); FVS3(75ml); FVS4(100ml); FVS5(125ml); FVS6(150ml) for very soft binder

FS1 (25ml); FS2(50ml); FS3(75ml); FS4(100ml); FS5(125ml); FS6(150ml) for soft binder

FMS1 (25ml); FMS2(50ml); FMS3(75ml); FMS4(100ml); FMS5(125ml); FMS6 (150ml) for medium soft binder

Acrylic Binder Film Preparation

Finish films were prepared on glass plates measuring 10×5×0.5 cm as per the formulations shown in Table II. The acrylic finish formulations (25 ml) were taken on the glass plates and allowed to dry at 60°C. The film-forming properties and physical properties of acrylic binder films were investigated.

Determination of Contact Angle

The contact angle of various solvents on acrylic binder films, dyed crust leather, and finished leather were measured using an ACAM contact angle instrument. Water, DMSO and hexadecane were the solvents used for the contact angle measurements. It is the quantitative measure of the wetting of solid (leather/film) by liquid. The interfaced tensions between solid liquid (SL), liquid vapor (LV), and solid vapor (SV) which occur when a drop of liquid is resting on a solid surface like leather/film and creating a contact angle, may be defined as the drop being in equilibrium while it is at rest.

Measurement of Work of Adhesion

The work of adhesion can be defined from Young's equation and Young-Dupre relation, $Wa = \gamma LV (1+ \cos\theta)$, where Wa is the work of adhesion that was measured using θ, the angle in the contact angle (degrees).[7]

Measurement of Adhesion of Finish

The adhesion force of finished leather was measured according to IUF 470.[15] Samples from all the crust and finished leathers of 5×14 cm were cut from the official sampling positions of the leathers.

Determination of Flexing Endurance

Measurement of the Flexing resistance of finished leathers was carried out by IUP 39[16] from samples of crust and finished leathers that were cut from the official sampling positions of the leathers.

Determination of Wet and Dry Rub Fastness

Measurement of Wet and Dry rub fastness test of finished leathers was carried out according to IUF 450.[17]

Determination of Water-Vapor Permeability

The Water vapor permeability of the finished leathers was measured according to IUP 15.[18]

Determination of Physical Strength Characteristics

The various strength characteristics such as tensile strength and elongation at break were measured as per IUP 6,[19] and tear strength as per IUP 8.[20]

Determination of Organoleptic Properties

The organoleptic properties enable us to assess the quality of leather produced for diverse applications such as fullness, smoothness, grain smoothness, grain fullness, and color. The leathers were scored from 0-10, having higher ratings indicating superior properties, according to the evaluation of experts.

Results and Discussion

The surface charge of the crust leather to be finished and the finish formulations of a particular type of leather determine the final properties, characteristics, and surface behaviour of the final leather. The finishing chemicals play a significant role in improving the surface properties (like fullness, covering and grain smoothness) and reducing the anisotropic property with respect to the feel of the finish in the final leather. There are a wide variety of acrylic binders that influence the functional surface properties of the leather. It is of prime importance to know how each of the acrylic binders behaves in influencing the surface characteristics of leather with respect to its charge, surface energy and work of adhesion. Using Young's equation, the surface free energy of the acrylic films, crust and finished leather was calculated from the contact angle values as given below in equations 1 to 8.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}} + \sqrt{\gamma sv^{p}}\sqrt{\gamma lv^{p}}] \quad (1)$$

Where θ is the contact angle

γlv = liquid- vapor surface energy

γsv^{d} = solid- vapor interfacial energy of non-polar component

γlv^{d} = liquid- vapor interfacial tension of non-polar solvent

γsv^{P} = solid- vapor interfacial energy of polar component

γlv^{P} = liquid- vapor interfacial energy of the polar component

In the case of non-polar component, the polar component will vanish.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}}] \quad (2)$$

Substitute the non-polar component in equation 1. The polar component was calculated using equation 3.

$$\gamma lv(1+\cos\theta) = 2[\sqrt{\gamma sv^{d}\gamma lv^{d}} + \sqrt{\gamma sv^{p}}\sqrt{\gamma lv^{p}}] \quad (3)$$

The total surface energy of the crust leather is the sum of both polar and non-polar components.

$$\gamma sv = \gamma sv^{p} + \gamma sv^{d} \tag{4}$$

Van Oss- Chaudhury- Good (OCG) thermodynamic approach can also be used to determine the surface free energy components of solids.[21-22]

In the current study, the polar component of surface energy, is expressed in the form of two components i.e., Lewis's acid and Lewis's base (γs^{+} and γs^{-}) parameters respectively.[23] To calculate these values in these experiments, three liquids such as water, DMSO and hexadecane were used.

$$\gamma lv(1+cos\theta) = 2\sqrt{\gamma s^{LW}\gamma l^{LW}} + 2\sqrt{\gamma s^{+}\gamma l^{-}} + 2\sqrt{\gamma l^{-}\gamma s^{+}} \tag{5}$$

For the non-polar component, the polar component in equation 5 was reduced to:

$$\gamma lv(1+cos\theta) = 2\sqrt{\gamma s^{LW}\gamma l^{LW}} \tag{6}$$

By substituting the known values non-polar components were calculated.

To calculate the Lewis acid parameter or the cationic nature of the surface, one can use polar and moderately polar contact angles and surface tension values. Since moderately polar was very small value compared to the polar value, it is neglected in equation 5 and the equation is reduced to

$$\gamma l(1+cos\theta) = 2[\sqrt{\gamma s^{LW}\gamma l^{LW}} + 2\sqrt{\gamma s^{+}\gamma l} \tag{7}$$

By substituting Lewis's acid parameter in equation 5, Lewis's base parameters were calculated.

The total surface energy is the sum of polar and non-polar components.[24]

$$\gamma s^{total} = \gamma s^{LW} + \gamma s^{P} \tag{8}$$

For the black dyed crust leather, contact angle values were measured at several regions such as the butt, backbone, neck, shank and belly. The contact angle values for the different regions of the leather were 78.42°, 73.47°, 69.01°, 66.02° and 62.43° for polar solvent (water). Due to spontaneous dispersion on the leather surface, measuring the contact angle value for moderately polar and non-polar solvents for crust leather is negligible. According to the above values, the butt region has the highest contact angle, while the belly region has the lowest. It was also found that each region of the crust shows a different value. In order to reduce the anisotrophicity of finish values in acrylic finished leathers, acrylic finish films were cast and placed on microscopic slides. The surface energy and work of adhesion were calculated using the contact angle values.

Contact Angle and Surface Energy and Work of Adhesion Parameters of different Acrylic Binder Films

The surface related parameters viz., surface energy and work of adhesion of very soft, soft, medium soft and hard binders were calculated based on the contact angle values for the films cast on the glass plates made with different liquids, viz., water, DMSO and hexadecane.

The contact angle values of polar solvent (water) showed an increasing trend from 60.23° to 87.75° for four different binder films in the trend, medium soft acrylic binder < soft acrylic binder < very soft acrylic binder < very hard acrylic binder. The higher contact angle values for hard binders indicate a non-smooth discontinuous film being formed. Hence, the hard binder cannot be used for the base coat, where film formation is completely not possible. The hard binder is used for specific finished leathers like crackle finish. Resin binders with smaller water contact angles were ideal for base coat because they spread quickly across the surface of the leather, which in turn facilitates the degree of adhesion.

The contact angle values of moderately-polar solvent (DMSO) showed a different trend, which can be attributed due to the nature of the monomers present and the behaviour of the acrylic polymer in presence of solvents in the binder film. The values for this moderately polar solvent ranged from 25.31° to 57.30° in the trend, very soft acrylic binder < very hard acrylic binder < medium soft acrylic binder < soft acrylic binder. For non-polar solvents, the values ranged from 7.80° to 20.54° in the trend, soft acrylic binder < medium soft acrylic binder < very soft acrylic binder < very hard acrylic binder. For leather finishing, the contact angle values of polar solvent are predominant, hence it is used for the entire finish film study for leather finishing.

The total surface energy value of a very hard acrylic binder is low in comparison to the other binders. The polar part of the surface energy (γsv^{p}) is very low for the hard binder and hence it does not form a continuous film. Comparatively, the surface energy values of the other three binders were greater, indicating that they had better adhesive qualities. It can also be seen that the difference between polar and dispersive surface energy values follows the trend of very soft binder (17.83 m/Nm) > soft binder (11.76 m/Nm) > medium soft binder (9.33 m/Nm). This indicates that the adhesion of the finish to the leather will follow a similar trend. However, we observed that the total surface energy values follow a reverse trend in comparison to the difference in polar and dispersive values. Hence, it can be concluded that the total surface energy is higher for very soft binders and hence, it binds better to the leather surface and requires more energy to remove the finish from the leather when compared to the very hard acrylic binder.

Table III

Contact Angle and Surface Energy and Work of Adhesion Value for Binders coated on a Microscopic Slide

S. No	Chemical name	Contact Angle (degree)			Surface Energy (m/Nm)			Work of Adhesion (mJm^{-2})		
		Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1	Very Hard Acrylic Binder	87.75	26.79	20.54	25.75	3.93	28.69	75.65	83.28	53.19
2	Very soft Binder	64.96	25.31	10.92	26.98	9.16	41.27	103.62	83.78	54.44
3	Soft Acrylic Binder	63.89	57.3	7.80	27.22	15.46	42.68	104.84	67.77	54.68
4	Medium Soft Acrylic Binder	60.23	50.6	8.65	27.16	17.83	44.99	108.95	71.93	54.63

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Very Soft Binder

Based on the results from Table III, a separate set of experiments were carried out to assess the surface energy and work of adhesion of individual binders in combination with other chemicals like pigments, fillers, wax emulsion, protein binder and water added to the finish season for finishing of leathers. The experiment was conducted to understand the binding capacity of the acrylic binder to the pigment particles. The surface contact angle for different pigment binder ratios (@1:0.5 to 1:4) (PABR) of very soft binders were evaluated. The other finishing chemicals such as fillers, wax emulsion, protein binder, and water were kept constant along with pigment and the resin binder concentration alone was varied based on the PABR. The leathers were finished and the values for surface energy and work of adhesion are reported in Table IV.

The surface contact angle of leathers finished with varied PABR of very soft binder were found to increase with increase in binder concentration. The contact angle for the polar component was greater than the moderately polar and non-polar solvents, because of its higher water affinity compared to the moderately polar and non-polar solvents. The surface energy of the finished leather was calculated by combining both dispersive and non-dispersive components. There are several interactions taking place in the adhesion/cohesion between atoms and molecules during finishing of leathers that results in a surface energy. Dispersive interactions in leather finishing process are those caused by temporary fluctuations in the charge distribution of atoms or molecules during pigment binder interactions. Polar interactions are non-dispersive wherein Coulomb interactions between induced and permanent dipoles, such as hydrogen bonding taking place during the film formation of pigment binder interactions in finishing of leathers.[24]

The dispersive component of surface energy values for different PABR finished leathers showed a decreasing trend. However, beyond the PABR of 1:3, there was no major difference in the value of surface energy. A similar pattern was also observed in the polar component of the surface energy. Hence, it can be concluded that a ratio of 1 part of pigment requires 3 parts of very soft binder to form a film that was optimal surface energy for a better performance in finished leather. The physical properties of the finished film also followed a similar pattern as shown in Table VII. From the above observations, it can be concluded that the surface of polymer macromolecules tends to reorient or restructure in order to increase the surface concentration of both polar or non-polar moieties depending on the polarity of the surrounding phase; this phenomenon is attributed to the thermodynamic driving force to minimise the surface free energy. This indicates that a lower surface energy value in the finished film will need a less amount of energy for the finished film to be removed from the leather surface.

The higher values of adhesion work observed in Table IV indicates that higher energy is required to remove the finish from the leather. Hence, from Table IV, it can be seen that the work of adhesion value is lower for the higher PABR finished leathers indicating less energy is required to remove the finish from the leather. More so ever, the work of adhesion values is higher for polar solvents than for moderately polar and non-polar components, following a similar trend to surface energy values. The electrostatic force between the acrylic resin surface and the leather surface is important for controlling the film formation of acrylic resin towards binding of pigment in leather finishing. The cohesive force exerted by the interaction of acrylic resin molecules is greater than the solid-liquid (leather surface/water) interaction. As the binder concentration increases the lower the work of adhesion, so lesser energy is required to remove the finish from the leather surface.

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Soft Binder

The surface energy and work of adhesion of soft acrylic binders in combination with other chemicals (pigments, fillers, wax emulsion, protein binder and water) was also carried out in line with very soft binders to understand the binding capacity of the soft acrylic binder

Table IV

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Very Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	76.47	50.31	21.57	25.61	7.71	33.32	89.84	72.1	53.01
1:1	77.21	51.73	23.19	25.32	7.46	32.78	88.92	71.25	52.72
1:1.5	78.57	53.82	30.36	23.86	7.4	31.26	87.23	69.97	51.17
1:2	79.49	54.19	35.67	22.58	7.65	30.23	86.08	69.74	49.79
1:2.5	81.38	56.43	36.95	22.25	6.81	29.06	83.71	68.32	49.42
1:3	82.62	57.28	38.51	21.84	6.45	28.29	82.15	67.78	48.97
1:3.5	83.54	57.65	39.02	21.71	6.14	27.85	80.99	78.84	48.81
1:4	84.01	57.92	39.52	21.57	6.11	27.57	80.40	67.37	48.66

to the pigment particles. The surface contact angle for different pigment binder ratios (@1:0.5 to 1:4) (PABR) of soft binders was evaluated based on the results given in Table V. The surface contact angle increased as the soft binder concentration in the finished leathers increased. The effective binding capacity was observed at a PABR of 1:2.5, where the film starts to increase the surface hydrophobicity reducing the wettability of the leather surface. From Table V, it can also be observed that the contact angle of the polar component (water) had a greater contact angle than the moderately polar (DMSO) or non-polar solvent (Hexadecane) used for the study. This is due to high water affinity as the polar group was larger degree of contact angle. Combining the dispersive components (γsv^d) and polar component (γsv^p) of the leather surface values form the contact angle reveals the surface energy of the finished film. The dispersive component of surface energy exemplifies a constant trend upto PABR of 1:2.5 with little variation beyond this PABR. The polar component of surface energy also showed a similar pattern. The work of adhesion value is lower for the higher PABR finished leathers and do not increase drastically beyond PABR of 1:2.5. The surface energy and adhesion work of the finished leather as observed in Table V indicate that they follow a similar trend to very soft leathers with the optimal energy values reaching at PABR of 1:2.5. Similar patterns were also evident in the soft binder finished film's physical characteristics, as shown in Table V.

Table V

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	79.97	46.49	34.53	22.87	9.55	32.42	85.48	74.29	50.09
1:1	80.04	52.11	34.89	22.79	7.67	30.47	85.39	71.02	50.01
1:1.5	81.13	55.39	38.25	21.91	7.27	29.18	84.03	68.99	49.04
1:2	81.59	56.54	41.04	21.16	7.43	28.59	83.45	68.26	48.19
1:2.5	83.45	57.54	49.92	18.58	8.92	27.50	81.11	67.61	45.16
1:3	84.92	58.42	50.13	18.49	8.26	26.77	79.28	67.04	45.08
1:3.5	86.04	59.72	51.74	18.03	7.97	26.00	77.83	66.18	44.48
1:4	86.63	60.05	52.01	17.94	7.71	25.65	77.08	65.96	44.38

Correlation between Surface Energy and Work of Adhesion Parameters for various PABR of Medium Soft Binder

The surface contact angle for various pigment binder ratios (1:0.5 to 1:4) of medium soft binder was also assessed. The surface contact angle increased with PABR up to 1:2 beyond which there was no major increase and hence optimized this PABR in the medium soft finished leathers. The polar group shows the higher degree of contact angle in medium soft binder finished leathers, indicating that the cohesive forces associated with water are larger than the forces involved with water-finished leather surface contact. The solid content of medium soft binder was higher when compared to soft and very soft binder. Hence, the contact angle of finished leather film was higher. The film on the leather surface had a better coverage and uniformity that resulted in larger contact angle values. As the binder concentrations increased contact angle increased up to 1:2 PABR as it makes the surface become hydrophobic in nature. The surface energy values showed a decrease with increase in PABR of medium soft binders up to PABR of 1:2. This indicates that lesser energy is required to remove the finish film from the leather surface beyond this PABR and hence we were optimized the ratio as 1:2 for medium soft binder finished leathers. The higher values of adhesion work for medium soft finished leathers observed in Table VI indicates that higher energy is required to remove the finish from the leathers up to 1:2; beyond this ratio there was not much variation of significance. Hence from Table VI, it can be concluded that work of adhesion value is required for the higher PABR of 1:2, which is the optimized ratio for medium soft binder finished leathers.

Pigment Volume Concentration (PVC) is a universal acceptance in the finishing process of leather industry worldwide. Pigment volume concentration in the finishing season is the volumetric percentage of pigment present, which is relative to the total solids present in both the pigment and the binder. Hence, the entire finishing process works on the total solids of these chemicals used for finishing of leathers.

It's perceived by many technical experts that a pigment (with varied total solids) will bind to the leathers surface with different binders (with varied total solids) at specified PB ratios as they result in identical values of the pigment volume concentration. However, this is not the case. The entire calculation of pigment-binder volume calculations is based on the total solids of the pigment and in relation to the total solids present in the binder. Ideal recipe development for finishing for enhanced physical and chemical properties of final leathers will be based on total solids and the volume concentration of pigment and binder majorly.

From the current study, it is also established that a ratio of pigment to binder 1:2 is sufficient for medium soft, 1:2.5 for soft and 1:3 for very soft binder both in terms of surface energy and work of adhesion values. It clearly establishes the fact that a pigment with a total solid of 22% required two parts of medium soft binder of 40% total solids, two and half parts of soft binder of 30% total solids and three parts of medium soft binder of 22% total solids to completely bind the pigment to the leather. There are also several other factors that influence the adherence of pigment to binder: (1) Fundamental packing characteristics of pigment; (2) type of binder employed; (3) types and amounts of special agents present; and (4) fineness of grind of the system.

The pigment volume concentration (PVC) of a finishing solution is the volumetric percentage of pigment contained in the total solids of the leather finish system that does not include any volatiles. It is the concentration at which there is enough binder present to completely

Table VI

Contact Angle and Surface Energy and Work of Adhesion Values for various PABR of Medium Soft Binder

PABR	Contact Angle (degree)			Surface Energy (mN/m)			Work of Adhesion (mJm^{-2})		
	Water	DMSO	HD	γsv^d	γsv^p	γsv	Water	DMSO	HD
1:0.5	78.13	50.01	31.75	23.54	8.28	31.82	87.78	72.28	50.83
1:1	79.13	50.54	33.45	23.13	8.12	31.25	86.53	71.96	50.39
1:1.5	81.02	51.48	35.01	22.75	7.58	30.33	84.16	71.40	49.97
1:2	82.67	53.25	36.85	22.28	6.99	29.27	82.09	70.33	49.45
1:2.5	83.48	54.05	37.23	22.18	6.62	28.80	81.07	69.83	49.34
1:3	84.31	54.93	38.12	21.95	6.53	28.28	80.01	69.28	49.08
1:3.5	85.09	55.19	38.86	21.75	6.22	27.94	79.03	69.12	48.86
1:4	86.39	55.98	39.57	21.67	5.75	27.42	77.34	68.61	48.64

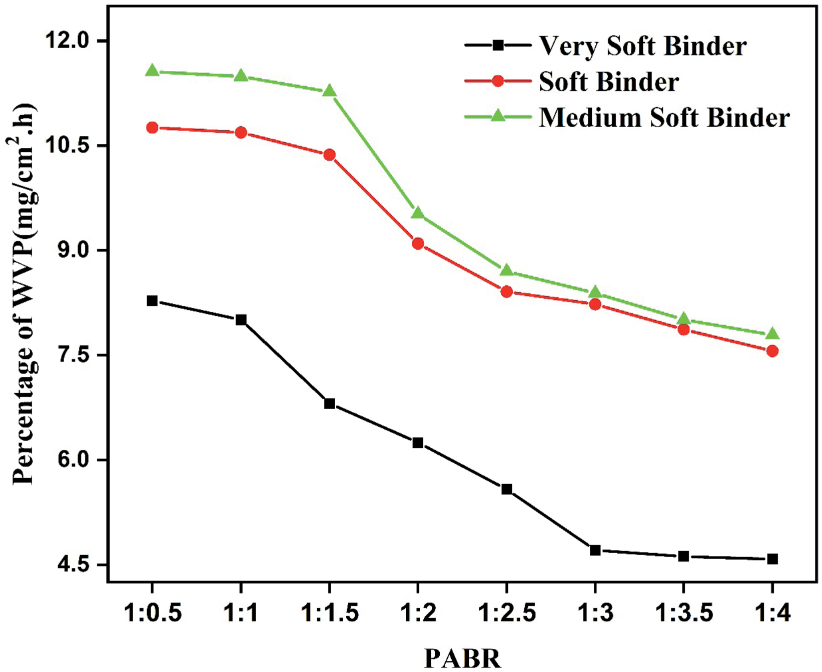

Figure 1. Plot of %WVP finished shoe upper leather versus P/B ratios.

fill the voids during the film formation on the leather surface.[25] When the pigment binder system reaches a critical pigment volume concentration (CPVC), the appearance and behaviour of the finish film on the leather surface is noticeably changed. Fundamental packing features of the pigments, the kind of binder used, types and quantities of special agents present, and the system fineness of the grind, particle size etc. all have an impact on CPVC of the leather finish system. The CPVC of individual binders used is determined by the degree of dispersion or agglomeration.[26] An agglomeration is a collection of two or more distinct pigment particles that are held together by the force of adhesion and have a tendency to stay together as one whole. A widely distributed pigment system exhibits a higher CPVC than an agglomerated pigment system. The leather finish system basically needs higher CPVC and is mainly influenced by the type of binder used. The part of the binder that was firmly adsorbed to the surface of the pigments is known as the "bound vehicle" solids. The ingredients present in the binders for leather finish systems that are also known as the "interstitial binder" are needed to fill the spaces left by the pigment particles when they are packed as tightly as possible given their dispersion. The fraction of the binder over and above the interstitial binder plus the bound vehicle solids is referred to as the "excess binder".[27] It is this excess binder that covers the pigment particle completely and does allow it to come out during wet rub fastness as soon as the film is completely formed. It is for the same reason that the finish recipe for a type of leather will have a mixture of all the three binders (soft, very soft and medium soft) with the ratios being changed to the required softness of the finish. Thus, there shall always be an "interstitial binder" and also the "excess binder" present in the finish system that protects the grain layer of the leather, binds completely to the leather as well as give the desired properties required for the type of the leather. The higher the CPVC, the smoother the surface and better the properties of the finish in the final leather; lower CPVC exhibits thixotropic effect.

Water Vapor Permeability

Water Vapor Permeability of leather determined by the rate of transmission of water vapor through leather in terms of milligrams per unit area and for a specified period. In general, unfinished leather will always show higher water vapor permeability than finished leather due to the blockage of the pores by the film.[28] Here in this work, the coating of different pigment to binder ratios on the leathers and its effect on permeability was studied and shown in Figure 1. From Figure 1, it divulges that with the increase in the concentration of binder, there is a decrease in the water vapor permeability. Amongst the binder types, the very soft binder showed less permeability than the soft and medium types. This may be due to the good covering of pores by low molecular weight components in a very soft binder. Whereas the medium and soft binders showed an almost equal range of high permeability. The presence of medium and long acrylic chains in soft and medium binders could not completely cover the nanopores present on the leather surface. Because of that medium binder will be better in order to make a permeable leather. And also, the 1:0.5 to 1:1.5 pigment to binder ratio showed higher permeability than other ratios. Hence, the water vapor permeability results confirm that the type of binder and its ratio greatly affect the permeability of leather.[29]

Finish Adhesion Properties of Finished Leather

Finish adhesion towards leather can be determined by two factors: adhesion to the substrate and cohesion within the film. Adhesion depends on the penetration of the finishing formulation either

Table VII
Adhesion Properties of Optimum PABR of various Binder

Binder Type	Finish Adhesion (N/mm)		Color Fastness to Circular Rubbing (grey scale)		Flexing Endurance (×500,000)	Lastometer	
						Distension at Grain Crack	Load at Grain Crack
	Dry	Wet	(Wet Rub)	(Dry rub)		mm	Kg
Very Soft	3.19	1.01	4/5	4/5	Excellent	8	22
Soft	2.33	0.80	4/5	4/5	Fine Grain Cracks	7	21
Medium Soft	1.32	0.71	4/5	4/5	Fine Grain Cracks	7	21

by particle size and force of action like spray or impregnation. Cohesion depends on the cohesive force within the film, which was proven to increase with decreasing particle size. Hence, it is important to understand the adhesion properties of the finished film and the grain crack resistance of the leather after coating with three types of binders. Considering the solid content of the binder, the very soft binder had a lower Total Solids content (TS -25%) and smaller particles than the soft (TS-30%) and medium soft binders (TS-36%). Higher the solid content and lower the particle size, better is the film forming characteristics and penetration of binder into the micropores of the leather. Hence, the very soft binder can coat the leather uniformly, whereas the medium type will load the leather instead of uniform coating. Similarly, the particle size of all the acrylic binders were found to be in the range of 90-140nm; lower the size of binder, the higher the impregnation/ penetration into the finish film. Similarly higher the size, more covering of the finish will be provided. From the finish adhesion property shown in Table VII divulges that due to the very small particle size, the very soft binder showed greater adhesion than medium and soft. The results are well correlated with the leather surface energy and adhesion properties.

In general, the particle size of the pigment and binder is crucial in forming the film on the leather surface. As a result, it affects the leather's surface energy and film adhesion. The good adhesion of film on the leather surface can be attained by choosing the proper pigment to binder ratio. In that way, the pigment to binder ratio was maintained at optimum ratio, the high binder concentration was chosen to get adequate binding of all pigment particles to leather, which leads to better adhesion of pigment. To understand the color transfer from leather, the wet rub and dry rub fastness was studied, and the results are shown in Table VII. At the optimized ratio of PABR, all types of binder showed good and similar fastness values indicating the better anchoring of pigment particles at higher concentrations of the binder.

To predict the film cohesion, the results of vamp flexing for leathers finished with various binders are depicted in Table VII. Throughout 10,000 cycles, all leather samples with various binders exhibit good flexing resistance, no remarkable changes were observed, and no cracks could be seen. This exemplifies the finish film's tight bond with the leather. At 500,000 cycles, the very soft binder shows no grain cracks, and the medium and soft binder showed slight creasing and cracks on the surface. The results indicate that poor cohesion in medium and soft binders caused the grain crack, whereas good cohesion in very soft binders with pigment showed good resistance against the flexing. Good flexing resistance of very soft binder is also due to the smaller particle size. Lastometer results also confirm the same observation that the distension and load were higher in the case of very soft binder than a medium and soft binder.

Organoleptic Properties Analysis

The finished leathers of all finish types were evaluated for organoleptic properties by hand and visual evaluation. The organoleptic properties such as finish film uniformity, grain smoothness, fullness, color of optimum PABR of finished leathers are given in the Table VIII. Higher numbers indicated a better property. The finish film uniformity was higher in case of very soft and soft binders, and the medium binder showed poor uniformity due to the large particle size. Grain smoothness and uniformity were interconnected based on the film coating on the surface. Both very soft and soft binder showed similar trend in grain smoothness than medium soft binder coated leather. Color shade and feel were also good for very soft binder as the grain is not loaded.

Table VIII
Organoleptic Properties of Optimum PABR of various Binder

Binder Type	Finish Film Uniformity	Grain Smoothness	Finish Surface Feel	Color Shade
Very Soft	8	8	8	9
Soft	8	8	7	8
Medium Soft	7	7	6	8

Conclusion

The study demonstrates that surface energy values play an important part in understanding surface behavior depending on the charge of the leather's surface. Because of the hydrophilic nature and particle size of the binder, the very soft binder had greater PABR than the soft and medium soft binders. The greater the surface energy values, the better the adhesive power of the binder. A better selection of binder quality and concentration is required for a better finishing procedure. It is difficult to evaluate the rub fastness test from a rheological standpoint, since the finish performance is dependent on several functions such as leather structure, application, technique, and chemical performance. The leather with higher polarity (i.e., low contact angle and higher surface energy) resulted in better work of adhesion. Hence, the present study indicates that the type of binder and PABR influence the vapor permeability of leather based on the type and solid content of binder. Adhesion and cohesion were greatly affected by the binder type; good adhesion was found in case of soft binder and good grain crack resistance in case of very soft binder. Based on the organoleptic properties, the very soft binder finished leather showed good grain characteristics than other types of binder. Thus, the study ensures that choosing correct quality and quantity of chemicals used in the finishing process, which helps us to get desired finishing. More so ever, a judicious quantity and quality of binders will be required for the type of leather based on the finish properties required.

Acknowledgments

The authors thank authorities of CSIR-CLRI, Tamil Nadu, India for providing necessary facilities during the period of research. We also thankful to CSIR-Integrated Skill Initiative Program NWP0100 for their financial support. CSIR-CLRI Communication number is 1890.

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