



ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
CHEMICAL AND BIO-ENGINEERING DEPARTMENT
LEATHER TECHNOLOGY STREAM
STUDIES ON EFFECT OF DIFFERNT PIGMENT AND BINDER
COMBINATIONS ON SURFACE PROPERTY OF FINISHED LEATHER

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ABBREVIATIONS AND ACRONYMS

SFE	-	Surface Free Energy
PCSE	-	Polar Component Of Surface Energy
NPCSE	-	Non- Polar Component Of Surface Energy
TSE	-	Total Surface Energy
SL	-	Surface Layer
PU	-	Polyurethane
PUTC	-	Polyurethane Top Coat
CAB TC	-	Cellulose Acetate Butyrate Top Coat
PVC	-	Polyvinyl Chloride
VOC	-	Volatile Organic Compound
TS	-	Tensile Strength
EB	-	Extension At Break
YM	-	Young's Modulus
ML	-	Maximum Load
ME	-	Maximum Extension
WCA	-	Water Contact Angle
MICA	-	Methyl Iodide Contact Angle
HDCA	-	Hexadecane Contact Angle
DMSO	-	Dimethyl Sulfoxide
LIDI	-	Leather industry development institute
CSIR	-	Council for scientific and industrial research
CLRI	-	Central leather research institute
TC	-	Top coat
FC	-	Finish coat

ABSTRACT

The present work attempts to analyze the surface and physical properties of leathers finished with various combinations of binders and pigments by keeping other auxiliaries constant. The contact angles of liquid drops resting on the leather surface have been used to evaluate surface energy, acidity, basicity components of the surface energy, polarity and work of adhesion. Contact angle values have been measured for chrome tanned and conventionally re-tanned crust and finished leather made by varying pigment and binder combinations. The wettability of finished leather has been correlated with the contact angle values: the higher the contact angle value the less wetting is observed. Complete wetting can be obtained when the contact angle value is zero i.e. the drop of liquid spread spontaneously on the surface and partial wetting is obtained when the contact angle value is in between 0° and 90° . Acrylic binders with different film forming properties, protein, polyurethane and butadiene binders have been combined to prepare different finish formulations. Pigment to binder ratio for acrylic system and acrylic with polyurethane binder system have been optimized from the information obtained from contact angle values which have direct relation to degree of wetting. And the results have been correlated with wet and dry rub fastness, finish adhesion, vamp flexing value, water vapour permeability and water proofness. It has been observed that when the surface of leather is coated with acrylic binder the contact angle value due to polar solvents(water) , non polar solvents(hexadecane) and moderately polar(DMSO) and methyl iodide show that as the thickness of coating increases, the contact angle value decreases for the base coat and sharply increases when top coat is applied. Top coats have the ability to increase the contact angle and they improve the performance properties of leather such as water resistance, fastness, finish adhesion etc. Cationic and anionic finishing formulations have been compared to study their effect in modifying the surface of finished leather based on contact angle values, wet and dry fastness to circular rubbing and water resistance. It has been observed that leathers finished using anionic finishing technique shows better wet rub fastness and water resistance effect compared to cationic finishing technique.

Key words:- contact angle, surface energy, cationic finishing, anionic finishing, work of adhesion, acidity, basicity

CHAPTER- 1

INTRODUCTION

1.1 Introduction to the problem addressed

The object of finishing is to give a treatment of coatings to the grain surface to protect it against dirt, staining, wetting, mechanical stresses like rubbing, scuffing, flexing etc., levelling or evening out the colour of the grain surface, hiding grain blemishes and upgrading its quality, improving the aesthetic appeal and the sales value of the product. By the finishing process, the grain surface of the leather is coated with various substances and is then submitted to different mechanical operations, depending upon the purpose intended whereby the appearance of leather can be highly influenced to make it more useful, attractive and appealing to users. Finishing may be employed to impart colours, a uniform shade, special patterns, a smooth or grained or printed/embossed surface, lustre (Matt or glossy) as well as opaque (covered) or transparent (aniline/semi-aniline) appearance to the leather surface. Finishing operation is the most vital part of the processing of leather as the final product is judged by its appearance, evenness of colour and surface, feel, handle, break, gloss etc. Hence it is usually the finishers who have to face the complaints or blames, if anything goes wrong. They are also expected to correct whatever faults that have occurred during the earlier operations [1].

Finishing was once considered as an art and was kept a secret but today with the introduction and availability of a wide variety of leather finishing chemicals and mechanisation, finishing is no longer that secret. However, in spite of the innumerable finishing auxiliaries available and marketed by the firms providing details like general composition and properties of the products, mode of application with formulation for different types of finishing of leather, finishing is still dependent upon the finisher's ability of judging and blending of different auxiliaries to make his own combination to give the best finishing effect. Also, he keeps in mind the high qualities required from finishing, like adhesion, flexibility, durability against weathering and aging, durability against dry and wet rubbing, resistant to peeling, cracking on flexing, light fastness, resistant to the various mechanical operations involved in finishing and permeability to water vapour thus ensuring the hygienic conditions.

The absorption of surface and anchorage and adhesion of finish film can be affected by the surface charge and presence of fatty substances. In the case of chrome tanned crust leathers,

the final PH is around 3.5 and this means the surface has cationic residual charge. Most of finishes used in leather finishing are anionic in nature and too much of residual cationic charge may not allow the finish film to anchor well. This combined with the presence of fatty matter will result in poor adhesion of the finish film. The absorptive nature can be assessed by putting a drop of water on the surface and measuring the time taken for absorption. In case, the leather is absorbing less water that means the leather surface may have materials which are hydrophobic. In this case the water contact angle will be more so that the water molecules will form spherical beads rather than spreading on the surface. In which case, traditionally clearing coats are applied to improve the absorptive nature. Clearing coats contain a water miscible solvent like isopropyl alcohol or diacetone alcohol along with a mild alkali like ammonia. The solvent clears the surface fat and ammonia reduces the surface cationic charge on the surface. Sometimes the surface non- uniformity is reduced and made more level by using a dye solution along in which case the coat is called stain coat [2].

When a leather technician wants to make soft leather excessive anchorage is not required because it causes hardening of the surface of leather hence too much clearing coat is counterproductive. In such cases traditionally people use cationic oil ground to seal the surface of the leather so as to avoid excessive sinking of finishing chemicals. This is called sealing coat. In this case we are blocking the absorption of excess chemicals by incorporating the cationic charge on the surface of the leather. Care should be taken to avoid excessive use of the cationic oil ground. Usually 100-150 gram per liter is used to get the optimum effect. When the cationic oil ground is used in excess amount the season coat cannot be adhered properly to the surface of leather, in such case ammonia can be used to reduce the cationic charge.

In conventional pigmented leather finishing technique, the natural look and feel of leather is usually lost because of heavy loading of pigments and binders which in turn affect the profitability of a given company. Even though the leather chemical industries are developing different finishing chemicals for up gradation of the surface defects and blemishes, the understanding of effect of each finishing chemicals and auxiliaries on surface and optical property of leather is still limited among leather technicians and researchers. A buyer's first consideration when faced with the leather is probably its feel. "Plastic" finishes with a cold, synthetic feel, or finishes which are too rigid and do not show good levelling and integration with the leather, should be avoided by means of suitable selection from the first phases of

making the leather. Efforts to improve the situation on leather already finished are difficult and largely ineffective, even if the wide range of feel modifiers can help.

In this work, the overall objective has been to understand the surface energy parameters of different finishing of leather and relate these properties to the quality of finishing. Further, the work has attempted to optimize the quantity, nature and the combination of different finishing chemicals to obtain optimal finishing properties for different types of leathers.

Thus to quantify the amount of finishing chemicals especially binders and pigment in finishing of shoe upper leather goat crust having similar grain quality were selected and finished by varying the concentration of different binders. Contact angle values were measured for leathers finished with different finish formulations. From contact angle value polar and non polar component of surface energy, the degree of wetting, work of adhesion were calculated. In addition to this, effects of other finishing chemicals and top coats on the surface and physical properties were also determined.

The amount of surface coating applied to the leather influences whether or not the item can be described as genuine leather. If the leather has a surface coating, the mean thickness of this surface layer, however applied, has to be 0.15mm or less, and does not exceed 30% of the total thickness of the leather.

The results of this study is especially helpful to develop finishing technology for special type of leathers like water resistance, self care, light weight and high water vapour permeability and etc.

1.2. Statement of the Problem

Globally the quality of hides and skin is declining dramatically due to different ant-mortem, post mortem and process defects at different leather processing stages. So that the value obtained from hide and skin is substantially decreasing from time to time. The problem is more pronounced in developing countries like Ethiopia because of different parasitic defects like “echek” which is more common in sheep and goat skins. In addition to this, flaying defects due to knife cuts during slaughtering is the major quality problem especially in cow hides. The cutting value of leather can only be maximized by using proper understanding of leather finishing techniques. However, the science and technology of leather finishing is poorly understood by different finishing technicians and leather industries because of complexity of surface properties of different leathers, polymer chemistry and technology and

the trade secret of chemical companies. Hence the effect of different finishing chemicals and auxiliaries on surface and optical property of leather is still poorly understood among leather technicians and researchers. Quality inconsistency is one of the main problem in leather finishing which is due to improper combination of binders and pigments because there is no scientific information given for the quantity of each used based on the type of leather to be finished.

1.3. Objective of the Study

1.3.1. General objective

The main objective of this work is to quantify and analysis of different combination of pigment and binders on surface property of finished leather and finish leather films.

1.3.2. Specific objectives

- Study of surface morphology of each pigment to binder relationship by stereo microscope
- To determine the optimum pigment binder (p/b) ratios for different binders and pigments
- To determine the effect of each finishing auxiliaries on the physical properties of leather.
- To relate surface properties like contact angle, surface energy and work of adhesion with different types of binders.
- To correlate different finishing auxiliaries to the surface properties.
- To give direction for the leather finisher to quantify the amount of chemicals used so as to get the quality leathers by employing optimum amount of finishing chemicals as per the quality of raw materials and intended product quality
- To study the wettability of finished leather by polar and non-polar solvents.

1.3.3. Scope of the study

This thesis work covers preparation of finish formulation by varying pigment to binder ratios and keeping other auxiliaries constant and evaluates the surface property and the quality of leather coated by respective pigment–binder combinations. The study also correlates the film forming property of different binders with the physical properties and addresses the optimum pigment to binder ratio for efficient utilization of the chemicals.

1.3.4. Significance of the research

- It will be helpful for profitability of the tanner by optimizing and in few cases reducing the excess use of pigments and binders.
- It will help to reduce quality inconsistency of finished leather and overcome the problem of surface defects with minimum chemicals and cost effective manner
- It will provide scientific explanations for the use of different binders and other finishing auxiliaries
- It gives good understanding on surface morphology of finished leather by different pigment and binder combination
- It helps to understand the nature of different binders and pigments because the chemicals used by a given manufacturer are kept as secret.

1.3.5 Organization of the Thesis

This thesis is divided into five chapters. The first chapter deals with the general introduction to the problem, objectives of the work and scope of the work. The second chapter deals with the literature review and past work done in this area. The third chapter, Materials and Methods, involves description of the materials and their design used to solve the given problem. It deals with the preparation of different finish formulation by employing commercially available finishing chemicals by varying the type and quantity of resin binders and top coats to study the surface property by the help of contact angle measuring instrument and physical properties with the help of physical testing equipments respectively. Besides it lists the models and assumptions used in the entire thesis work. The fourth chapter, Results and Discussions, presents the results obtained and the discussion thereof. The fifth chapter, Conclusions and Recommendation, gives the conclusion from the results obtained and some points recommended for future work that is possible in this area.

CHAPTER-2

REVIEW OF LITERATURE

2.1. Introduction

The finishing technique of leather can greatly vary mainly depending on the purpose of the leather. Leather for shoes needs thick, water and scuff resistant coating while leathers for garment and gloves require light finishing. Shoes in warm countries to wear in towns and mainly in rooms needs only thin coatings. Leather for car upholstery to be used in sunny parts needs special coating resistant to high UV radiation in the polymers and pigments used. The fastness properties determine greatly the character of the finish [3].

Visual evaluation of leather depends on its surface. As a rule, finished leather surface is treated in such a way that it emphasizes its natural beauty and conceals its minor defects. The surface of the leather in the over most cases the grain, was treated in ancient times with a protective season. Leather needs a closing and sealing of the porous surface against humidity, dust, dirt and to make the surface an attractive appearance. Development of polymer chemistry and technology makes it possible of changing leather surface in many ways. Apart from chemical stability i.e. resistance to damaging factors like air, oxygen, water and its impurities, it has to be firmly attached to the substrate. The surface tension existing at the ground coat interface during applying i.e. when the coat is liquid affects effectiveness of coat applied. The capability of joining the two substances (adhesion) and internal coherence (cohesion) are responsible for the stability of the coat, together with reactions occurring between the coat layers [4].

The surface properties of finished leather will vary based on the type of the finishing auxiliaries, the nature of crust leather and mechanical operations used. The surface energy, surface charge, work of adhesion, wettability on different solvents, covering effect, the grain character, optical properties etc are very important parameters to characterize finishing. Scientifically finishing is the reduction of surface charge by using polymeric coating chemicals and auxiliaries this in turn increases abrasion resistance of leather and decreasing friction on the surface. The surface charge of the leather is a measure of its polar nature and capacity to react with polar substances. Generally surface charge densities of crust leather depend decisively on the kind of tannage and are of particular importance for all post tanning processes such as neutralization, re-tanning, , dyeing and fatliquoring [5].

Therefore studying the charge characteristics of coating materials is important to see the surface property of finished leather. Coating of leather depends on the surface charge of crust leather, binders, pigments and feel and flow modifiers but no sufficient scientific information is given for the effect of each auxiliary on surface property of leather. Contact angle value is simple and accurate technique to quantify the surface energy and work of adhesion of different finish formulation. Finishing layer should be able to be easily cleaned. There should be no spot formation due to water and the most important one is the binding of that layer to the leather has to be strong so that it should stay on the leather even in the presence of water. This can be measured by using standard test method called finish adhesion.

2.2. Surface Tension, Surface Energy, Contact Angle and Adhesion

2.2.1 Surface Tension

The origin of surface tension in a liquid is the forces of attraction between the molecules that make up the liquid. In the absence of other forces, this mutual attraction of the molecules caused the liquid to coalesce to form spherical droplets. This can be seen, for example, when rain falls on a freshly waxed car body. As a general rule, the greater the proportion of polar groups (e.g. O-H groups) in a molecule the stronger the attractive forces between them. Strong attractive forces give rise to a high surface tension and a tendency to form discreet droplets on a surface rather than wet it evenly. The large proportions of -O-H groups in water are responsible for its high surface tension. Alcohols, with their smaller proportion of O-H groups, have lower surface tensions. Clearly, all things being equal, the lower the surface tension of a liquid coating, the easier it will be to form a satisfactory wet film from it [6].

Surface tension can be thought of as the force that holds a liquid together. In the depths of a volume of liquid, each molecule is surrounded on all sides by other molecules; the forces between them balance out and the entire mass is in equilibrium. The situation is different at the surface of a liquid. At a liquid-air interface for example, the molecules at the surface are being attracted by the surrounding liquid but not by the air. The forces are imbalanced and consequently the liquid behaves as if had a stretched skin [7].

In leather finishing also the binders used at the bottom and base coat should contain smaller polar groups compared to binders used at the top coat because a molecule having lesser content of polar groups have better adhesion effect and have small water contact angle this

improves binding of top coats on the surface. And top coats have more polar groups so that the water contact angle is higher which causes the surface of leather not to be wetted easily.

2.2.2 Measuring Surface Tension

Every liquid has a specific surface tension value. Liquids with high surface tensions, such as water (72.8m N/m), demonstrate a high intermolecular attraction and a strong tendency to bead up (form spheres). Liquids with low values have a weak tendency toward sphere formation that is easily overcome by countering forces. A variety of methods are available for measuring liquid surface tension [8].

Most common ones are capillary rise method, drop weight method, wilhelmy plate method, maximum bulk pressure method and dynamic method.

Table 1 Surface tension of some liquids

Liquid	Surface tension (m N/m).
Sulphur hexafluoride	5.6
Trifluoroacetic acid	15.6
Methanol	22.1
Acetone	24
Dimethylformamide(DMFA)	26.3
Hexadecane	27.47
Dimethyl sulfoxide(DMSO)	44
Ethylene glycol	48.4
Methyl iodide	50.8
Formamide	59.3
Glycerol	63.1
Diiodomethane	70.2
Water	72.8
Mercury,metal	490.6

Source: From Dean, J., Ed., *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, 1985

The total surface tension component (γ) can be broken down to polar (γ^p) and non polar (γ^d) components according to the following equation

$$\gamma = \gamma^d + \gamma^p$$

The polar and non polar component of surface energy values for some of the liquid used in this research are described in table 2 below.

Table 2 Polar and non polar components of surface Tension

Type of solvents	Surface tension and its components				
	Total Surface tension values (<i>m N/m</i>)	Non – polar component (m N/m)	Polar component (m N/m)	Acidic component(m N/m)	Basic component (m N/m)
Hexadecane(non polar)	27.47	27.47	0	0	0
Water(polar)	72.8	21.8	51	25.5	25.5
DMSO(moderately polar)	44	36	8	0.5	32

2.2.3 Surface free energy

The atoms at the surface of a condensed- phase material are in a very different environment compared to those atoms from its interior. This difference arises from the asymmetric environment; in the bulk material, each atom is surrounded by similar ones and they experience no net forces. However, those at the surface see this only on one side of the interface. In addition, the various influencing factors exerted by the environment act only on the outmost atoms [9]. These atoms consequently have a different energy distribution from the inside, and are in a higher energy state at the surface. This energy excess is one wants to measure. Differences between the energies of atoms or molecules located at the surface and in the bulk of a material manifest themselves as surface tension(or surface free energy), γ . The surface free energy of non-metallic material always has non-polar, γ^d and may have a polar component, γ^p [10].

Qualitatively, surface tension acts in any surface, trying to minimize the surface area, i.e. it is a contractile force. Thus, it is a measure of the tendency of all areas to become as small as possible.

The work which has to be expended in order to increase the size of the surface of a phase is referred to as the surface free energy. As energy per unit area, the surface free energy has unit

mJ/m², wherein the equivalent unit mN/m is frequently used. Among the most important surface parameters that were found responsible for the various functionalities in nature, like self-cleaning, adhesion, low friction, etc., are wettability, hydrophobicity and/or hydrophilicity and surface energy. Since these are critical for solid–liquid properties, which are also the key for all lubricated surface conditions.

The wettability of solids with various liquids is of a great practical importance for many industrial processes, such as catalysis, flotation, making protective coatings, varnishing, gluing, and printing. Studies on the properties of the surface layer (SL) of various materials, including the wettability and SFE, are the subject of intensive scientific research for over forty years. Low energy surfaces are difficult to wet and can give poor results for coating, painting, and printing [8]. These quantities are being assumed as important criteria for evaluation of adhesion properties of solid polymers. They are especially useful for the analysis of the effects of modification of the SL of polymeric materials.

The energetic of solid surfaces and their effect on the interaction with liquids play an important role in a variety of applications such as adhesive bonding, polymer coatings, printing, etc, where a high degree of wetting is desired. In other applications such as water and ice repellency and anti-sticking, easy-cleaning or self-cleaning surfaces, wetting is undesirable. In other words surfaces which have more free energy shows less contact angle value whereas solid surfaces which have less surface energy signifies high contact angle.

The thermodynamics between a liquid and a solid were first described by Thomas Young in 1805[11]. The so-called Young's equation relates the surface tensions of a liquid, a solid and a gas surrounding them to the contact angle formed between the liquid and the solid substrate.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \text{-----} (2.1)$$

Or

$$\gamma_{SL} = \gamma_S - \gamma_L \cos\theta \text{-----} (2.2)$$

Where, γ_S is the SFE of a solid, γ_{SL} – the SFE Corresponding to the solid-liquid interface, γ_L – the SFE of a measuring liquid, and θ - the contact angle between the solid and the measuring liquid. This equation and the measured value of the contact angle are still being used as the basis for calculating the SFE of polymeric materials. Adamson [12] defined wetting as the case where the contact angle between the liquid drop and the solid surface approaches zero. Non-wetting was defined as the case where the contact angle is greater than 90°. Based on thermodynamic considerations a liquid will completely wet a solid surface, provided that the surface energy of the solid is greater than that of the liquid. The higher the

difference between the surface energies of the liquid and the solid, less wetting is expected. Generally, when the water contact angle is less than 90° the surface is considered hydrophilic. When the water contact angle is greater than 90° the surface is considered to be hydrophobic [11].

The surface property of crust leather has been studied and reported that different re-tanning and fatliquoring systems influence the surface property of leather [12]. Because of coating chemicals most of which contain polar and non polar groups the property of finished leather will vary substantially. Hence it is important to experimentally analyze and quantify the effect of each finishing auxiliaries on the final leather. Modification of the surface of leather have significance to develop new technologies which enable the leather technologist to produce different finished leathers which have special properties like self-cleaning, anti-soiling, water repellence, superior fastness property, etc.

The surface or interface of the leather has been assumed as the limit of separation of the two phases. In heterogeneous systems, this limit of separation is very important for the behaviour of the whole. Adhesion depends on interfacial tension and the state of the surfaces. One can assume that adhesion is a consequence of the possibility of perfect contact at every point between two surfaces. But if we break a glass rod into two and bring the two ends together, it is no longer possible at room temperature to join them. The force that has been used to break the system has left on the two surfaces and created the internal tension, which resists external projection. So it needs energy like heat to become a single continuous system. It is common in the coatings industry to refer to low energy and high energy surfaces. Polyethylene and polypropylene are examples of low energy surfaces. The forces between the hydrocarbon molecules that make up the polymers are weak and consequently polar liquids tend to form droplets on the surface rather than spread out. It is difficult to coat low energy surfaces but fortunately there are numerous ways of converting low energy into high energy surfaces. All the methods aim to form oxygen containing species at the surface and this oxidation can be achieved by exposure to ultraviolet radiation, plasma or corona discharge or by flame or acid treatment. Surface energy is quantified in terms of the forces acting on a unit length at the solid-air or the solid-liquid interface [13].

According to the theory of permanent dipole interactions between the liquid and the solid

$$\gamma_{lv}(1 + \cos\theta) = 2[\sqrt{\gamma_{sv}^d \gamma_{lv}^d} + \sqrt{\gamma_{sv}^p \gamma_{lv}^p}] \text{-----} (2.3)$$

Where θ = contact angle

γ_{lv} =liquid- vapour surface energy

γ_{sv}^d =solid- vapour interfacial energy of non polar/dispersive component

γ_{lv}^d =liquid- vapour interfacial tension of non polar solvent

γ_{sv}^p =solid- vapour interfacial energy of polar component

γ_{lv}^p =Liquid- vapour interfacial energy of polar component

In the case of non polar liquids, the polar component will be vanished, and then equation [2.4] can be reduced to

$$\gamma_{lv}(1 + \cos\theta) = 2[\sqrt{\gamma_{sv}^d\gamma_{lv}^d}] \text{-----} (2.4)$$

By rearranging terms, the non polar component of surface energy can be expressed as:

$\gamma_{sv}^d = \left(\frac{\gamma_{lv}(1+\cos\theta)}{4}\right)$ where, θ is contact angle for non –polar liquid and γ_{lv}^d and γ_{lv} are equal for non polar liquids.

Van Oss- Chaudhury- Good(OCG) thermodynamic approach can be used to determine the surface free energy components of solids. A similar comparison can be made by considering the Van Oss, Chaudhury and Good [13] model in which the solid/liquid work of adhesion is expressed as a sum of three terms:

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_s^+\gamma_l^-} + 2\sqrt{\gamma_s^-\gamma_l^+} \text{-----} (2.5)$$

Where θ = contact angle

γ_{lv} =liquid- vapour surface energy

γ_s^{LW} = the Lifshitz–van der Waals (non-polar) component of the surface free energy

γ_s^+ and γ_s^- the Lewis acid parameter and the Lewis base parameter, respectively.

From the contact angles of at least three liquids of known surface tension parameters ($\gamma_L, \gamma_s^{LW}, \gamma_s^+$ and γ_s^-) equation (2.5) can be used to determine the van Oss, Chaudhury and Good parameters for the surface free energy of the solid.

Thus, by considering three polar liquids, it is theoretically possible to determine the Lifshitz–van der Waals (non-polar) component, γ_s^{LW} of the surface free energy of polymers. This result can be compared to the value obtained with the equation (2.4)

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} \text{-----} [2.6]$$

Equation (2.6) can be used for determination of non- polar component of surface energy by using the contact angle of non polar liquids such as hexadecane, diiodomethane, α -bromonaphthalene and etc. By using this value it is possible to determine the Lewis acid and

Lewis base component of surface energy of the given liquid this in turn help to know the charge characteristics of the surface of the given solid [13].

In this study the charge characteristics of the surface of finished leather crust leather and finished leather have been determined. This is useful to modify the surface of the leather with help of different polymeric materials such as binders and top coats. Three liquids such as water, hexadecane and dimethyl sulfoxide (DMSO) were used.

2.2.4 Contact Angle

The definitions of surface tension and surface energy have involved consideration of the behaviour of liquids in contact with solids and the formation of droplets or thin films. One convenient way of quantifying this behaviour is to measure the angle θ formed by the liquid-solid and the liquid-liquid interfaces: -If θ is greater than 90° the liquid tends to form droplets on the surface. If θ is less than 90° the liquid will wet the surface easily. Consider a liquid drop resting on a flat, horizontal solid surface (Fig. 1). The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapour interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapour interface in the droplet profile). The interface where solid, liquid, and vapour co-exist is referred to as the “three phase contact line”. Figure 1 show that a small contact angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, a contact angle less than 90° indicates that wetting of the surface is favourable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavourable so the fluid will minimize its contact with the surface and form a compact liquid droplet. For example, complete wetting occurs when the contact angle is 0° , as the droplet turns into a flat puddle.

For super hydrophobic surfaces, water contact angles are usually greater than 150° , showing almost no contact between the liquid drop and the surface, which can rationalize the “lotus effect” liquid tends to spread out over the surface and when the liquid forms a thin film, θ tends to zero.

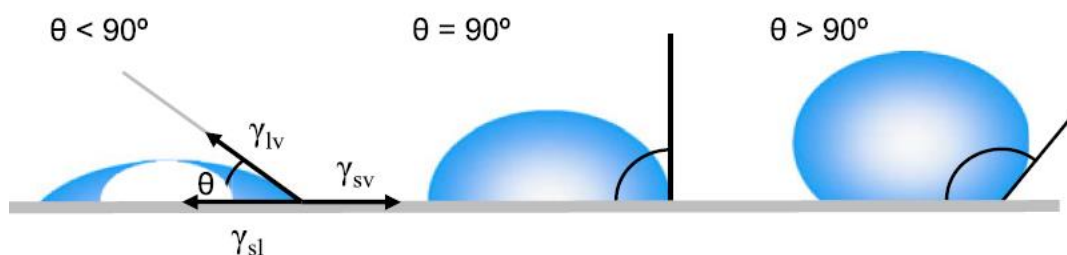


Figure 1 contact angle representation on different solid surfaces

Furthermore, contact angles are not limited to the liquid-vapour interface on a solid; they are also applicable to the liquid-liquid interface on a solid. Ideally, the shape of a liquid droplet is determined by the surface tension of the liquid. In a pure liquid, each molecule in the bulk is pulled equally in every direction by neighbouring liquid molecules, resulting in a net force of zero. However, the molecules exposed at the surface do not have neighbouring molecules in all directions to provide a balanced net force. Instead, they are pulled inward by the neighbouring molecules (Fig 2), creating an internal pressure. As a result, the liquid voluntarily contracts its surface area to maintain the lowest surface free energy. From everyday life, we know that small droplets and bubbles are spherical, which gives the minimum surface area for a fixed volume. This intermolecular force to contract the surface is called the surface tension, and it is responsible for the shape of liquid droplets. In practice, external forces such as gravity deform the droplet; consequently, the contact angle is determined by a combination of surface tension and external forces (usually gravity). Theoretically, the contact angle is expected to be characteristic for a given solid-liquid system in a specific environment [14].



Figure 2 surface tension of liquid molecules on solid surface

2.2.5 Adhesion

Adhesion can be defined as degree of binding to the surface of the leather of a finishing layer used to improve the leather's physical characteristics. The finish must stick when it is applied; otherwise it would peel or crack. For this reason the finishing technician must pay particular attention to obtain the highest possible degrees of adhesion. Surface tension, surface energy and adhesion are all interrelated [15]. The numerical difference between the surface tension of a coating and the surface energy of a substrate has a profound effect on the way in which the liquid coating flows out over the substrate and on the strength of the adhesive bond between the substrate and the dry film. If the surface tension of the coating is greater than the surface energy of the substrate then the coating will not spread out and form a film [16]. As we increase the surface energy of the substrate, we can reach a stage where the coating will spread out and form a film but, when dry, has poor adhesion. Further increases in the surface energy of the substrate will result in easier wet-film formation and better dry-film adhesion. It is important to emphasise that surface energy is only one aspect governing the complex phenomenon that we refer to as adhesion. Adhesive testing involves the application of force to remove the coating from the substrate. The intention is to measure the force needed to overcome the forces of adhesion between coating and substrate. In practice however, the cohesive strength of the coating and of the substrate both have an effect on how easy it is to remove the coating. In fact there is a supportable case for saying that there is no such thing as a true adhesive failure since, at the molecular level, all failures are cohesive failures of the coating on the substrate [18].

Work of adhesion, W_a can be calculated from Thomas young equation as follows:

$$W_a = \gamma_{lv}(1 + \cos\theta) \text{-----} [2.7]$$

Where,

γ_{lv} is liquid -vapour interfacial tension.

θ is the liquid- solid contact angle

From equation [2.7] one can deduce that the work of adhesion is inversely proportional to the contact angle i.e. the higher contact angle the less adhesion effect. For performance finishes like water resistant, self care and for hydrophobic surfaces the water contact angle will be more than 90° , hence the work of adhesion will be very small.

2.3. Technique of application of finishing chemicals

2.3.1 Bottom Coat

The bottom coat may be sealing, impregnation coat or clearing coat. The object of sealing coat is to seal the grain to control the excessive penetration of the season coat and the aim of impregnation coat is to enhance the grain tightness by filling the gap between the grain and corium major by using binders which have smaller particle size. The season coat should give a leveled and uniform filmed color coating and not overload the grain. Sealing should uphold firmly on the leather surface. The objective of the clearing coat is to make the grain devoid of any oils or fats and to improve the absorbance of the season coat by the leather. In other words, by applying the sealing coat we are increasing the contact angle or wetting angle so as to reduce excessive sinking of the finishing chemicals into the inner part of the leather [18].

2.3.2 Season Coat

The season coat is to impart a desired color to the leather and level out the surface defects. The effects like glossy or matt, soft or hard feel can be brought about by proper choice of auxiliaries added to the season coat. This coat can be done either by pad or hand spray or Auto spray. By spraying on we can achieve levelness in film formation. This stage is the main finishing step to obtain the required covering effect. Usually different combination of binders and pigments together with fillers and waxes can be used. In this coat the binders used should have required softness and flexibility in order to form continuous film [18].

2.3.4 Top Coat

Top coat serves the purpose of protecting the season coat. It gives properties like appearance, handle, fastness to wet and dry rub resist to hot plating and reduces tackiness of the binders used in top coat. Commonly available top coats are lacquer based products. The most common lacquer used in leather finishing is nitrocellulose derivatives like cellulose acetate butyrate(CAB) [18].

2.4. Classification or type of finishing system

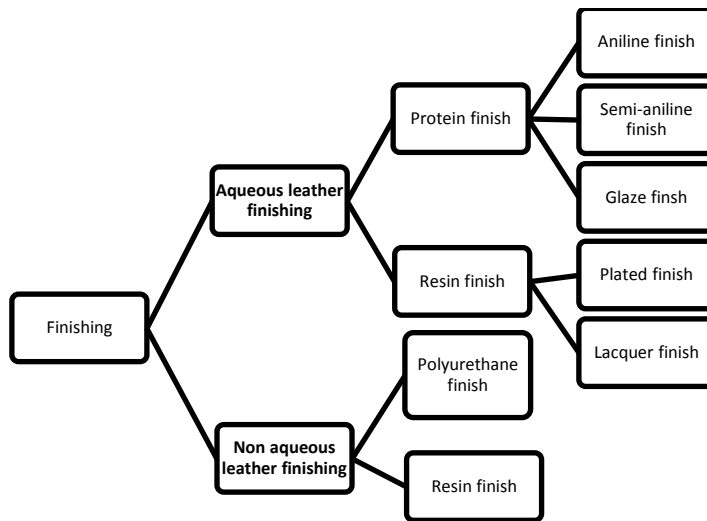


Figure 3 Block diagram for classification of leather finishing

2.4.1 Protein Finish (Aqueous)

Shoe uppers, lining leathers of goat, sheep, cattle any leathers of various types for leather goods which are protein finished and glazed still occupy an important position in the export demand of finished leathers. This type of finish uses binders mostly based on proteins. The film formed is not continuous, which facilitates the friction glazing at high temperature. The leathers will have a natural look and feel. The finish would also be resistant to cold weather [1].

2.4.2 Aniline Finish

In the recent years, the practice of coating leathers with a heavy opaque, plastic like finish has been abandoned due to the simulation of the leather imitation materials by their manufactures. Aniline finish is a transparent/translucent finish, which keeps the natural appearance so that the original grain pattern of leather surface is easily visible. The leather manufactures and finished goods manufacturers are anxious to preserve the natural look and handle of leather and hence finishing with thin coats are done through which the grain pattern is more or less visible. Aniline finish is done only in full grain leathers to retain the natural grain clearly visible. Aniline leather need not be completely free of pigments. The finish may be leered out with small amounts of finely dispersed pigments [18].

So the main feature of aniline leather is its natural appearance and handle so that the original grain pattern of the leather surface is best retained when the leather is dried out after uniform and level dyeing and fat liquoring without any surface treatment of finishing coats.

2.4.3 Semi-aniline or aniline look or mock-aniline finish

These types of finishing are more adopted for plated finished leather. The leathers are more or less heavily re-tanned and invariably the leathers are snuffed on the grain lightly or deeply depending upon the defects in the grain surface. After initial impregnation the grain surface may be coated with a good covering of opaque pigments to hide the defects. The finisher then uses his skill to give a slightly darker tone on the top using sprits soluble dyestuff, transparent organic pigments/colored lacquer emulsions etc., so that they look like aniline leather. This finish is in between real aniline and pigment (opaque) finishing.

2.4.4 Glaze Finish

This is special type of leather finishing system to make highly shiny shoe upper leather with help of protein binders. Goat is mainly used for making glaze finish. For this type of finishing technique glazing machine is used. Initially for glazing casein pigments, polymeric substances and natural substances like shellac, linseed oil are used in these finishes for getting filling, glossy and smooth feel. Glazed aniline leather can also be produced by plated (polymer) finish using polymer binders [1].

2.4.5 Resin Finish (Aqueous or Non Aqueous)

This finish is primarily based on polymer emulsions and top coated with lacquer. Currently most of the finishing activity is done by using this technique because of more proportion of poor quality raw materials worldwide. The film formed during such finishing technique is continuous and thermoplastic. The resin finished leathers can only be plated at pressure and temperature and not capable of being friction glazed. Resin finishing provides more filling effect compared to protein finishing technique. Unlike protein finish, the film is internally plasticised and hence possesses intrinsic elasticity. The new easier form of film forming products like acrylates or vinyl or butylenes polymers or polyurethane or nitrocellulose are offered by the chemical industry. The new modern finishes have been accepted by the tanner as it is possible to upgrade the poor quality raw material which is the main objective of leather finishing.

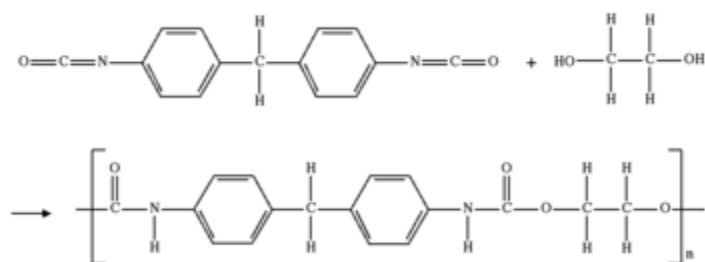
2.4.6 Lacquer Finish

This finish is generally based on nitrocellulose or cellulose nitrate. Here both lacquers (solvent dilutable) and lacquer emulsions (water dilutable and solvent dilutable) are used. But recently, solvent dilutable lacquers are not recommended because of environmental issue since they generate considerable amount of VOC [1].

2.4.7 Polyurethane finish (non- aqueous)

Urethane finishes have come into extensive use in leather finishing in the current decade. Polyurethanes represent a class of versatile, high performing polymers. The reaction of polyisocyanates with polyols is the basis for polyurethane chemistry.

Polyurethanes are amide esters of carbonic acid of the formula



Courtesy Wikipedia

The best known simple urethane is ethylcarbonate. The most widely used method for the synthesis of urethane is the reaction of diamide polyisocyanates with polyols (polyether or polyester polyols). The characteristics of the finish film depends on the nature of the polymer binder used and hence the nature of the polyurethane system with respect to these characteristics have been dealt here with some of the polyurethanes, they are highly compatible both in cationic and anionic systems. This finish is based on urethanes (both reactive and non reactive polyurethane systems). This finish gives a film, which has exceptionally excellent abrasion resistance, balance of flexibility and toughness, high gloss, gloss retention, solvent resistance, good covering, better handle, softness and levelness, brilliancy of the finish, dry and wet rub fastness, and better adhesion. At the same time, the finish has one disadvantage in that it makes the leather look like plastic. Urethanes are normally used as top coats for leathers finished with polymer emulsions. Urethanes are reactive finishes where the film is formed on the leather by the reaction of the isocyanate pre-polymers containing residual OH groups with additives containing isocyanate groups. The polyurethane is formed with the development of high molecular weight by the reaction of NCO groups with -OH groups.

2.4.9 Opaque or Covering Finish

Finish using covering pigments for hiding the grain defects and damages or for covering the very uneven drum dyeing. Here covering pigments are used along with polymer (resin) dispersions and other auxiliaries. Sometimes little dye solutions is also added to brighten the

finish. Finally they are top coated with lacquer emulsions or lacquers. In addition there are a variety of finishing systems and finishes like metallic finishes, two tone finishing, antique finishing, rub off/brush off finishing, burnish type finishing, transfer of gold, silver and other metallic foils, transfer of PVC films, polyurethane films etc., marbled and fancy finishing and so on.

2.4.10 Compact Finishes

Now a day everything becomes sophisticated in the industry easy way of applying, handling and with less labor. The compact resin binder will be used as single binder for the finishing of garment leather, upper leather and upholstery leather. It give excellent wet/dry resistances and a soft and natural feel, good adhesion and long lasting film which remain unchanged even after dry drumming and staking. This can be used in the place of season coat but initially pre bottom or base coat should be given and then normal topcoat can be applied [2].

2.4.11 Cationic finish

Cationic finishing products were first available for tanning and finishing leather from the time modern ideas on finishing began to take a hold on the industry in the 1930s. New technologies, including acrylics, copolymers and polyurethanes were all anionic in form and only recently has there been resurgence in the application of cationic technology in the leather industry. Products such as pigments and fillers with an anionic charge have little natural affinity for leather and, therefore, call for the use of resins and binders to provide the necessary levels of adhesion to the leather surface. Nevertheless they provide excellent physical properties. In contrast, cationic finishes are meeting requirements for a finish which may be best described as a 'skin cosmetic' rather than 'paint' while performing to the same high aesthetic standards as anionic finishes [19]

2.5 Application of finishes

There are essentially two methods of application (i) by pad / brush and (ii) by spray. In most cases the two methods are used in combination. In recent years another application method has been developed is roller coating. Application of finish by using roller coating machine has better transfer efficiency and this in turn help to minimize wastes generated during finishing operation.

2.6. Major constituents in leather finishing that can modify the surface of the leather

2.6.1. Acrylic binders

Until about 50 years ago protein based aqueous finishes were exclusively used for finishing all types of leather especially those with full grain structure. This resulted in a surface having many natural defects and it became necessary to have selective cutting for making foot wear and other leather articles - a laborious and time consuming job. The tanner in course of time developed a re-tanning process to homogenize the structural differences and to have a uniform surface appearance; grain was possible to be corrected by buffing with emery paper to remove most of the surface blemishes or defects. The traditional method of protein finishing of such leathers was found not to meet the rigid demands and the development of acrylic polymer emulsions was very handy to finish such leather.

Acrylic resins are manufactured by reacting (polymerizing) various quantities and ratios of acrylic monomers. Each acrylic monomer will contribute to different properties. Different polymer combinations are possible resulting in products with different and specific characteristics. Acrylic emulsions are tiny insoluble resin particles uniformly dispersed in water. The acrylic emulsions used for leather are film forming i.e. on evaporation tiny resin particles flow together to form a durable uniform film. Acrylic monomers can also be emulsified with other classes of monomers like vinyl chloride, styrene, vinyl acetate, butadiene to form copolymers.

The unique combination of the properties makes acrylic resins most suitable and ideal surface appearance enhancing and upgrading the quality. Minor surface defects and imperfections are covered and better and more uniform quality leather could be made from even lower quality grades. These binders unlike protein binders are internally plasticized and hence they possess intrinsic elasticity which will help the leather finish to remain for long time without cracking. The thermoplastic character of the polymer emulsions makes the grain surface tacky and therefore such finished leathers are given top coats based on protein binders and formaldehyde, or lacquer emulsions or lacquers or polyurethanes.

2.6.2. Polyurethane binders

The second largest polymer group used in finishing is polyurethanes. There is a wide variety of this type of binders, which can be divided into two principal groups [20].

Aliphatic polyurethane: These products are widely used as their properties satisfy nearly all requirements. Their range is extended from extremely small particle-sized binders to products

with extraordinary covering power. It can be stated that polyurethane binder possesses the best physical and mechanical properties found in finishing polymers.

Aromatic polyurethane: These are generally more economical in use. Although they provide excellent adhesion, the light fastness is poor.

2.6.3. Butadiene binders

These binders provide particularly high covering power and therefore find applications mainly on buffed leathers and splits. Their use is limited on long life articles, such as upholstery and automotive leathers, or on white leathers because of their reduced light fastness. Butadiene polymers are cross-linked by polysulphides, and their properties are modified by different copolymers. The butadiene monomers ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) provide elasticity while styrene ($\text{CH}_2=\text{CHPh}$) and acrylonitrile ($\text{CH}_2=\text{CH}-\text{C}=\text{N}$) monomers give tensile strength, and oil and solvent resistance, respectively. Their disadvantages are oxidation and discoloration due to residual double bonds in their polymer chains [1].

2.6.4 Protein binders

Protein binders are used on a large scale in the leather industry, and are based on casein, albumin and synthetic polyamides. They belong to the group of non-thermoplastic binders so they do not soften when temperatures are increased in finishing. Leathers can therefore be plated and embossed at high temperature without becoming tacky. In addition these binders can be used to provide a strong glazing effect. When used with acrylic, butadiene or polyurethane binders, the natural tackiness that these products exhibit is reduced. Protein binders withstand the hot iron test, but in order to enhance the fastness to wet rub, cross linking with formaldehyde or polyaziridine is required [2].

2.6.5. Colouring materials, Pigment Pastes and dye solutions

In leather finishing dry pigment colours (inorganic or organic), which are not miscible with water are normally dispersed using dispersing agents or with other vehicles like casein, plasticizers, wetting agents, preservative etc. The dry pigments are ground and dispersed using equipments like ball mill, cone mill, triple roll mill, or similar equipments. The vital properties required for leather pigment are; colour, strength of staining, hiding power, texture, absorption, fastness to light, fastness to heat and temperature and resistance in various media in which the pigment pastes are likely to come into contact (viz., alkali, acid, formaldehyde, solvent, etc.)

The quality of pigment paste depends upon the particle size and shape of original dry pigment colours and degree of dispersion besides the above-mentioned properties. Pigments are broadly divided into inorganic and organic. Inorganic pigments have better covering power than organic pigments. Pigment paste are marketed into two categories viz., pigment dispersed in finely divided form with dispersing agents and protective colloids containing no pronounced binders (casein free pigment pastes). The later type does not overload the grain surface and there is no encrustation of the pigment pastes which are known for their transparency and brilliancy are also marketed and these are both suitable for glazed and plated finishing. Though in general, organic pigments are known for their poor resistance to light, heat, temperature and alkali and give bronzy effect, selected pigments are used which are very handy in making aniline, semi aniline and special effects on opaque or covering finishes.

Tinting Strength of pigments

Tinting Strength is the amount of a colored pigment required to tint (color) a given weight of a white pigment to produce a given shade. Tinting strengths are always relative to a standard sample of the pigment under test, and for two samples of the same pigment, the tinting strength is a measure of the difference in particle size and distribution. Comparative tinting strengths of white pigments in a standard blue pigment show that the tinting strength of rutile titanium pigment exceeds that of all other listed pigments. The tinting strength of a pigment is independent of its hiding power. Relatively transparent pigments can have a high tinting strength.

Table 3 Type of pigment and their tinting strength

s/no	Type of pigments	Tinting strength
1	Rutile titanium pigment	1850
2	Anatase titanium pigment	1350
3	Zinc sulfide	900
4	Antimony oxide	400
5	Lithopone	300
6	Zinc oxide	200
7	White lead	100

Refractive Index of different pigments

When light falls on a pigmented paint film, part is reflected back whilst some enters the film. The light, which is reflected back, interacts with the pigment on the way back through the film. The black and strongly colour pigments absorb the light to obliterate any surface, whereas the white pigments Confer opacity solely by scattering of light.

Table 4 paint materials and their refractive indices values

Paint materials	Refractive index
Rutile titanium dioxide	2.76
Anatase titanium dioxide	2.55
Zinc sulphide	2.37
Antimony oxide	2.09
Zinc oxide	2.02
Basic lead carbonate	2.00
Basic lead sulphate	1.93
Barytes	1.64
Calcium sulfate (anhydrite)	1.59
Magnesium silicate	1.59
Calcium carbonate	1.57
China clay	1.56
Silica	1.55
Phenolic resins	1.55-1.68
Malamine resins	1.55-1.68
Urea-formaldehyde resins	1.55-1.60
Alkyd resins	1.50-1.60
Natural resins	1.50-1.55
China wood oil	1.52
Linseed oil	1.48
Soya bean oil	1.4

The higher the refractive indexes the more covering effect has been obtained. From the above table, titanium dioxide which is white pigment has superior covering property.

In protein finishes, only anionic dyestuffs can be used for brightening the aqueous finishes. Because of the opposite charge, basic dyes cannot be mixed with protein finishes as they may precipitate. As normal anionic dyestuffs contain additives, for finishing concentrated

dyestuffs are marketed and used. Metal complex dyes with special molecular structure which are soluble in solvents like alcohol, diacetone alcohol, dimethylformamide, oxitol are used not only for colouring lacquers but also sometimes in protein finish.

2.6.6. Wax Emulsions

Wax emulsions are one of the most important leather finishing materials. Popular waxes are carnauba wax, micro crystalline wax, montan wax, shellac wax, paraffin wax etc., and other modern synthetic waxes of different hardness. In leather finishing, waxes as emulsions are used as aqueous dispersing agents along with other finishing agents to improve what is known as waxy feel in the trade. Wax emulsions are particularly important in resin finishing helping release in hot plating. Leathers which are finishing based on acrylic polymers when plated at pressure and temperature have a tendency to stick to the plates. The use of wax emulsions (low melting waxes) in suitable quantities along with resin binders reduces the tendency to stick on to the plate due to the melting of the dispersed wax and releasing the leather from the plate. This plate releasing wax dispersions should be used in optimum quantities as if excess used in bottom coats may no longer adhere properly.

2.6.7. Feel Modifiers

Feel modifiers gives the final finished leathers an excellent touch, silky, smooth and also this place a major role in avoiding the removal of finish by tape test method, it also improves the dry and wet rub fastness. Feel modifiers have two way of touch one is slippery feel and other one is waxy feel there are two separate products which can be introduced according to the final product of the buyer's sample.

2.6.9. Nitro cellulose (N.C.) lacquers and lacquer emulsions

These auxiliaries are predominately used for the top surface coating of the already finished leathers (mostly polymer finished in order to make them glossy, remove tackiness and make water fast is resistant to dry and wet rubbing. In leather finishing normally nitrocellulose of viscosity 1/2 second to 20 seconds are used, to produce the effect desired on a specific type of leather. NC is not soluble in water but only in solvents.

Though NC lacquers give fastness and good gloss, they have a tendency to make the leather more artificial. A later development is the use of lacquer emulsion which is NC lacquer containing some amount of water. Lacquer emulsions are of two types (I) water dilutable lacquer emulsion and (ii) solvent dilutable lacquer emulsion. [31].

2.7 Pigment volume concentration (PVC).

Pigment volume concentration (PVC):- it is the ratio of total pigment volume to sum of pigment volume and resin binder volume .while calculating PVC for leather finishing the governing parameter will be total solid. Mostly of pigment have total solid around 40% except black pigment (20-30%) whereas for binder depending the type it will varies but most of them have solid content in between 24-40%.

The concept of pigment volume concentration (PVC) is defined as the percentage of pigment volume in the total volume solids of the paint.

$$PVC\% = \frac{\text{Volume of Pigment X100}}{\text{Volume of Pigment} + \text{Volume of Binder}}$$

In the above formula, since the amounts of the pigment and the binder are on volume basis, two finishing formulations can have an identical pigment-binder (wt %) ratio, but very different PVC values, simply by using pigments of different densities.

Maximum gloss and durability are achieved at low PVC, and maximum opacity at either moderate or very high PVC. The finish formulated with low PVC, shows an excess of binder present which results in a well bound film giving a high gloss level, and good chemical, water and abrasion resistance.

2.8. Properties of polymers used in leather finishing

Though there are vast number of synthetic resins used for coating purpose, but a very limited of them have usages in leather finishing. The synthetic resins which are used for leather can be broadly classified into two groups-(1) synthetic resins for aqueous leather finishes and (2) synthetic resins for non aqueous leather finishes. The resins for the first group should be either soluble in a suitable organic solvent so that the solution, after spraying and evaporation of solvent, produces a lacquer- like film on the leather surface. In both the aqueous and non-aqueous systems only those can be selected which fulfil certain requirements. The properties of resins for bottom coat are different from pigment coat. Similarly the resins for pigment coat and top coat differ significantly. But there are certain properties which are, more or less, common for resins of all the three coats mentioned above and few of them are mentioned below [1].

2.8.1 Softness and elongation

All resins used in leather finishing should be soft and extensible so that the films formed may stretch with the leather without cracking. The softness of course differs from coat to coat. The

resins for top coat are harder and less extensible than resins for intermediate/season coat. Similarly a resin for intermediate coat is harder and less extensible than resins of ground /bottom coat. But in comparison to resins used for coating metals, wood paper and textile, the resins for top coat of leather finishing are softer and more extensible.” this immediately eliminates a great number of well-known and widely used synthetic resins, such as phenol-formaldehyde, and urea formaldehyde resins, because they are too hard and lacking in stretch. To be suitable for leather finishing purpose, a resin must have stretchiness between 300 to 1000% according to its use in different coats. Most of the softer types of resin of stretchiness with this range produce tacky film of low tensile strength, low melting point, and poor resistance to abrasion [2].

2.8.2. Glass transition temperature (T_g)

Most of the resins behave differently at different temperatures. A resin may be hard, brittle and may not form a film at higher temperature. polymethyl acrylate, as for example, is brittle and does not form film at a temperature below 8⁰c. But above this temperature it is a soft and excellent film forming polymer. Thus the temperature at which an amorphous material like glass, high polymer etc. changes from a brittle, vitreous state to a plastic is called the glass transition temperature (T_g) of that material. Leather is used at the atmospheric pressure which may go as low as -10⁰c in cold countries like north of Canada, Russia, Alaska, south Argentina, etc. So the glass transition temperature for the resins, to be used for leather finishing must be lower than -10⁰c. Except (T_g) all other properties of methyl acrylate are suitable for preparing leather seasons for ground and intermediate coats, and so this polymer is copolymerized or grafted with polymer of butadiene whose (T_g) is as low as -85⁰c. Thus by copolymerization or by grafting the T_g of resin can be modified. When two or more different types of polymers are joined together, the process is called grafting, whereas in copolymerization two or more different types of monomer are polymerized. A grafted polymer of methyl acrylate and styrene will show properties of both methyl acrylate and styrene, but copolymer of methyl acrylate and styrene possesses different a resultant property [1].

Table 5 Approximate glass transition temperatures of some polymers

S/No	Type of polymer	Glass transition temperature, T _g ⁰ c
1	polyethylene	-125
2	Polydimethylsiloxane	-123

3	Polybutadiene	-85
4	Polyisobutylene	-70
5	Cis-1,4-poly isoprene	-70
6	Poly(n-butyl acrylate)	-54
7	Poly vinylidene fluoride	-39
8	Poly ethylene	-20
9	Poly propylene	-18
10	Polymethyl acrylate	8
11	Poly-n-butyl methacrylate	22
12	Poly vinyl acetate	30
13	Poly ethyl methacrylate	65
14	Polyvinyl chloride	82
15	Polyacrylonitrile	98
16	Poly styrene	100
17	Poly methyl methacrylate	105
18	Poly methacrylonitrile	120

Source:- S.S.Dutta , Introduction to principle of leather manufacture

2.8.3 Polymer emulsions for impregnation

Emulsions of smaller aqueous medium, these penetrate the leather surface instead of surface deposition. The object of this impregnation is to deposit the resin between the grain layer and corium thus strengthening the zone so as to overcome the tendency of loose grain and pipe break. To regulate the penetration, solvents and penetrators/drivers are used along with impregnating resins. Sometimes lubricating agents like sulphated oils are also used in small quantities depending upon the softness required.

2.8.4 Mechanism of film formation

The principal mechanisms by which binders form films are reaction with oxygen from the air (oxidation), evaporation of the solvent from the vehicle (solvent evaporation), or chemical cross linking (polymerization). The coating film attained by these mechanisms can be either thermoplastic or thermosetting. Thermoplastic materials deform and soften on exposure to heat. Thermoset materials do not deform and remain hard upon heat exposure. However, with both oxidation and most polymerization film-forming mechanisms, solvent evaporation occurs initially, followed by a subsequent chemical reaction consisting of either a reaction

with oxygen or chemical cross linking. Solvent evaporative coatings also are called thermoplastics because, when heated, they become plastic and can soften and deform. Oxidation and chemically cross linked coatings “set” and harden when cured; they do not soften or deform on heating and, therefore, are called thermosets [12].

The film produced from a top coating material should have transparency, toughness, light fastness, non-tacky nature and water-repellency. To determine these properties 10mm of the prepared emulsion diluted to double volume with water is poured into a rectangular glass plate and spread throughout the total area of the plate. The level of the plate is adjusted with spirit level so that the thickness of film will be uniform throughout. The liquid is dried to form film by drying overnight and further conditioned.

2.9. Technique of colour quantification in leather dyeing and finishing

The perception of colour can be very subjective and linked to the impression and perception of the individual, as the sensitivity of the eye being a very personal characteristic [15].

Colour can be quantified by using colour scanning instruments. It is characterized by CIE guide line, the colour difference ΔE , L^* indicates the lightness and a^* and b^* the chromaticity coordinates. Positive values of a^* Show the red direction, and negative values the green direction, whereas positive values of b^* show the yellow direction and negative values the blue direction. The centre is achromatic (i.e. neutral).

The ΔE value can be calculated as follows:

$$\Delta L = L_{sample} - L_{standard}$$

$$\Delta a = a_{sample} - a_{standard}$$

$$\Delta b = b_{sample} - b_{standard}$$

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

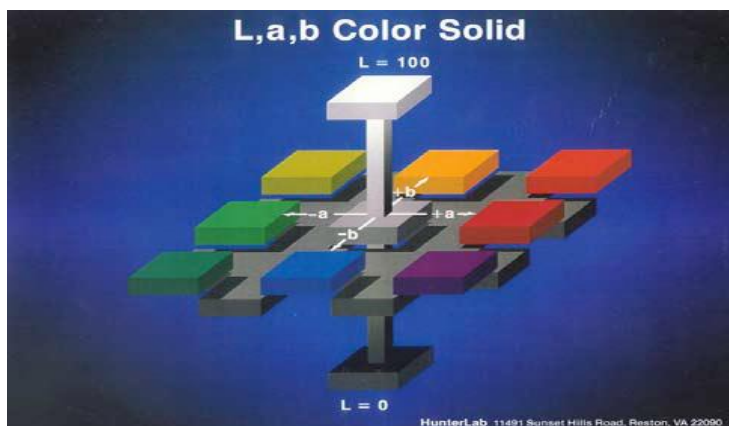


Figure 4 Representation of three dimensional colour space

Color forecasts for leather products vary depending upon the fashion demand and the colours for different products vary from one season to another. Even if finished leather is made with all the necessary sensory and functional properties needed for an end-use, it may be rejected if the colour is not matched to the buyer's sample/swatch. Hence, colour matching assumes great importance in leather dyeing and finishing.

Manual colour matching is very difficult job due to the usual trend in tannery for evaluating the new color developed is done by the team containing more than 3 or 4 leather technologists having several experience in color matching but the color perception differs from person to person so that the color matching work is usually tiresome. Nowadays computerized colorimetric instruments are available in the market which has simplified color matching process.

The delta E (ΔE) value is important parameter which determines how far the color of the sample is deviated from the standard or customer swatch. The smaller ΔE value indicates the less color variation against customer swatch. Therefore one has to calculate ΔE value to decide whether the given sample is closer in color to the customer sample or not. A dye is a coloured substance that imparts its own colour to the substrate with which it is chemically treated with. In contrast, the pigments, another class of colorants used in leather industry in finishing impart colour to the substrate not by chemical reactions but by superimposition and the colouration is restricted to the surface alone but with dyes we get diffusion (penetration) into the fibre matrix as well.

2.10. Commonly used mechanical operations in leather finishing modifying the surface of the leather

2.10.1 Embossing and plating of leather

Plating of leather during the course of finishing is an operation of fundamental importance as a guarantee of adhesion, good levelling of the film, and the final appearance and feel of the leather. General fastness also tends to increase considerably after heavy finishes are plated, because of the closed, continuous and compact layer that the thermoplastic film creates on the leather. Embossing on the other hand allows a suitable design to be impressed, giving character to an article or contributing towards the masking of defects in other cases.

Perfect embossing and good behaviour during plating are, however, always assisted by the presence in finishing coats of some polymeric resins, which also improve the final handle and do not affect adhesion of the subsequently sprayed coat. A final aspect to bear in mind is the

embossing of finishing coats with fine artificial grain which must resist lasting. In this case it is fundamental to use a suitable resin which is capable of retaining the embossed pattern permanently, even on splits [4].

2.10.2. Ironing

Hand ironing is still used certain types of leathers like kids, box calf etc, for removing the wrinkles and smoothening the surface. The hot iron flattens the grain gives a perfectly smooth surface. Weights of 12-20 kg., hand irons are used. They are electrically heated and temperature can be adjusted and maintained by thermostat[4].

2.10.3. Glazing

Finishes prepared based on protein binders (non thermoplastic) are usually glazed. Leathers, which are finished with (resin) binders being thermoplastic cannot be glazed but usually plated at temperature and pressure in hydraulic press. The coating of glazable lacquers should be even so that there is no polymer coated surface straight away coming into contact with glazing cylinder. Glazing machines differ only from one another in design (inclined or level bed). The glazing cylinder may be of glass or agate or steel. Agate is quite hard and gives very good gloss. Most of the reptile leathers are glazed in small glazing than other types of leathers. Too much fat on the grain does not produce gloss. It is also necessary that the leathers are dried well before glazing [4].

2.11 Water and Oil Repellence in the Finishing of Leathers

The demand for leathers with high water resistance has recently become even more pressing. This is particularly true for garment leathers which need to be protected from casual soaking and not be hardened after drying. An anti-soiling effect is also appreciated. Normally after tanning and post-tanning processes, water-resistant leathers have to be finished. A problem arises due to the scarce adhesion of normal finishing mixtures. Moreover, the products used for finishing must not damage the hydrophobic effect obtained during tanning operation.

The same problem is present when finishing water-proofing military shoes and sports shoes, as well as upholstery leathers, where water repellence is an important aspect of the article. These considerations leads us to treat leather water-proofing as a sole subject, regardless of the final article. Water repelling agents still find two large fields of application in leather finishing. The first is the finishing of very absorbent leathers, which have to retain a soft and natural appearance. If you use directly finishing products on these spongy and open leathers,

they may excessively penetrate into the cross-section leaving the leathers hard, wrinkled and not uniform, and more applications are necessary.

If you use a hydrophobic agent before starting the finishing, absorption can be controlled and reduced, the appearance will be more uniform and the final effect very natural.

2.12 Wet and Dry Rub Resistance of Finishing Coats

Finishing which is well-conducted according to the traditional rules provides for adequate protection and fixation of the finish, based on the fundamental principle of working with soft coats on the lower layers, progressively using harder coats until the final protective finish with the maximum degree of hardness. This procedure normally guarantees a good degree of general fastness resistance.

Frequently, however, fashion requirements oblige the finisher to create soft, light, unprotected coats, as a result of which it is much more difficult to achieve the required degree of resistance, and presupposes the careful selection of components and their technical application. A further, and frequent, cause of a reduction in general rub-resistance is the application of a feel-modifier as the final top coat. Such products are usually greasy substances which have the undesirable side-effect of plasticizing and softening the coat on which they are used.

The use of unsuitable organic pigments may be a further cause of poor final resistance, independent of the polymers and fixing agents used in formulating the coats. Some organic pigments are excessively soluble in solvent, or tend to bleed layer by layer until they reach the surface. Eliminating this problem is not easy, but a urethane-type water fixing agent may be useful as an isolator followed by a cellulose or vinyl coat sprayed very dry, if possible with several spray coats. The pigment pastes produced should be carefully evaluated from this point of view, and maximum degree of resistance possible with products of this type.

As a final consideration, it is wise to maintain the pigment volume concentration at the highest levels by using suitable binders which are polyurethane as far as possible, or at least comprising tenacious cross-linking polymers.

2.13. Factors that affect finish adhesion

The surface of the leather must have an absorption which the experienced technician may judge immediately to be correct or not, using effective and well known empirical methods. Scientifically absorptivity of leather can be checked by measuring contact angle using digital microscope which has camera mounted perpendicular to the test sample which have the size similar to microscopic slide where the drop of water is going to be applied. If the crust leather

is highly absorptive, the drop of water sinks immediately if not the liquid forms droplet on the surface of leather sample.

Crust leather which showed poor absorption effect has less wettability this in turn causes poor adhesion. That means the solid –liquid contact angle is higher. This is not recommended before applying the top coat so the binders used in base coat should have good wettability i.e. the water contact angle should be as low as possible.

The percentage humidity of the leather, if excessive, may render adhesion difficult. The ideal relative humidity is 13-15%. Leather which is too dry may also give rise to absorption difficulties, so it is always important to check relative humidity with particular care. When finishing leather with poor absorption - that is leather on which the finishing coat has poor wetting power - it may be necessary to degrease the surface of the leather in more serious cases, or more frequently, reduce, without however exceeding, the surface tension of the finishing solution by using polar solvents such as cellulose or alcohol with traces of surfactants.

An effective method of increasing the absorption of the polymers is to increase considerably the dry content in the finishing mixture. Generally, an increase in the binder/pigment relation tends to improve adhesion. It should be remembered that synthetic polymer emulsions with fine particles penetrate rapidly into the leather, whereas polymers dissolved in water, even if they have a slower penetration speed, tend to penetrate more deeply. The presence of excess soluble salts in the leather is sometimes a further cause of poor adhesion.

CHAPTER -3

MATERIALS AND METHODS

3.1. Introduction

In this chapter, the required materials and methods to study the effect of different binder and pigment in surface properties of finished leather were described. The chapter proceeds with the description of characteristics of different commercially available finishing chemicals used for the study. Several finish formulations were prepared to study the surface property of finished leather by varying binders and pigments alternatively and keeping other auxiliaries constant. Contact angle value for different solvents such as water, methyl iodide, DMSO and hexadecane were determined for the respective finish formulations by the help of optical microscope having digital camera mounted perpendicular to the test sample where the drop of solvents going to be applied. The detail procedure for preparation of sample in order to determine contact angle, and the design of the whole experiments were described. The experiments were also conducted to study the advantage and disadvantage of anionic and cationic finishing technique, the effect of pigment to binder ratio on the surface and physical properties of finished leather, film forming properties of different binders, effect of commonly used top coats on the surface of the leather and etc. In addition to this the procedure and methodology to conduct the entire physical tests were also explained.

3.2. Materials

Wet blue leather from goat skin and cow hides were made to be ready for post tanning operation by using conventional post tanning process techniques in order to produce dyed crust leather for finishing process. The leathers which have similar grades were selected for experimental work.

Different finishing chemicals, which are described in the table-3.1 and laboratory equipments and instruments (universal testing machine, contact angle measuring instrument, vamp flexing machine, water proofness machine, rub fastness testing machine, water vapour permeability tester, optical microscope, Lastometer, oven, glass wares and glass plates (for film formation) were used.

Table 6 the nature of finishing chemicals used in the experiment

s/no	Chemical name	Nature	remarks
1	B1 27047	Medium soft aqueous waxy protein binder	
2	B1 507	Soft protein binder	
3	BM 388-FO	Beauty maker	
4	LW 65416	Clear CAB lacquer water born, hard	
5	HM 51760	Handel modifier, aqueous modified silicon emulsion	
6	HM 51251	Water dilutable silicon emulsion	
7	RA 1216	Very hard acrylic binder	Tg= 53°C
8	B1 27154	Aqueous protein binder	
9	LS 65258	Clear NC lacquer solvent borne	
10	RA 17	Very soft acrylic binder	
11	RA 2354	Medium soft acrylic binder	Tg= -29°C
12	RA 27006	soft acrylic binder	
13	FI 50	Filler wax	
14	PP25824	pigment, brown	
15	PP25884	Pigment, red	
16	WT2586/13886	Water based pu top coat	
17	B1 1370	Aqueous protein binder	
18	XR79053	Water dilutable imine ester crosslinking agent	
19	HM183	Hand modifier, water dilutable silicon emulsion	
20	WT25853/13892	Dull waterborne aliphatic PU dispersion for producing high performance finishes	
21	WT13400	Clear high gloss waterborne acrylic co-polymer emulsion	
22	WR 22409	Water repellent,modified polyfluorocarbon emulsion	
23	Lepton aqua top TG	Water based top coat	

3.3. Methods

The methods used to reach at each specific objectives of this study are described in the following sub-titles.

3.3.1 Crust preparation

Thirty pieces of goat wet blue having similar size and grades were purchased from the market. The materials were sammed to remove the excess moisture content and to flatten the surface for subsequent mechanical and chemical operations. Since the materials were designed for production of dyed crust for shoe upper leather, it was shaved with a thickness of 1-1.2mm with strict control to maintain thickness uniformity. After thickness was adjusted, the re-tanning fat-liquoring and dyeing were conducted by conventional post tanning process for shoe upper production. Description of the process for post tanning operation is indicated at the back (annexure-1).

3.3.2. Finished upper leather preparation

Different finish formulations were prepared by varying concentration and type of pigment and binders alternatively fixing other ingredients constant. Types of Acrylic binders like very soft, soft and medium soft and polyurethane binders have been employed for a given pigment by varying binder concentration. In addition to this different formulation were prepared by using PU binders with or without cross linkers and using some performance chemicals. Finish formulation by using cationic chemicals were also prepared. The formulations were sprayed by using hand spraying machine on crust leather maximum of three coats. As described in the tables below, all the formulations were prepared at the same time and equal volume of the season was sprayed on crust leather having the same area. In all cases three coats were applied in between each coats, the leathers were allowed to be dried to avoid the quality inconsistency.

For anionic finishing technique, different commercially available acrylic resin binders, different PU top coats and cationic finishing chemicals were selected from stahl chemical company for whole experiments and one litre finish formulation were prepared at different p/b ratios by using each a single binder as well as combining the three binders at different p/b ratios. The three resin binders were chosen for experimental work based on their 'Tg' values and universal applicability.

Table 7 Finish formulation prepared by varying the concentration of very soft binder (RA-17)

Types of chemicals	Finish formulations					
	F1(in ml)	F2	F3	F4	F5	F6
Pigment	100	100	100	100	100	100
Filler Wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Resin binder	50	100	150	200	250	300
Water	790	740	660	640	590	540
Total	1000	1000	1000	1000	1000	1000

Table 8 Finish formulation prepared by varying the concentration of soft binder (RA27006)

Types of chemicals	Finish formulations					
	F7	F8	F9	F10	F11	F12
Pigment	100	100	100	100	100	100
Filler Wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Resin binder	50	100	150	200	250	300
Water	790	740	660	640	590	540
Total	1000	1000	1000	1000	1000	1000

Table 9 Finish formulation for base coats by varying the concentration of medium soft resin binder (RA-2354)

Types of chemicals	Finish formulations(gm)					
	F13	F14	F15	F16	F17	F18
Pigment	100	100	100	100	100	100
Filler Wax	30	30	30	30	30	30
Protein	30		30	30	30	30
Resin binder	50	100	150	200	250	300
Water	790	740	660	640	590	540
Total	1000	1000	1000	1000	1000	1000

Table 10 Finish formulation by using combination of acrylic binders

Types of chemicals	Finish formulations(gm)					
	F19	F20	F21	F22	F23	F24
Pigment	100	100	100	100	100	100
Vs- resin binder	25	25	25	50	50	50
S- resin binder	25	25	25	50	50	50
Ms- resin binder	50	75	100	150	200	250
Filler Wax	30	30	30	30	30	30
Protein	30	30	30	30	30	30
Water	740	615	660	640	590	540
Total	1000	1000	1000	1000	1000	1000

Note :VS- very soft, S- soft, MS- medium soft

Table 11 Base coat finish formulation for application of performance chemicals at the top coat.

A. Season formulation

Chemical name	Quantity(gm)	Remark
PP11832	50	3x plain plate before top coat
RA 1079	50	
RU3989	50	
FI50	20	
B ₁ 507	20	
WATER	150	

After applying the season based on the above formulation the leathers were allowed to dry and plain plated. To study the effect of PU top coats with cross-linker and PU top coat without cross linker and water repellence effect, the following formulations were prepared below.

Table 12 Different types of PU top coat formulations with cross-linker

Type of chemicals	Formulations(the quantity is in gram)					
	PUT1	PUT2	PUT3	PUT4	PUT5	PUT6
WT2586/13886	80	0	0	100	0	0
B1 1370	20	20	20	0	0	0
XR79053	2	2	2	2	2	2
HM183	3	3	3	3	3	3
WT25853/13892	0	80	0	0	100	0
WT13400	0	0	80	0	0	100
WATER	100	100	100	100	100	100

Table 13 Finish formulation prepared by using different PU top coats with speciality chemicals

Type of chemicals	Formulations(the quantity is in gram)					
	PUT1A	PUT2A	PUT3A	PUT4A	PUT5A	PUT6A
WT2586/13886	80	0	0	100	0	0
B1 1370	20	20	20	0	0	0
XR79053	2	2	2	2	2	2
HM183	3	3	3	3	3	3
WT25853/13892	0	80	0	0	100	0
WT13400	0	0	80	0	0	100
WR 22409	15	15	15	15	15	15
WATER	100	100	100	100	100	100

Table 14 Cationic finish formulations

chemicals	Finish formulations(quantity in grams)							
	Cat-1a		Cat-1b		Cat-2a		Cat-2b	
	SC	TC	SC	TC	SC	TC	SC	TC
PP 17732	25	-	25	-	50	-	50	-
BI 17737	100	-	100	-	100	-	100	-
RU 17702	50	-	50	-	50	-	50	-
FI 1292	25	-	25	-	-	-	-	-
FI 17701	25	-	25	-	75	-	75	-
LW65377	-	100	-	-	-	100	-	-
FI 77055	-	-	-	-	50	-	50	-
MA 27108	-	-	-	100	-	-	-	100
Water	500	100	500	100	650	100	650	100

Table 15 Experiment with butadiene

S.No	Chemicals	Experiment	control
	Pigment	100	100
	butadiene binder	200	200
	filler wax	-	30
	protein binder	-	30

Table 16 Film forming property of different binders

chemicals	Binder combinations									
	C1	C2	C4	C5	C6	Ac1	Ac2	Ac3	Ac4	Ac5
RA-1216	15	25	10	10	10	0	0	0	0	0
RA-27006	30	25	30	40	50	15	15	15	15	15
RA-2354						15	15	15	15	15
Ra-17						15	15	15	15	15
FI-50							10	10	10	10
B ₁ 27154								10	10	10
PP25824(IP)									15	0
PP25884(OP)										15

Note: the values are in grams

3.3. Finish film formation

Finish films were formed by combining soft and hard acrylic binders with and without protein binder, filler wax and pigments and the tensile strength were measured.

Finish films were formed by using the appropriate substrate for casting the formulations described in table 16. In this experiment glass plates having 25*15cm dimension were prepared and the calculated amount of formulations were poured on the required area and allowed to dry at 60⁰c. After the film were dried the film forming nature of acrylic and protein binders were studied. The dried films were used to determine, young's modulus, elongation, tensile strength and contact angle.

3.3.1 Finish film tensile strength determination

Glass plates having dimensions 25cm by 15cm have prepared and different binder combinations with known volume were poured uniformly and film forming nature of different binders and binder combinations were studied. The samples have allowed drying at room temperature for tensile strength measurement. After the films have dried the samples were prepared by cutting with 10mm width in the direction along the glass plate and across the glass plate. The thickness of the film sample is measured at five different points and the average value has taken for calculation. The tensile strength and percentage elongation have been tested by using Instron universal testing machine by setting the clip pressure of 3 bars and testing speed of 100mm/min for all samples.

$$\textit{tensile strength} = \textit{load/area}$$

$$\textit{where, Area} = \textit{width} \times \textit{thickness}$$

3.4. Adhesion of finish test /SATRA TM 411 sole bond test

This test is intended to determine the strength of finish adhesion to the leather surface. Force required pulling the leather away from its surface finish layer, the force being applied steadily at an angle of about 90⁰ to a rigid adherent plate to which the finished side of the leather has been bonded. The finished side of a strip of leather is bonded to a PVC plate by means of heat activated adhesive film. Force was applied to the free end of the strip to peel the leather from the finish over a distance and measured by using universal testing machine.

The tests were conducted for all the finish formulations described in table-7, 8, 9 and 10.

The apparatus used to conduct the experiment were universal tensile testing machine with 100±5mm/minute speed and force-distance recording facility, adherent plate holder with

provision to attach with tensile testing machine, hook link made of steel wire 1-2mm diameter and 25cm long for attaching the free end of leather specimen, IR lamp capable of heating the adherent plate up to 80°C , weight piece of mass 4.5 kgs to press the test sample for at least 12 hours and adherent plate comprising of hard 70 mm x 20 mm x 3 mm width PVC. For each experiment four leather samples were cut to 100 mm x 10 mm dimension from the leather, two from along direction and two from across direction. 2mm diameter hole was punched on either side of the test piece leaving 1cm from the edge and the surface was cleaned with petroleum ether. The PVC plates were slightly snuffed and PU adhesive (generally used for shoe sole attaching) was applied on each plate. After the plate was completely dried, the coated PU were activated by heating the plate with IR activator at 80°C and the finish side of the leather strip were immediately placed on the adhesive side of the plate leaving 10mm freely on the either side of the plate. All the test specimens were cured for 4 hours prior to operating the anistron machine. The test specimen was attached on the machine with help of sample holding jigs. And the machine was adjusted based on the standard. Finally the average force versus distance graph and also type of failure observed during the test were recorded. The experiment was repeated for the remaining three samples. For wet finish adhesion test, the half tested samples were immersed in distilled water for an hour and similar procedure was followed and the result was recorded.

3.5. Flexing endurance of finished leathers: SATRA 25:1992/BALLY TM 55

Flexing endurance is one of the wear properties of leather. If leather surface coating (finish) is not properly applied with correct proportions and following all technical procedures, the finish surface upon bending repeatedly develops cracks, flaking, brittle and delamination.

For all the finish formulations prepared by varying the concentration and type of resin binder, both wet and dry flexing endurance test were conducted. The tests were performed by the machine called vamp flexing machine. In performing the test first the test specimens were folded along the longer sides so that the finish side facing inward and one end of the folded specimen were clamped in upper clamp and the other end was clamped on lower clamp. The tests were conducted based on the above standard. For dry flexing test, the test specimens were flexed for 10,000 and 500,000 flexes and the finish damage were observed by magnifying glass and the type of damage were recorded. For wet flexing endurance test, first the test specimen was gently immersed in to water for approximately 30 seconds prior to clamping it on to the machine. The test specimen was clamped on to the machine in similar way to that of dry flexing but the number of flexing was adjusted for 10000 and 100000

flexes based on the above standard and the finish damage observed were assessed experienced expert with help of magnifying glass and the type of damage were recorded.

3.6 Color fastness to circular rubbing – SATRA TM 8:1992

i. Dry Rub Test

The test specimen was cut about 75mm square from the finished leather. And the specimen was placed on the horizontal platform and a felt pad was secured on the spindle and brought in contact with the test specimen. The weight was adjusted to $24.5 \pm 0.5\text{N}$ and the machine was operated for 512 revolutions. After the required revolutions were completed, the leather and the felt pad were removed from the machine. To assess the colour change and transfer of colour (degree of staining) standard grey scales were used. The number of cycles and the colour change and colour transfer depend up on the type of leather and customer's requirement.

ii. Wet Rub Test

Clean white felt pad was immersed in cold water and boiled until all the felts are completely wetted. After complete wetting, the felts were allowed to be cooled. The felts were removed one by one and excess water was slightly squeezed out prior to attaching it to spindle. The loads were adjusted to 7.1N forces. The spindle was brought into contact with leather specimen for 60 seconds and the machine was allowed to operate for 256 cycles and the colour change and colour transfer form test piece to felt pad was assessed based on the grey scale.

3.7. Water vapour permeability— ISO 14268/IUP15/EN 20344

Water vapour permeability is the unique property of leather. Under normal conditions about 5 grams/ hour sweat is produced by a human when the atmospheric condition is between 30–35°C. Under industrial working condition, the sweat produced by a human foot is around 10 gram/hour. This sweat has to be sent out to the outside of the shoe for comfort wear. Leather footwear has the ability to absorb the sweat produced and transmit to the upper part of the leather through wicking process. Once it reaches the upper surface, the sweat evaporates into atmosphere. This process is known as Water vapour permeability or water vapour transmission. This is possible by the porosity characteristic of leather. Filling, finishing and fat liquoring processes in leather making reduces this water vapour transmission property to a greater extent.

Based on the above standards

Water vapour permeability (wvp), $\text{mg}/\text{cm}^2/\text{hr}$ is equal to:

$$W_{vp} = \frac{7.640 \times w}{d \times d \times t}$$

Where, w is the mass difference in mg

$$W = w_1 - w_0$$

W₀ is initial mass of the leather and the dried silica jells.

W₁ is the final masses after the moisture from the leather is transmitted to silica jell within 8 hrs.

d is the diameter of the leather sample in mm

t is the time in taken for moisture transmission form water to silica jell

3.8. Determination of water resistant property, SATRA/ STM 606D

A test piece were formed into the shape of a trough and flexed whilst partially immersed in water. The time taken for water to penetrate through the test piece is measured. The method also allows the percentage mass of water absorbed and the mass of water transmitted through the test piece to be determined. In addition to this the time taken for penetration of water through the cross-section was determined. In this experiment percentage water absorption and the time taken for water to penetrate to the cross-section were determined for shoe upper leather finished with different PU based binder combinations and cationic binders.

3.9 Determination of contact angle

Contact angle is very important technique to understand wettability of polymeric surface up on different polar solvents and non polar solvents. Three solvents are usually used for contact angle measurements which are water (highly polar), DMSO (moderately polar) and hexadecane (non polar).The contact angle values will vary based on the type of coating when a drop of these solvents are applied on the surface of finished leather by using micropipette, the drop position were adjusted, and the contact angle picture were taken by using the camera which is mounted on the microscope. For all the contact angle measurement, the following instruments were used.



Figure 5 contact angle instrument

3.9.1. Contact angle for the crust leather

The crust sample was cut into appropriate rectangular shape with size similar to microscopic slide with dimension of 3cm by 1cm. The contact angle for the dyed crust leather was measured with the help of contact angle measuring instrument described in fig 5. By using three different solvents highly polar (water), medium polar (methyl iodide) and completely non-polar (hexadecane) contact angle value were measured and recorded

3.9.2. Determination of contact angle for binders

Different binders were coated on microscopic slid and allowed to dry completely in the desiccators. After the coating has dried, the contact angle was determined by the help of the instrument described above similarly three different solvents were used i.e. water, hexadecane and methyl iodide and the values were recorded.

3.9.3. Determination of contact angle for finish formulations

Different finish formulations were prepared and applied on crust leather by using hand spray technique and the samples have prepared similarly and the contact angle have been determined similarly with the above solvents and the values have noted.

3.10 Surface energy calculation

By using young's equation, the surface energy of any solids can be calculated from the contact angle value.

Surface energy of chrome crust leather can be calculated as follows

$$\gamma_{lv}(1 + \cos\theta) = 2[\sqrt{\gamma_{sv^d}\gamma_{lv^d}} + \sqrt{\gamma_{sv^p}\gamma_{lv^p}}] \text{-----} (3.1)$$

Where θ = contact angle

γ_{lv} =liquid- vapour surface energy

γ_{sv^d} =solid- vapour interfacial energy of non polar component

γ_{lv^d} =liquid- vapour interfacial tension of non polar solvent

γ_{sv^p} =solid- vapour interfacial energy of polar component

γ_{lv^p} =Liquid- vapour interfacial energy of polar component

In this experiment, two liquids were used to calculate the polar and non-polar component of surface energy, water and hexadecane respectively.

In order to calculate Non polar component of surface energy, the polar component in equation [3.1] will vanished and the equation will be reduced to the form:

$$\gamma_{lv}(1 + \cos\theta) = 2[\sqrt{\gamma_{sv}^d \gamma_{lv}^d}] \quad (3.2)$$

By rearranging terms, the non polar component of surface energy, γ_{sv}^d can be expressed as

$$\gamma_{sv}^d = \frac{\gamma_{lv}(1+\cos\theta)^2}{4} \quad (3.3)$$

Where, θ is contact angle

For hexadecane, $\gamma_{lv} = 27.47\text{mN/m}$

Hence, equation [3.3] reduced to

$$\gamma_{sv}^d = \frac{27.47(1+\cos\theta)^2}{4} \quad (3.4)$$

By combining equations [3.3] and [3.4], the polar component of surface energy, γ_{sv}^p can be calculated as follows:

$$\gamma_{sv}^p = \frac{[\frac{\gamma_{lv}(1+\cos\theta)}{2} - 2\sqrt{\gamma_{sv}^d \gamma_{lv}^d}]^2}{\gamma_{lv}^p} \quad (3.5)$$

Where,

θ = contact angle

γ_{lv} = total surface tension of liquid

γ_{lv}^d = non polar component of surface tension Value for a given liquid

γ_{lv}^p = polar component of surface tension for a given liquid

For water, the total, polar and non polar surface tension values are given in literature these are:

$$\gamma_{lv} = 72.8\text{mN/m}$$

$$\gamma_{lv}^d = 21.8\text{mN/m}$$

$$\gamma_{lv}^p = 51\text{mN/m}$$

By substituting the above surface tension values for water and non polar component of surface energy value, γ_{sv}^d obtained by using equation [3.4], the polar component of surface energy for the given solid material i.e. leather can be calculated and equation [3.5] can be reduced to:

$$\gamma_{sv}^p = \frac{[\frac{72.8(1+\cos\theta)}{2} - 2\sqrt{\gamma_{sv}^d * 21.8}]^2}{51} \quad (3.6)$$

Here, $\cos\theta$ value will vary based on the water contact angle, θ and γ_{sv}^d depend on the hexadecane contact angle value, θ

Therefore it is possible to calculate the polar and non polar component of surface energy values by using equation [3.6] and [3.4] respectively.

And the total surface energy, γ_{sv} will be the sum of polar and non polar components, i.e.

$$\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p \text{-----} (3.7)$$

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

A similar comparison can be made by considering the Van Oss, Chaudhury and Good (OCG) model [13] in which the solid/liquid work of adhesion is expressed as a sum of three terms:

In these approach, the polar component of surface energy, γ_{sv}^p is expressed in the form of two components i.e. Lewis acid and Lewis base (γ_{s^+} and γ_{s^-}) parameters respectively. To calculate these values in these experiments, three liquids such as water, hexadecane and dimethyl sulfoxide (DMSO) were used.

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_{s^+}\gamma_l^-} + 2\sqrt{\gamma_{s^-}\gamma_l^+} \text{-----}(3.8)$$

Where θ = contact angle

γ_{lv} =liquid- vapour surface energy

γ_s^{LW} = the Lifshitz–van der Waals (non-polar) component of the surface free energy

γ_{s^+} and γ_{s^-} = the Lewis acid parameter and the Lewis base parameter, respectively.

From the contact angles of at least three liquids of known surface tension parameters ($\gamma_L, \gamma_s^{LW}/\gamma_{sv}^d, \gamma_l^+$ and γ_l^-) equation (3.8) can be used to determine the van Oss, Chaudhury and Good parameters for the surface free energy of the solid.

Thus, by considering three polar liquids, it is theoretically possible to determine the Lifshitz–Van Der Waals (non-polar) component, γ_s^{LW} of the surface free energy of polymers. This result can be compared to the value obtained with the equation (3.2)

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_s^{LW}\gamma_L^{LW}} \text{-----} (3.9)$$

Equation (3.2) can be used for determination of non- polar component of surface energy by using the contact angle of non polar liquids such as hexadecane, di-iodomethane, α -bromonaphthalene and etc. In this paper contact angle and surface tension values of water and DMSO were used as polar liquids. By using these values it is possible to determine the Lewis acid and Lewis base parameters of surface energy of the given liquid this in turn help to know the charge characteristics of the surface of the given finished leather [13].and it can be expressed as a square root of geometric mean of the Lewis acid(γ_{s^+} and Lewis base (γ_{s^-}) parameters [1].

Mathematically;

$$\gamma_{sv}^p = 2\sqrt{\gamma_{s^+}\gamma_{s^-}} \text{-----} (3.10)$$

CHAPTER-4

RESULTS AND DISCUSSION

4.1. Determination of contact angle and surface energy

4.1.1 Contact angle and surface energy value for dyed crust and different finish formulations.

The crust sample was cut into appropriate rectangular shape with size similar to microscopic slide i.e. 3cm by 1cm. The contact angle for the dyed crust was measured with the help of contact angle measuring instrument which is microscope where digital camera is mounted on it to take the droplet pictures on the test specimen. Three different solvents highly polar (water), less polar (methyl iodide) and completely non-polar (hexadecane) have chosen and the values were described as follows:-

Table 17 Contact angle values for crust leather for shoe upper (black)

Sample no.	contact angle values			Remarks
	WCA	MICA	HDCA	
B1	69.01	ND	ND	In each cases one drop of the solvents
B2	80.69	ND	ND	

B3	80.66	ND	ND	(approximately 5µl) were applied
B4	66.02	ND	ND	
B5	85.61	ND	ND	
B6	73.47	ND	ND	
B7	78.12	ND	ND	
B8	83.59	ND	ND	
B9	62.43	ND	ND	
Average	75.51	-	-	

ND=not detectable

From table 17 one can conclude that the surface contact angle with less polar solvent (methyl-iodide) and non polar solvent (hexadecane) for the crust leather is negligible i.e. the drop of the liquid was spontaneously dispersed on the surface of the leather this might be due to the imbalance between the solid – liquid interfacial energy and the cohesive force of the molecules of the solvents. But in the case of water the contact angle is approximately more than 75⁰C which is indication of hydrophobic nature of the given leather. The cohesive force which is due to the interaction of the molecules of water /surface tension of water is more than the solid- liquid (leather surface /water) interaction. Therefore the molecule of water tends to form droplets rather than spontaneously spreading as it was observed in the case of methyl iodide and hexadecane. The higher value of the contact angle indicates the slower wettability of the surface by respective liquids in contact with the surface.

By using equation [3.1], it is possible to determine the surface energy of crust leather and finished leather finished with different finish formulations as follows. As it has described in table-17 above, the average value of contact angle for the crust leather is 75.51 in degrees. By using equation [3.1], it is possible to calculate polar and non polar components of surface energy and hence total surface energy. For the surface energy calculation, contact angle for water and hexadecane were used.

Surface energy calculation for two liquid systems.

Consider the contact angle for hexadecane to be zero and for water to be 75.51⁰

Θ of water=75.51⁰

Θ of hexadecane=0⁰

γ_{lv} for water=72.8mN/m

γ_{lv} for hexadecane= 27.47mN/m

It is possible to calculate the total surface energy by using equation (3.1) as follows:

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

In the case of hexadecane, the polar component will be vanished because it is highly non-polar substance, therefore;

The above equation becomes:

$$\begin{aligned} \gamma lv(1 + \cos\theta) &= 2[\sqrt{\gamma sv^d \gamma lv^d}] \\ 27.47\text{mN/m} (1+\cos 0) &= 2[\sqrt{\gamma sv^d * 27.47\text{mN/m}}] \end{aligned}$$

By rearranging the values

$$\gamma sv^d = 27.47\text{m N/m}$$

In similar way, the polar component of surface energy (γsv^p) can be calculated, by considering the contact angle value of water and its polar and non polar component of surface tension values as follows:-

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

By substituting the values

$$72.8\text{mN/m}(1 + \cos 75.81) = 2[\sqrt{\frac{27.47\text{mN}}{m} * \frac{21.8\text{mN}}{m}} + \sqrt{\gamma sv^p * 51\text{mN/m}}]$$

By rearranging terms, the polar component of surface energy will be:-

$$\gamma sv^p = 8.53\text{m N/m}$$

From the polar (γsv^p) and non polar (γsv^d) component of surface energy values one can see that there is inverse relationship between surface energy and contact angle i.e. the higher contact angle the smaller the surface energy and vice versa.

The total surface energy of the solid material (crust leather) is the sum of polar and non polar components.

$$\gamma sv = \gamma sv^p + \gamma sv^d = 8.53\text{m N/m} + 27.47\text{m N/m} = 36\text{m N/m}$$

The above surface energy value is the specific for the particular crust leather taken for the control. The magnitude will vary based on the type of re-tanning and fat-liquoring chemicals used. Any surface treatments like coating and different mechanical operations have significant influence on the surface energy value.



Figure 6 water contact angle values on crust leather

Effect of different leather finishing chemicals like binders, pigments, fillers, waxes, top coats and feel modifiers have significant influence on the magnitude of surface energy values. It has been observed that the surface energy parameter value was reduced by finishing the given crust leather by the help of different pigments and binder combinations and other leather finishing ingredients. By using the contact angle value of hexadecane and water with the finished leather the surface energy for each binder pigment combinations applied on the surface of leather, individual binders coated and dried on the microscopic slide and different finish films have been calculated in similar fashion described above and the results are shown in the following tables.

Table 18 Contact angle value for each binders coated on microscopic slide and the corresponding surface energy values

S.No	Chemical name	Contact angle value for different types of solvents			Surface energy (m N/m)		
		Θ of Water(w)	Θ of Methyl iodide(mi)	Θ of Hexadecane(hd)	γ_{sv}^d	γ_{sv}^p	γ_{sv}
1	B1 27047	52.273	49.126	17.416	26.23	17.00	43.23
2	B1 507	35.788	46.536	12.54	26.82	34.18	61.00
7	RA 1216	87.753	26.787	20.54	25.75	3.93	28.69
8	B1 27154	15.420	37.316	25.826	24.80	45.63	70.43
10	RA 17	64.963	25.305	10.92	26.98	9.16	41.27
11	RA 2354	60.234	50.598	8.65	27.16	17.83	44.99
12	RA 27006	63.888	57.298	7.80	27.22	15.46	42.68

The contact angle value for the above binders showed that hard binders like RA-1216 have higher contact angle value. Such kinds of binders are not suitable to use at the base coat and also cannot be used as universal binder with respect to film forming property of view. It was observed that such binder cannot form a film at room temperature (see fig 10c). Because the glass transition temperature, T_g (the temperature above which the polymer forms a film) is higher than the room temperature.

RA-2354, RA-27006 and RA-17 can be used in base coat since they have lower contact angle value compared to RA-1216. And hence the surface of the leather before applying the top coat is easily wettable. But if they are used at the top coat the surface of the leather can be easily affected by different soiling agents such as dust, dirt, fats and oils because of their tackiness.

The wettability of the surface of leather has to be good before applying the top coat otherwise the top coat cannot adhere to the surface of the leather whenever such hard binder is used at the base coat in larger proportion. Resin binders having lower water contact angle are ideal for base coat since they can easily spread on the surface of the leather this in turn facilitates degree of adhesion.

4.1.2 Contact angle and surface energy values for different finish films.

Finish films prepared on glass plates with dimension 25cm by 15cm were cut into a dimension equivalent to microscopic slide i.e. 3cm by 1cm and the contact angle value were determined in a similar way by using the microscope. Similarly from contact angle values the corresponding surface energy values were calculated. One can easily deduce that the surface energy is inversely proportional to the contact angle/wetting angle.

Table 19 contact angle values for the finish films

Binder combinations	Type of solvents			Surface energy(m N/m)		
	Θ of water	Θ of Methyl iodide	Θ of Hexadecane	γ_{sv}^d	γ_{sv}^p	γ_{sv}
C1	49.27	38.351	11.12	26.96	25.30	52.26
C4	33.92	28.52	14.24	26.33	35.44	62.08
C5	29.25	25.87	12.38	26.84	37.92	64.76
C6	39.29	26.02	10.62	27.00	31.88	58.88
Ac1	29.33	29.72	29.55	24.02	40.16	64.18
Ac2	53.29	36.87	9.37	27.10	37.67	64.77
Ac3	55.94	51.68	33.92	23.00	23.57	46.57
Ac4	40.10	37.71	32.467	23.35	34.08	57.43
Ac5	42.61	37.85	14.24	26.63	29.98	56.62

The above results on the table 19 show that the contact angle value is less than 90° for all formulations which is ideal for application of the formulation at the base coat. From the surface energy value one can deduce that the finish film created by using formulation AC3 indicate lower surface energy and film formed C4, C5 and AC2 showed higher surface energy which provides better adhesion effect if it is used at the bottom coat where as if these formulations are used at the top coat the performance of finish such as fastness, flexing endurance, water resistance etc. to be poor and the surface will be more tacky. Therefore the finish formulation used at the bottom coat should have higher surface energy where as finish formulation used at the top coat should have lower surface energy.

4.1.3. Physical and strength properties of finish films created by different resin binders.

From the graph below the strength property and the flexibility of the finish film were varied when hard binder is incorporated into the finish mix. Young's modulus (which indicates the degree of stiffness) has declined dramatically when the amount of soft binder increases this indicates that the flexibility of the finish film increases as the proportion of soft binder increases. In fig 7 below maximum young's modulus were observed in the case of finish film, C1 which were made by using more proportion of hard binders as compared with the remaining finish films. This shows that hard binders reduce the flexibility of films. Films formed by soft acrylic binders AC2, AC3, AC4 and AC5 have higher ME values than that of C1, C4, C5 and C6. the ME value clearly shows the flexibility of the films. In addition to this, the maximum load, ML was observed in the case of films formed by incorporation of hard binder in the given soft binder.

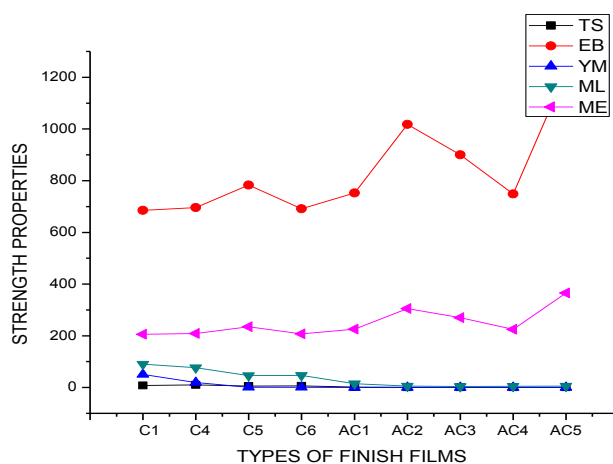


Figure 7 strength properties of films formed by combination of hard and soft resin binders and protein binders.

Properties of finish film formed by protein binders

The films formed by protein binder were observed to be discontinuous and less flexible in nature. And the elasticity was observed to be very less compared to acrylic binders. And the colour of the film was yellowish in nature and also the clarity was very less i.e. not transparent like acrylic binders. Acrylic binders have superior clarity (see fig 10c). The Young's modulus in the case of protein binders is more than that of resin binders. In addition to this when hard binder is added to soft binder the Young's modulus was increased significantly

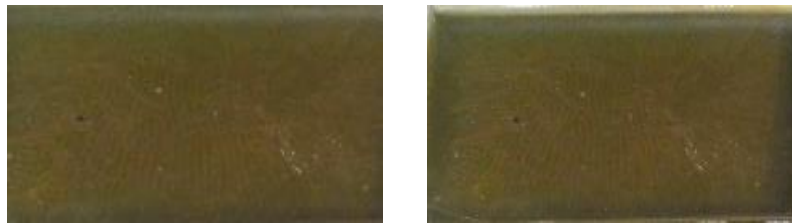


Figure 8 Films created by protein binder

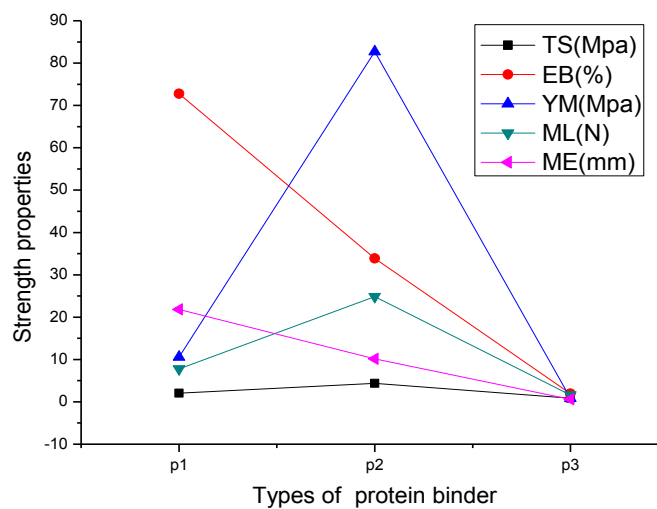


Figure 9 strength properties of different protein binders

(Note: TS=tensile strength (Mpa), EB=%extension at break), YM= Young's Modulus (Mpa), ML=Maximum load (N), ME=Maximum extension (mm), P₁= B1 27154, P₂= B1507 and P₃= B1 27047

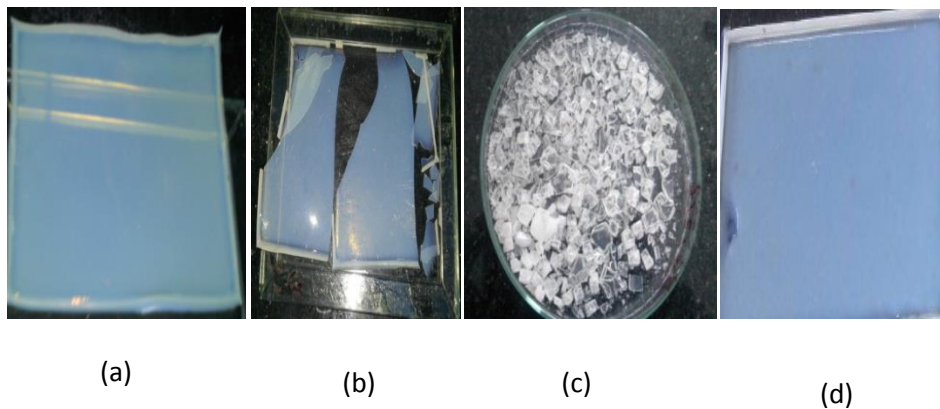
As it has indicated in the above graph, the three protein binders have different strength properties. Protein binder, P₂ shows maximum Young's Modulus that means the film formed by such kind of binder is stiffer than that of the film formed by P₁ and P₃. Since the protein binder P₃ shows least Young's Modulus value this might be due to incorporation of some

chemicals which have the properties that can modify the binder in order to increase its flexibility. ME value is very high in the case of acrylic binders (see fig 7) as compared to protein binders indicated in fig 9. ME value is directly related to the flexibility of the film therefore it has been observed that the flexibility of protein binders is very less compared to the acrylic binders.

In the fig10 (C) below hard binder, RA-1216 cannot form continuous and flexible film but it can be used together with very soft acrylic binders since it has the ability to reduce the tackiness effect so Such binder cannot be used as sole binder in resin finishing but rarely used to make crackle finished leathers from lower grade raw material for up-gradation.

Figure 10 Finish films prepared by acrylic resin

(a)hard binder with soft at 1:2 ratio, (b) hard binder with soft at 1:1 ratio, (c) film formed by only hard acrylic binder(d) hard binder with soft at 1:3 ratio.



From the above pictures we can easily observe that as the concentration of hard binder increases, the film becomes brittle and its elasticity and softness decreases. This property significantly affects the property of the final leather to be produced. Therefore it is mandatory to choose the right binders based on the flexibility and softness of the final product. That means for leathers which require superior flexibility and stretchiness like garment and gloves, soft and very soft binders have to be used in larger proportion and for shoe upper leathers and other heavy leathers, medium soft binders are ideal.

4.1.4. Contact angle (CA) and surface energy (SE) values for different pigment acrylic binder combinations.

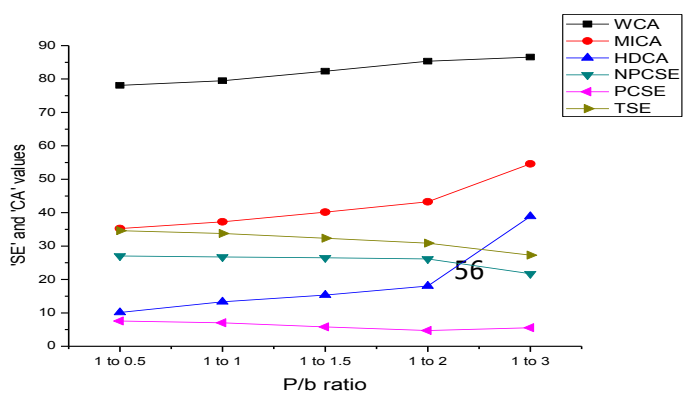


Figure 11 contact angle and corresponding surface energy values versus p/b ratios for acrylic binder (RA-17, RA-27006 and RA-2354) combinations

(Note: SE= Surface energy, CA= contact angle, WCA= water contact angle, MICA= methyl iodide contact angle, HDCA=hexadecane contact angle, NPCSE= Non polar component of surface energy, PCSE=polar component of surface energy and TSE= total component of surface energy).

From the graph it is clear that the water contact angle is higher than that of methyl iodide contact angle this is because of the higher surface tension of water compared to the substrate surface free energy(finished leather surface). In general the contact angle values show gradual increments when the p/b ratio increases whereas the surface energy values are gradually declining. The graph shows the maximum water contact angle and minimum surface energy of 86.56° and 20.33mN/m at p/b ratio of 1 to 3 respectively.

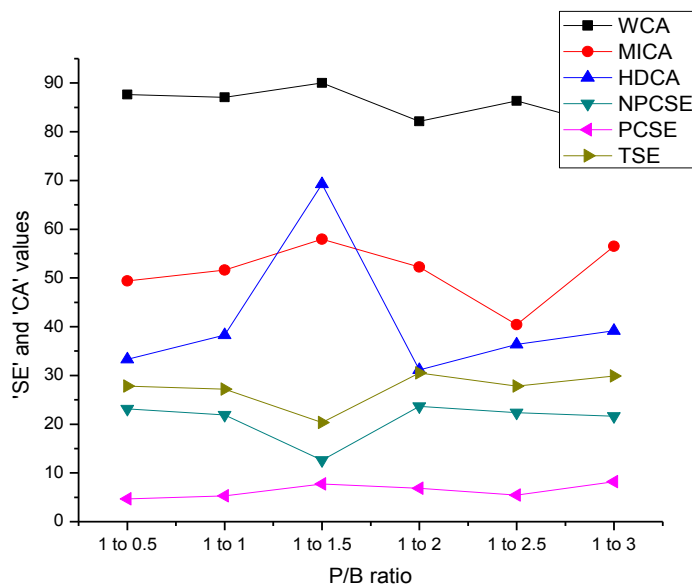


Figure 12 contact angle and surface energies for very soft resin binder (RA-17)

From the fig 12 it is evident that maximum contact angle value and minimum total surface energy was observed at p/b ratio of 1:1.5 and the PCSE does not show significant change as the ratio of p/b ratio varies. At p/b ratio of 1 to 0.5 and 1 to 1 higher NPCSE was observed.

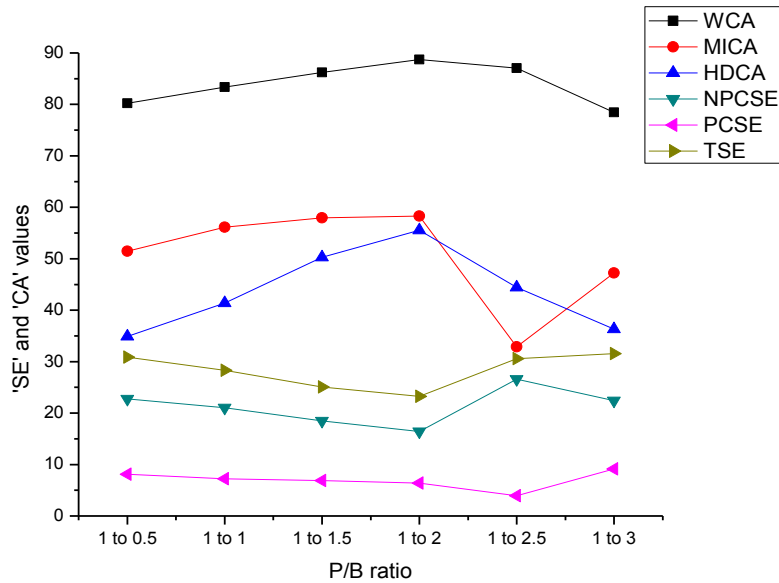


Figure 13 contact angle and surface energies for soft resin binder (RA-27006)

From the graph 13 it is clear that as the contact angle value increases the surface energy value decreases. Smaller surface energy values and higher contact angle (WCA, MICA and HDCA) values were observed at P/B ratio of 1 to 2. These values indicate that the surface of the finished leather is less wettable at this ratio because the higher the contact angle the surface of the solid is difficult to be wetted. And the graph shows that when the binder concentration increases beyond the limit the water contact angle value was observed to be decreased because the hydrophilic nature of the binder this in turn affect surface of finished leather i.e. the surface was appeared to be plastic, tacky and has poor fastness value.

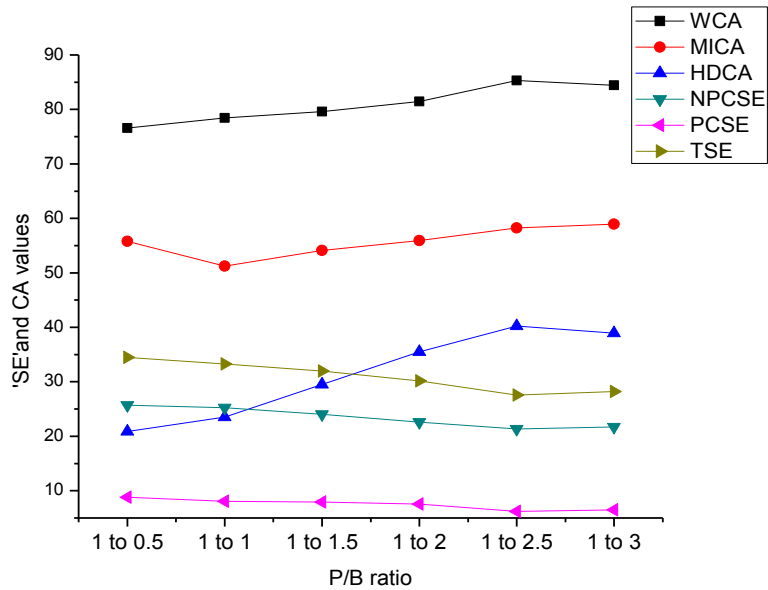


Figure 14 plot of contact angle and surface energy values versus P/B ratios for medium soft resin binder. (RA-2354).

From the graph in fig 14 higher contact angles and lower surface energy values were observed at P/B ratio of 1 to 2.5. This is the optimum value to get better finishing effect. That means at this ratio better fastness, flexing endurance and other surface properties were observed. It was also shown in the above graph that the contact angle value increases as the ratio of p/b increases up to ratio of 1 to 2.5 and beyond this value it starts to decrease gradually. But the total surface energy value was high at lower concentration of binder up to certain limit and then starts increasing. This result is better indication for a finishing technician in deciding the quantity of soft binder to be used.

Table 20 contact angle values for finished leather made by acrylic and PU binder combinations in base coat.

Specimen	Type of solvents			surface energy		
	Θ of Water	Θ of methyl iodide	Θ of Hexadecane	γ_{sv}^d	γ_{sv}^p	γ_{sv}
1	77.02	41.52	11.62	26.91	8.14	35.5
2	82.11	47.74	12.93	26.78	5.84	32.62

3	78.87	34.94	11.31	26.94	34.18	34.18
4	73.89	50.60	11.25	26.95	9.74	36.68
5	76.50	48.54	9.07	27.13	8.32	35.45
6	76.36	47.98	10.50	27.01	8.43	35.45
Average	77.46	45.22	11.11	26.6	7.91	34.87

Table 21 Effect of cationic oil ground on contact angle value

Specimen	Type of solvents			surface energy		
	Θ of Water	Θ of methyl iodide	Θ of Hexadecane	γ_{sv}^d	γ_{sv}^p	γ_{sv}
1	98.51	46.95	63.15	14.48	3.46	17.94
2	98.48	55.43	63.16	14.48	3.47	17.95
3	104.48	55.69	70.62	12.19	2.38	14.58
Average	100.51	52.69	65.64	3.71	3.06	16.75

From table 21 it is evident that the contact angle value is increased because of the oil ground used at the very beginning of the finishing operation. This hinders the excessive sinking of finishing season whenever the absorptive nature of leather is very high this in turn reduces the wettability of the surface. This technique is applicable whenever there is excessive sinking of finishing chemicals if the crust leather is too absorptive which can affect the natural look of the leather to be finished. The amount of oil ground used has to be optimum i.e. 100-150gram per 1000ml of Sealing coat mixture. If it is beyond this range there might be poor adhesion of the season since the water contact angle will be much far from 90°. Therefore the finishing technician has to control excessive use of oil ground.

4.1.5 Effect of number of base coats and use of CAB top coat on surface energy and contact angle value.

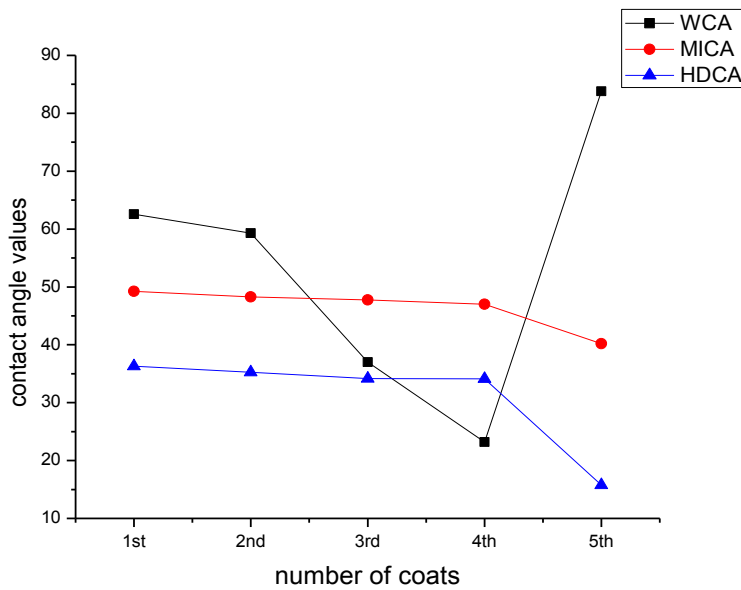


Figure 15 plot of number of coats versus contact angle values.

(Note: 1ST, 2nd, 3RD and 4th coats are base coats and the 5th coat is top coat with water based CAB lacquer).

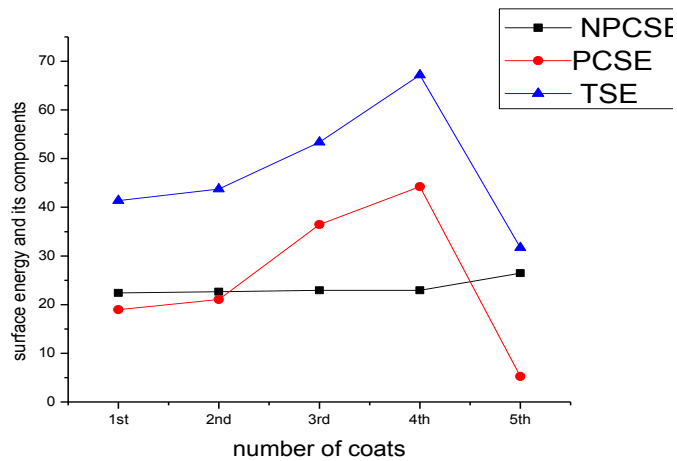


Figure 16 plot of number of finish coats VS Surface energy and its components.

In fig 15 and 16 the contact angle value and surface energy showed inverse relationship that means the higher contact angle the lower surface free energy and as the number of coat increases the surface energy also increased initially and decreased sharply when the top coat was sprayed and the water contact angle value also start slowly decreasing and then showed

sharp increase after the forth coat but the change in contact angle value for methyl iodide and hexadecane was not as high as compared to water contact angle. Because all the finishing chemicals used are water based and have polar groups, the change in water contact angle value is high during the coating process.

Table 22 contact angle value for cow crust

Specimen	Type of solvents		
	Water	Methyl iodide	Hexadecane
1cow	74.196	ND	ND
2cow	76.358	ND	ND
3cow	76.739	ND	ND
Average	75.764	ND	ND

Similar to goat crust leather described above the contact angle value in the case of hexadecane and methyl iodide cannot be detected because the droplet was spontaneously dispersed into the surface of the leather this because the solid –vapour interfacial energy is more than the surface tension of the liquid molecules i.e. the cohesive force within the liquid molecules is less than the surface energy of the solid material which is the crust leather. Therefore any coating technique altered the contact angle value which in turn affects the surface energy of the solid material.

Table 23 contact angle values for PU finished cow upper leather before plating

specimen	Type of solvents			surface energy(m N/m)		
	Θ of Water	Θ of methyl iodide	Θ of Hexadecane	γ_{sv}^d	γ_{sv}^p	γ_{sv}
1F	64.63	46.67	27.90	24.37	16.45	40.82
2F	61.58	40.65	28.23	24.30	16.83	40.72
3F	60.65	42.65	28.13	23.80	16.86	40.65
4F	60.24	40.36	28.23	23.62	17.79	41.41
5F	60.15	41.36	28.24	23.85	18.31	42.16

From the table 23, it is evident that contact angle value has changed when PU is used in base coat. The water contact angle value was decreased compared to the contact angle value of control crust whereas the methyl iodide and hexadecane contact angle value has increased significantly. This is because the nature of PU used is water soluble and it has the capacity to decrease the hydrophobic nature of chrome tanned crust leather so the surface becomes more hydrophilic compared to the control crust. Due to this the contact angle values in the case of less polar solvents have shown significant increment. In this case some chemicals having good performance effect has to be applied at the top coat to increase the contact angle value.

Table 24 contact angle values for PU finished cow upper leather after plating

SPECIMEN	TYPE OF SOLVENTS			surface energy(m N/m)		
	Θ of Water	Θ of methyl iodide	Θ of Hexadecane	γ_{sv}^d	γ_{sv}^p	γ_{sv}
1p	65.42	33.66	30.81	23.73	16.28	40.01
2p	58.13	37.35	30.14	23.89	16.83	40.72
3p	64.49	36.11	30.52	23.80	16.86	40.65
4p	63.23	43.77	31.32	23.62	17.79	41.41
5p	62.27	39.15	30.32	23.85	18.31	42.16

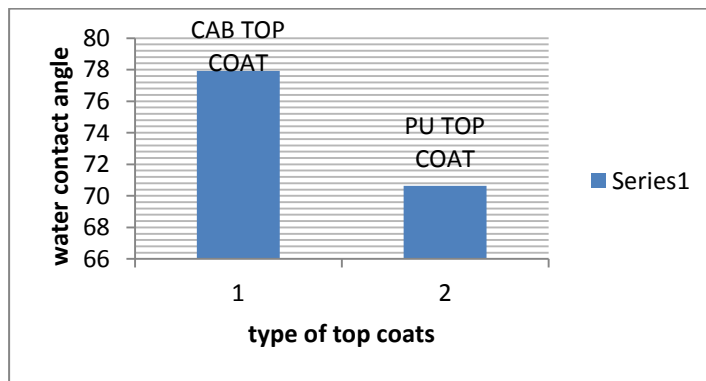
Table 25 Contact angle values for butadiene binder -black pigment combination

Specieman(cow black)	Type of solvents					
	Contact angle for water		Contact angle for Methyl iodide		Contact angle for Hexadecane	
	exp	Control	exp	control	Exp	Control
1b	25.29	33.40	33.46	47.99	Nd	28.854
2b	22.16	35.83	46.96	46.02	Nd	33.795
3b	30.46	34.80	35.58	56.48	Nd	32.001
4b	21.38	41.06	41.87	56.66	Nd	31.788
5b	20.88	35.30	44.70	47.80	Nd	34.359

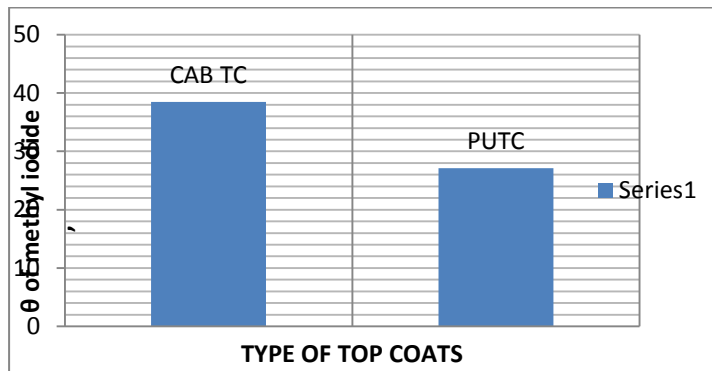
As it has described in table 25, the contact angle values in the case of butadiene binder was less than the control crust this shows that butadiene binder alone cannot be used for leather finishing. It was absorbed that in the case of hexadecane the drop was sinking spontaneously so that the hexadecane contact angle was not determined.

Figure 17 contact angle values for butadiene-pigment combination (2:1 ratio) after top coat.

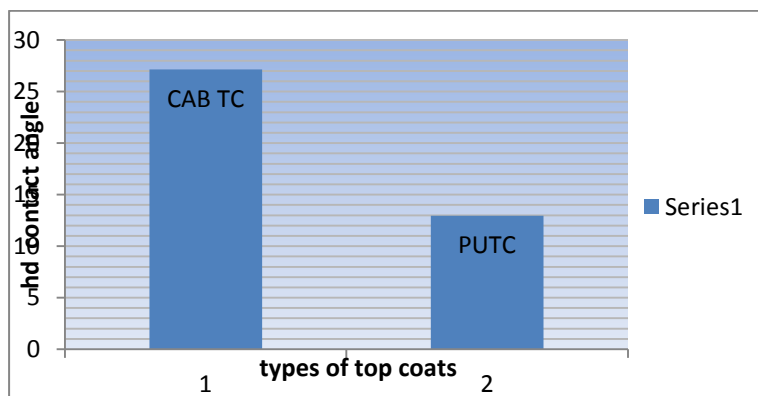
(a) water contact angle,(b) methyl iodide contact angle,(c) hexadecane contact angle



(a) Water contact angle



(b) Methyl iodide contact angle



(c) Hexadecane contact angle

From fig 17 (a),(b) and (c) showed that the contact angle value for CABTC is more than that of PU top coat this might be because of CABTC has more polar groups compared to PU TC. Therefore the choose of CABTC is ideal for making leathers which require special performance properties like self cleaning, water resistance effect and good fastness properties.

Table 26 contact angles for p-b combinations (1:2 ratios) by varying the type of binders.

Type of binders used	Contact angle value		
	water	DMSO	Hexadecane
B ₁ 27154	67.050	ND	ND
combination VS,S,MS(1:1:1)without filler	79.747	62.389	ND
Resin binder combination with filler	87.65	70.36	38.17
CRUST for control	75.829	ND	ND
RA-2354	87.094	60.347	ND
RA-27006	91.431	58.609	ND
RA-17	88.536	59.807	ND
B ₁ 27047	65.871	ND	ND

Note: - Vs= RA-17,S= RA-27006, MS=RA-2354

ND= not detected

4.1.6 Surface energy calculation for three liquid systems

By using the contact angle value of the three liquids it is possible to calculate the Lewis acid parameter (cationic nature) and Lewis base parameter (anionic nature of the surface of the resin finished shoe upper leather using equation [3.8].

Let's consider the contact angle values determined in the case of resin binder combination with filler in the table 26,

For hexadecane, since it has no polar component of surface tension value, equation [3.8] is reduced to:

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}}$$

Where

$$\theta = 37.17$$

$$\gamma^L = \gamma^L = 27.47 \text{ mN/m}$$

By substituting the given values

$$27.47(1 + \cos 37.17) = 2\sqrt{\gamma^S \gamma^L} + 2\sqrt{\gamma^S \gamma^L}$$

By rearranging terms

$$\gamma^S = 23.84 \text{ mN/m, non-polar component of surface energy}$$

To calculate the Lewis acid parameter or the cationic nature of the surface, one can use water and DMSO contact angle and surface tension values.

Since DMSO has very small γ^+ value compared to γ^- value, it is logical to neglect the last term in equation [3.8] and the equation is reduced to:

$$\gamma^L(1 + \cos\theta) = 2\sqrt{\gamma^S \gamma^L} + 2\sqrt{\gamma^S \gamma^L}$$

From table 2-2 and 4-10 for DMSO we can get

$$\gamma^L = 44 \text{ mN/m}$$

$$\gamma^L = 36 \text{ mN/m}$$

$$\gamma^- = 32 \text{ mN/m}$$

$$\Theta = 70.36$$

By substituting the above values

$$44(1 + \cos 70.36) = 2\sqrt{23.84 * 36} + 2\sqrt{\gamma^S * 32}$$

$$22(1.336) = 29.30 + \sqrt{\gamma^S * 32}$$

$$0.092 = \sqrt{\gamma^S * 32}$$

Squaring both sides and rearranging terms

$\gamma^+ = 0.003 \text{ mN/m}$, the Lewis acid parameter which signifies the cationic nature of the surface.

To calculate the Lewis base parameter (γ_s^-), one can use surface tension of water and the above surface energy components obtained in the case of hexadecane and DMSO.

For water

$$\gamma_l = 72.8 \text{ mN/m}$$

$$\text{WCA} = 87.65^\circ$$

$$\gamma_l^- = \gamma_l^+ = 25.5 \text{ mN/m}$$

$$\gamma_{LW} = 21.8 \text{ mN/m}$$

By using equation [3.8] and substituting the known values:-

$$72.8(1 + \cos 87.65) = 2\sqrt{23.84 * 21.8} + 2\sqrt{0.003 * 25.5} + 2\sqrt{\gamma_s^- * 25.5}$$

$$37.89 = 23.08 + \sqrt{\gamma_s^- * 25.5}$$

Solving for the unknown value and rearranging terms

$\gamma_s^- = 8.6 \text{ mN/m}$, Lewis base parameter which signifies the anionic nature of the surface of the leather finished with the above formulation indicated in table 26

The polar component of the surface energy can be estimated by using equation [3.10] as follows:-

$$\gamma_s^p = 2\sqrt{\gamma_s^+ \gamma_s^-}$$

By substituting the values

$$\gamma_s^p = 2\sqrt{0.003 * 8.6} = 0.32 \text{ mN/m}$$

The total surface energy is the sum of polar and non polar components

$$\gamma_s^{\text{total}} = \gamma_s^{LW} + \gamma_s^p$$

$$\gamma_s^{\text{total}} = 23.84 \text{ mN/m} + 0.32 \text{ mN/m} = 24.16 \text{ mN/m}$$

From the surface energy and its component values one can deduce that the coated surface of leather have more of non polar nature and the charge characteristics is mostly anionic in nature even though there is residual cationic charges.

4.2. Water vapour permeability

As it has been shown in fig 18, water vapour permeability decreases significantly as the proportion of binder increases. In addition to this, very soft binders resulted in lower water vapour permeability than soft and also soft binders showed lesser result than medium soft binders. Highest water vapour permeability was observed in the case of using combination of resin binders rather than using individual binders. From this experimental result one can deduce that the type and concentration of resin binder influence the water vapour permeability of shoe upper leather. Therefore it is better for the leather finishing technician to use right quantity and type of binder combination in order to get better permeability. And it is also advisable to use combination of binders rather than using a single binder in right proportion to get maximum water vapour permeability.

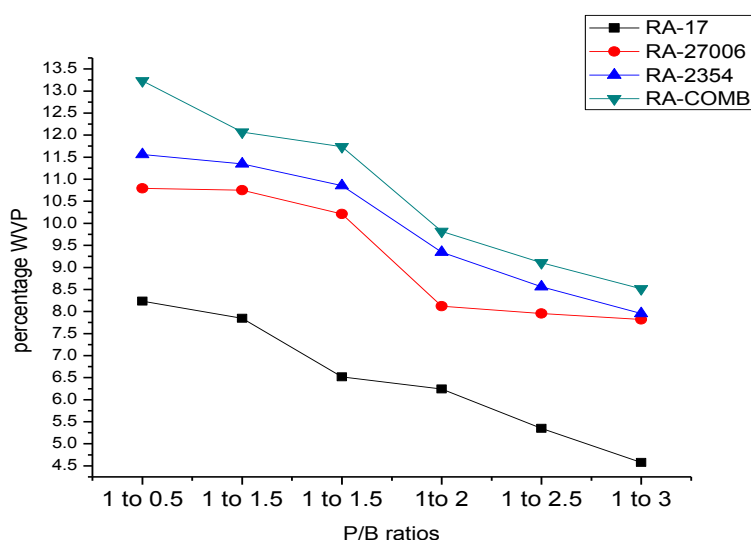


Figure 18 plot of % WVP finished shoe upper leather versus P/B ratios.

(For very soft (RA-17), soft (RA-27006), medium soft (RA-2354) and combination of the three (RA-comb) resin binders by fixing the other auxiliaries constant)..

Table 27 Determination of water resistance of flexible leather

S.No	Formulation name	Water resistance of flexible leather		remark
		% water absorption	Penetration	

			time(min)	
1	PUT1A	64.4	13.7	
2	PUT2A	42.3	54.3	
3	PUT3A	91.7	3.5	
4	PUT4A	87.7	4.6	
5	PUT5A	69.0	53.4	
6	PUT6A	61.2	4.4	
7	PUT1	111.1	24.5	
8	PUT2	87.7	23.0	
9	PUT3	116.1	15.7	
10	PUT4	100.7	10.1	
11	PUT5	81.4	23.2	
12	PUT6	95.0	9.4	
13	Cat-1a	129.2	1.2	
14	Cat-2a	128.9	0.4	
15	Cat-1b	158.5	0	
16	Cat-2b	109.0	0.4	
17	ccat	161.6	0	

Note: ccat is control dyed crust

From the table one can deduce that percentage water absorption is more in the case of cationic finishing technique. In addition to this water was penetrated immediately to the cross section of the leather finished with formulations cat-1a, cat-2a cat-3a and cat-4a and hence the water resistance effect is poor. As it has explained in determination of contact angle value, the value is lower as compared with all other anionic finishing techniques. Almost no difference in percentage water absorption was observed as compared with the control crust. From this result one can conclude that cationic finishing technique is not suitable to improve the water resistance effect and other performance properties but the main advantage of cationic finishing is to get good covering effect without affecting the natural look, flexibility and softness.

4.3. Finish adhesion values for leathers finished with different binders.

The finish adhesion result for finish formulations prepared by varying the concentration of binders in chapter-3, Table 7,8,9 and 10 have described in table 28 and 29, the corresponding load versus extension graphs have indicated in annexure-3 (i, and ii,)

Table 28 Finish adhesion test (Wet method) result for different p/b ratio

Specimen	Formulation name	p/b ratio	Max. load(N)	Average load(N)	Average peel strength (N/mm)	Max. load/width(N/mm)	Width (mm)	Type of failure
1	F10	1to 2	4.72	4.34	0.43	0.47	10	Fc
2	F10	1 to 2	7.28	5.02	0.50	0.73	10	Fc
3	F2	1to 1	3.42	2.58	0.26	0.34	10	TC
4	F2	1 to 1	4.16	3.34	0.33	0.42	10	TC
5	F6	1 to 3	5.75	4.76	0.48	0.57	10	TC and FC
6	F6	1to 3	4.28	3.36	0.34	0.43	10	TC and FC
7	F1	1 to 0.5	5.82	4.49	0.45	0.58	10	TC
8	F1	1 to 0.5	4.91	4.58	0.46	0.49	10	TC
9	F21	1 to 2	10.01	8.18	0.82	1.00	10	TC and FC
10	F21	1to 2	12.83	6.03	0.60	1.28	10	TC and FC
11	F3	1 to 1.5	9.99	7.10	0.71	1.00	10	TC and FC
12	F3	1to 1.5	7.57	5.17	0.52	0.76	10	TC and FC
13	F14	1to 1	7.74	6.07	0.61	0.77	10	TC
14	F14	1 to 1	4.08	2.74	0.27	0.41	10	TC
15	F16	1to 2	5.22	3.95	0.40	0.52	10	TC and FC
16	F16	1 to 2	6.98	3.71	0.37	0.70	10	TC and FC
17	F22	1to 3	10.87	8.02	0.80	1.09	10	TC and FC
18	F22	1 to 3	12.80	10.13	1.01	1.28	10	TC and FC
19	F15	1 to 1.5	4.01	3.12	0.31	0.40	10	TC
20	F15	1 to 1.5	3.25	2.25	0.22	0.32	10	TC

Note: FC= Finish coat, TC= top coat

From the table 28 one can easily see that the TC removal was observed in the case of the formulations which are made by p/b ratio below 1 to 2. This is because of insufficient binding

materials in the base coat formulation which is due to less amount of resin binders or the excess amount of filler wax used. It is also evident that the finish formulations made by p/b ratio greater than or equal to 1 to 2, the finish failure observed was removal of both TC and FC. This is because sufficient amount of binders used in the base coat made the top coat to adhere strongly with the base coat so that the top coat alone cannot be removed easily. One of the quality parameter used in determination of finish adhesion(average peel strength(N) per 10mm based on SATRA test method is acceptable (above 0.2mm) for all formulations. but the leathers finished by the above formulations were quite different in physical appearance and the degree of finish failure varies significantly when the p/b ratio varies. Maximum average peel strength (N) per load (mm) was observed in the case of finish formulations F21 and F22. Since the formulations were created by using combination of very soft, soft and medium soft resin binders. Therefore from this result one can deduce that better adhesion effect is observed when a finishing technician combines resin binders having different degree of softness.

Table 29 Finish adhesion test (dry) result for different p/b ratio.

specimen	Formulation name	p/b ratio	Max.load(N)	Average load(N)	Average peel strength(N/mm)	Maximum load/width (N/mm)	Width (mm)	Type of failure
1	F1	1 to 0.5	19.99	17.89	1.79	2.00	10.00	TC
2	F1	1 to 0.5	15.53	13.22	1.32	1.55	10.00	TC
3	F7	1 to 0.5	36.71	31.89	3.19	3.67	10.00	TC
4	F7	1 to 0.5	27.79	23.27	2.33	2.78	10.00	TC
5	F18	1 to 3	15.54	11.00	1.10	1.55	10.00	Tc
6	F18	1 to 3	12.84	8.29	0.83	1.28	10.00	Tc
7	F14	1 to 2.5	21.54	16.07	1.61	2.15	10.00	Tc
8	F14	1 to 2.5	19.84	15.07	1.51	1.98	10.00	Tc
9	F15	1 to 1.5	14.22	12.71	1.27	1.42	10.00	Tc
10	F15	1 to 1.5	18.27	14.27	1.43	1.83	10.00	Tc
11	F6	1 to 3	1.53	1.02	0.10	0.15	10.00	Tc
12	F6	1 to 3	9.98	9.98	8.07	0.81	10.00	Tc

13	F13	1 to 0.5	51.21	40.06	4.01	5.12	10.00	Fc
14	F13	1 to 0.5	22.98	19.80	1.98	2.30	10.00	Fc
15	F3	1 to 1.5	58.51	30.52	3.05	5.85	10.00	Tc
16	F3	1 to 1.5	19.52	16.06	1.61	1.95	10.00	Tc
17	F12	1 to 3	23.83	17.77	1.78	2.38	10.00	Tc
18	F12	1 to 3	28.72	16.15	1.61	1.95	10.00	Tc
19	F22	1 to 3	12.17	8.65	0.87	1.22	10.00	Tc
20	F22	1to 3	24.30	18.14	1.81	2.43	10.00	Tc
21	F21	1 to 2	13.24	7.06	0.71	1.32	10 .00	Tc
22	F21	1 to 2	5.15	1.69	0.17	0.51	10.00	Tc
23	F9	1 to 1.5	21.58	17.70	1.77	2.16	10.00	Tc
24	F9	1 to 1.5	10 .23	8.60	0.86	1.02	10.00	Tc
25	F5	1 to 2.5	14.66	9.85	0.99	1.47	10.00	Tc
26	F5	1 to 2.5	15.00	7.00	0.70	1.50	10 .00	Tc
27	F8	1 to 1	20.08	16.26	1.63	2.1	10.00	Fc
28	F8	1 to 1	26.44	18.78	1.88	2.64	10 .00	Fc
29	F4	1 to 2	19.12	13.67	1.37	1.91	10.00	Tc
30	F4	1 to 2	20. 28	14.18	1.42	2.03	10.0	Tc

From table 28 and 29 it evident that in the case of dry finish adhesion test, the strength parameters such as maximum load, average load, maximum load per width and average peel strength per width were higher compared to wet adhesion test. Average peel strength per width (N/mm) result were above 0.3N/mm for all the leathers finished with the above formulations except F6 and F21. This might be due to the greasy nature of the crust prior to applying the base coat. In other words any chemical which have a tendency to increase the contact angle of the crust leather above 90^0 before the base coat is applied decreases the average peel strength (N) per width (mm) value this is the indication of poor adhesion.

4.4. Determination of flexing endurance

In this experiment flexing resistance/endurance were tested for different finish formulations described in chapter-3 table-7, 8, 9 and 10 based on the international standards, SATRA TM25:1992/BALLY TM 55.

s/n	Formulation name	No. Of cycles	Along-dry	Across-dry	Along-wet	Across-wet
1	F4	10000	A	A	A	A
		100000			E	E
		500000	B	B		
2	F2	10000	A	A	A	A
		100000			E	E
		500000	D	D		
3	F3	10000	A	A	A	A
		100000			E	E
		500000	D	D		
4	F9	10000	A	A	A	A
		100000			C	C
		500000	C	C		
5	F22	10000	A	A	A	A
		100000			D	D
		500000	B	B		
6	F21	10000	A	A	A	A
		100000			D	D
		500000	C	C		
7	F1	10000	A	A	A	A
		100000			F	F
		500000	D	D		
8	F6	10000	A	A	A	A
		100000			D	D
		500000	C	C		
9	F7	10000	A	A	A	A
		100000			D	D
		500000	D	D		
10	F8	10000	A	A	A	A

		100000			D	D
		500000	D	D		
11	F14	10000	A	A	A	A
		100000			D	D
		500000	D	D		
12	F15	10000	A	A	A	A
		100000			F	F
		500000	D	D		
13	F16	10000	A	A	A	A
		100000			E	E
		500000	D	D		
14	F17	10000	A	A	A	A
		100000			C	C
		500000	C	C		

Table 30 Vamp flexing result for leathers finished with different formulations.

Note: A: no effect B: slight creasing C: slight pipiness D: marked creasing E: severe creasing F: severe pipiness G: slight crack H: marked crack

From the above table we can deduce that there was no finish failure observed for all the formulations in the case of 10000 cycles but different types of finish failures were observed in all leather samples finished by using the above formulations. Finish formulations F4, F2, F3 and F16 shown severe creasing, F14, F8, F7, F6, F21 and F22 shown marked creasing at 10000 cycles in wet flexing test. Based on the standard for all the leathers finished by the above formulations have shown acceptable result. From this one can deduce that vamp flexing is not strongly affected when the finish formulation contains p/b ratio ranging from 1 to 0.5 to 1 to 3 if and only if the crust have no looseness and the top coat applied is CAB diluted with water at the ratio of 1to1.

4.5. Determination of wet and dry rub fastness

In these experiments, Rub fastness was determined by using circular rubbing machine based on SATRA TM 8 procedure for different finish formulations prepared by varying the p/b ratio and for cationic and some performance finishing techniques prepared by different PU

binder combinations.. For dry rub fastness determination, the transfer of colour from test piece to felt pad were checked at 512 cycles and for wet rub fastness the colour fastness to felt pad were checked at 256 cycles and the test results are described in the following table.

Table 31 colour fastness to circular rubbing for resin finished leather

For leathers finished with different finish formulations prepared by varying concentration and type of resin binders in tables 7, 8, 9 and 10.

s/no	Formulation name	p/b ratio	Color fastness to circular Rubbing (grey scale)	
			dry	Wet
1	F4	1 to2	4	3/4
2	F5	1 to 2.5	3	3
3	F6	1 to 3	3	2 /3
4	F7	1 to 0.5	3	2/3
5	F8	1 to 1	3/4	3
6	F9	1 to 1.5	5	4
7	F10	1 to 2	5	4
8	F11	1 to 2.5	5	4
9	F12	1 to 3	5/4	4
10	F13	1 to 0.5	4	2
11	F14	1 to 1	4	3
12	F15	1 to 1.5	4	3
13	F16	1 to2	5	5
14	F17	1 to 2.5	5	5
15	F18	1 to3	5	5
16	F21	1 to 2	5	5
17	F22	1 to3	5	5
18	F1	1 to 0.5	4/5	4
19	F2	1 to 1	4	3
20	F3	1 to1 5	5	4

From the table 31 one can easily observe that for F6, F7, F8, F13 has shown poor fastness effect to rubbing. The possible reason is that the tackiness property of very soft binder (RA-17) which is directly related to fastness property. Therefore the finishing technician has to be aware of the nature of binder used before deciding the amount of binder to be added in a given finish formulation. Very soft binder in the case of the formulations F6, F5 were shown poor wet rub fastness when it is used in higher proportion. Form this result one can deduce that very soft binder is not recommended for shoe upper finishing in larger proportion and soft and medium soft binders are recommended in more proportion to get better fastness to rubbing.

4.5.1 Rub fastness result for cationic finish

Poor colour fastness to circular rubbing was observed in the table below in the case of cationic finishing this is because of the cationic nature of chrome tanned crust. Since the charge of the substrate/crust and the charge of cationic finishing chemicals have similar nature, the chemicals are loosely bound to the surface of the leather.

Table 32 rub fastness result for leather finished with cationic finishing technique

specimen	Formulation name	Colour fastness to circular rubbing	
		Dry at 512cycles	Wet at 256 cycles
		Felt pad	Felt pad
1	Cat-1a	3	1
2	Cat-2a	3	1/2
3	Cat-1b	3	1/2
4	Cat-2b	3	1

4.5.2 Rub fastness result for leathers finished by varying different PU top coat and performance chemicals.

Incorporation of performance chemicals into PU based top coats has improved the both dry and wet rub fastness value. This type of finishing is also recommended for finishing water resistance leathers. As the result shows below the both wet and dry rub fastness effect were increased when the performance chemicals were added to at the top coat. Leathers finished with the six different formulations such as PUT1A, PUTC2A, PUTC3A, PUTC4A, PUTC5A

and PUTC6A have shown maximum fastness because in each formulation performance chemicals were incorporated.

Table 33 rub fastness result for PU finished leathers with and without performance chemicals.

S.NO	Formulation name	Color fastness to circular rubbing	
		Dry at 512cycles	Wet at 256 cycles
		Grey scale	Grey scale
1	PUT1	4	3
2	PUT2	4/5	3
3	PUT3	4/5	3
4	PUT4	4	3
5	PUT5	4	3
6	PUT6	4	3
7	PUT1A	5	5
8	PUT2A	5	5
9	PUT3A	5	5
10	PUT4A	5	5
11	PUT5A	5	5
12	PUT6A	5	5

CHAPTER-5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The current research presents different finish formulations were prepared by using commercially available finishing chemicals to study the effect of pigment and binder combinations on the surface property of shoe upper leather. Contact angle was used as a parameter to study the effect of each finish formulations on the surface property of the leather. Water, methyl iodide, hexadecane and DMSO were used to measure the liquid-solid contact angle. The experimental result from contact angle value showed that coating with pigments and binders have increased the contact angle value compared to the control crust. And the corresponding value of surface energy were calculated by using Thomas young equation and the results showed that there is decrease in surface energy when the contact angle increases. It was observed that when the contact angle increases the degree of adhesion and the wettability of the surface of the leather were decreased. In addition to this the effect of top coats and other finishing auxiliaries other than pigments and binders on contact angle value were investigated. Fillers have the ability to increase the contact angle. CAB top coated leather showed more contact angle than PU and acrylic top coats. This value clearly showed that wettability is more in the case of PU and acrylic top coated leathers than CAB top coated leathers.

The effect of number of top coats on water contact angle value were determined ,and the experiment showed that the value were decreased gradually at the beginning of the coat because the top coats are water based so during the coating process the hydrophobic nature of the surface of chrome tanned leather have decreased. And finally the contact angle value were increased and the corresponding surface energy were reduced when CAB top coat were sprayed. In general when the coating chemicals have more polar groups the contact angle values were observed to be increased.

Physical tests like rub fastness, finish adhesion, water vapour permeability and flexing endurance were conducted for leather samples finished with different acrylic binder pigment combination, cationic finish formulations and PU binders with and without incorporation of performance chemicals. The physical test results showed that pigment binder ratio and the property of the given binder have significantly affected the above mentioned physical test

parameters. In the case of acrylic binder- pigment combination better result were obtained when we use combination of soft, medium soft and very soft binders at 1 to 3 p/b ratios but very soft binder has to be used in smaller proportion to minimize the tackiness effect. And better wet rub fastness and water resistance effects were observed in the case of acrylic resin finish and PU based finishing technique compared to cationic finishing technique.

Film forming property of different acrylic binders and protein binders were studied and the result showed that soft, medium soft and very soft acrylic binders form flexible, softer films and hard acrylic binders do not form film at room temperature where as protein binders form discontinuous and brittle film.

The wettability of the surface of leather has to be good before applying the top coat otherwise the top coat cannot adhere to the surface of the leather whenever such hard binder is used at the base coat in larger proportion. Resin binders having lower water contact angle are ideal for base coat since they can easily spread on the surface of the leather this in turn facilitates degree of adhesion.

RA-2354, RA-27006 and RA-17 can be used in base coat since they have lower contact angle value compared to RA-1216. And hence the surface of the leather before applying the top coat is easily wettable. But if they are used at the top coat the surface of the leather can be easily affected by different soiling agents such as dust, dirt, fats and oils because of their tackiness..

When RA-17, RA-27006 and RA-2354 are used independently with other finishing chemicals in base coat, optimum finish effect is observed at p/b ratio of 1 to 1.5, 1 to 2 and 1 to 2.5 respectively. And when these binders are combined the optimum value is observed at p/b ratio of 1 to 3.

The percentage elongation of the films prepared by soft, very soft and medium soft resin binders showed maximum value where as when the hard resin binder (RA-1216) the value has reduced. The Young's modulus which indicates the stiffness of the finish film were increased when hard binder is incorporated

5.2. Recommendation

Since almost all the customers in leather market in the world require the natural look of leather, a great care has to be taken in finishing so as to maintain the feel and natural look of the leather since it is the main parameter that determines the selling value of leather. In order to do this the finishing technician has to choose the right quantity of pigments and binders and other auxiliaries. Usually the natural feel of resin finished leather is poor even the leather finished with such technique appears to be plastic look. In order to get better natural look with good covering effect the ideal finishing technique is cationic finishing technique but the problem of cationic finishing is its poor wet rub fastness. Therefore to improve the wet rub fastness property of cationic finishing technique further study has to be undertaken to modify the surface of leather in such a way that the cationic finishing chemicals will adhere strongly with the leather surface.

It has to be recommended that a finishing technician has to check the glass transition temperature, solid content, degree of softness and etc. of the resin binders prior to preparing the finish formulation for particular product.

The amount of finish auxiliaries such as fillers and waxes have to be used in smaller quantity because such chemicals have a potential to reduce the performance property of the finished leather such as fastness, water repellence effect, adhesion and etc.

Further work has to be conducted in modifying the leather surface with appropriate finishing chemicals having special properties in order to produce leathers which have special effects like self cleaning, water resistant, super hydrophobic etc. by understanding the principle of science and technology of solid surface.

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ANNEXES

Annexure-1 Crust preparation for control

process	chemicals	Percentage	Time (min)	remark
Acid wash	water	150		
	Acetic acid	0.5		
	Wetting agent	0.5	40	D/W
Rechroming	water	50		
	acetic acid	0.5	10	
	BCS(chrome powder)	6	45	
Basification	Sodium formate	0.5	10	
	Sodium bicarbonate	0.5	3*10+30	Ph=4-4.2
Next day			10	D/W
Neutralization	water	100		
	Sodium formate(1:5)	0.5	10	
	Sodium bicarbonate(1:5)	0.5	3*10+10	PH=5-5.2
Retanning	water	80		
	Relugan RE(acrylic synthan)	2	20	
	DI(replacement syntan)	5		
	FB6(melamin resin)	5		
	MR70(phenolic synthan)	5		
	PF18(phenolic synthan)	5		
	GS(vegetable tannin)	5	45	
dyeing	dye	3	40	Check penetration of dye
fatliquoring	Sx20(synthetic)	3		
	Sx25(synthetic)	3		
	LP16(semi-synthetic)	3		
	GL(semi-synthetic)	2	60	

Annexure-2 Leather specifications

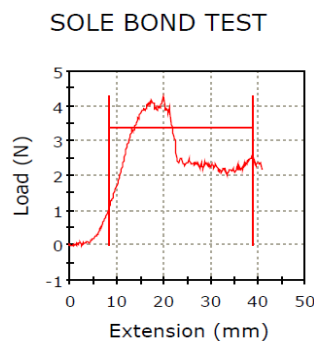
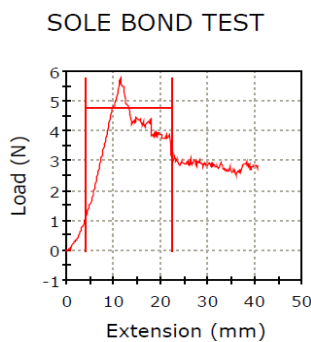
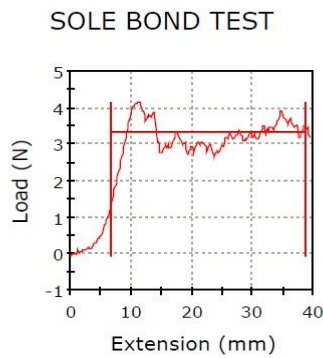
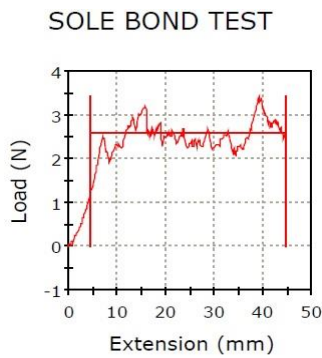
S.No.	Property	Guidelines	Test Method
1.	Extension at break for all leathers	40 – 80 %	ISO 3376
2.	Double hole stitch tear strength of leather	80 N/mm	IS 5914
3.	<p>Colour fastness to rubbing – Circular method</p> <p><u>Shoe uppers</u></p> <p>Colour change – grey scale rate</p> <p>1. Dry rubbing 512 rubs</p> <p>2. Wet rubbing 256 rubs</p> <p>Colour transfer to felt – grey scale rate</p> <p>1. Dry 512 rubs</p> <p>2. Wet 256 rubs</p>	<p>Min. 3</p> <p>Min. 3</p> <p>Min.3</p> <p>Min.3</p>	SLF 5
4.	<p>Flexing resistance – Bally method</p> <p><u>Upper leather</u></p> <p>1. Dry 100,000 flexes</p> <p>2. Wet 20,000 flexes</p> <p><u>Upholstery leather</u></p> <p>Dry 20,000 flexes</p>	No sign of finish crack, flaking of finish, delamination etc	ISO 5402-1
5.	<p>Flexing resistance – Vamp Method</p> <p>1. Dry 500,000 flexes</p> <p>2. Wet 100,000 flexes</p>	Not worse than slight crack and appearance of no salt spue	ISO 5402-2
6.	<p>Adhesion of finish</p> <p><u>Aniline leather</u></p> <p>1. Dry</p> <p>2. Wet</p> <p><u>Corrected grain finished leather</u></p> <p>1. Dry</p>	<p>2 N/10 mm</p> <p>2 N/10 mm</p>	

	<p>2. Wet</p> <p><u>Upholstery leather</u></p> <p>1. Dry</p> <p>2. Wet</p> <p><u>Patent leather</u></p> <p>1. Dry</p> <p>2. Wet</p>	<p>3 N/10 mm</p> <p>2 N/10 mm</p> <p>4 N/10mm</p> <p>3 N/10 mm</p> <p>5 N/10 mm</p> <p>3 N/10 mm</p>	ISO 11644
57	<p>Dynamic water penetration – Bally method</p> <p>1. Water penetration time</p> <p>2. Water absorption for 60 minutes</p> <p>3. Water transmission for 30 minutes</p>	<p>Min. 60 minutes</p> <p>Max. 30 %</p> <p>Max. 0.2 gram</p>	ISO 5403 -1
8.	<p>Dynamic water penetration – Maeser Method</p> <p>Water penetration cycles</p> <p>Excellent</p> <p>Very good</p> <p>Good</p> <p>Moderate</p> <p>Poor</p>	<p>> 20000 cycles</p> <p>15000-20000 cycles</p> <p>10000 -15000 cycles</p> <p>10,000-15,000 cycles</p> <p>< 5000 cycles</p>	ISO 5403 -2

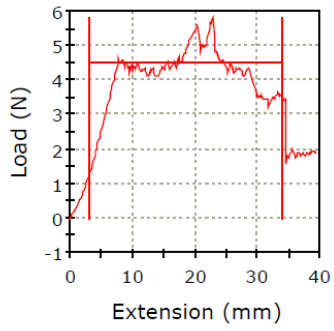
9	<p>Water Vapour Permeability (W.V.P) and Water Vapour Coefficient (W.V.C)</p> <p><u>Upper Leather</u></p> <ol style="list-style-type: none"> 1. Water Vapour permeability 2. Water Vapour coefficient <p><u>Lining Leather</u></p> <ol style="list-style-type: none"> 1. Water Vapour permeability 2. Water Vapour coefficient 	<p>Min. 0.8 mg/cm²/hour</p> <p>Min. 15 mg/cm²/8 hour</p> <p>Min. 2.0 mg/cm²/hour</p> <p>Min. 15 mg/cm²/8 hour</p>	ISO 14268
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Annexe-3 Finish adhesion test result

i) Graphical representation of finish adhesion (wet-2) by sole bond test for pigment binder combinations described in table 4.31a

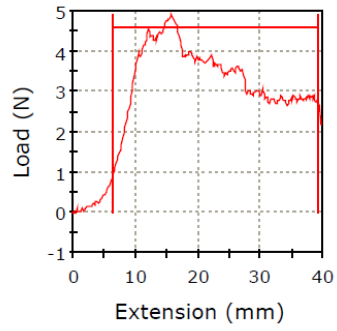


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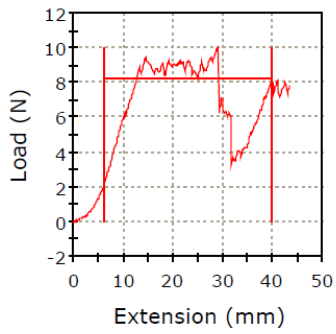
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SOLE BOND TEST



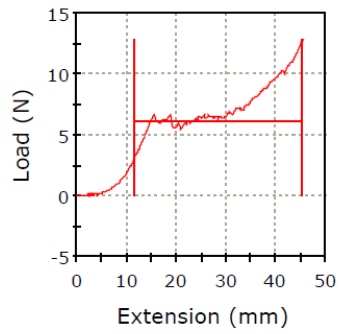
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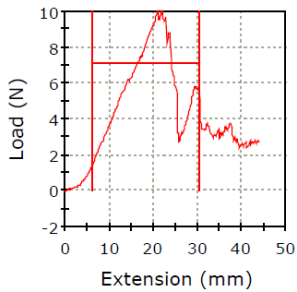
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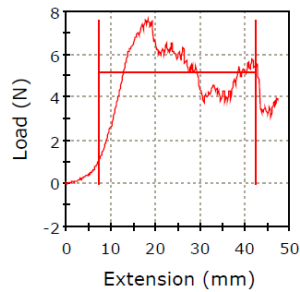
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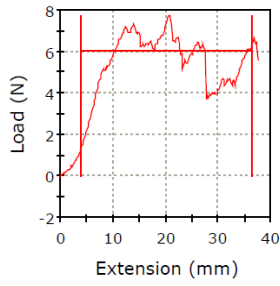
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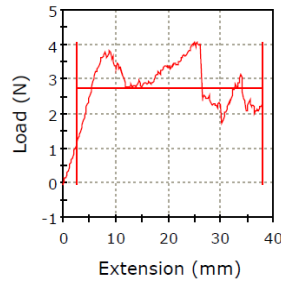
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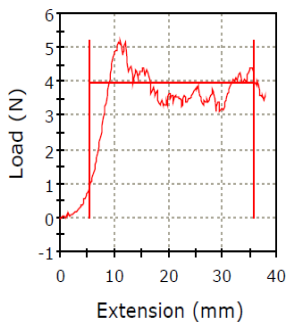
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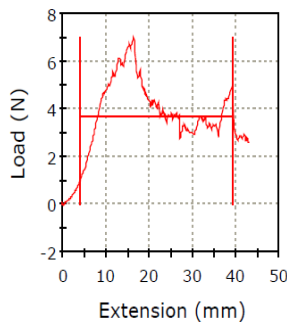
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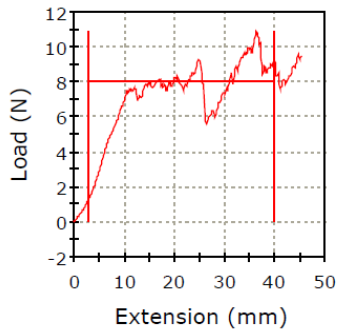
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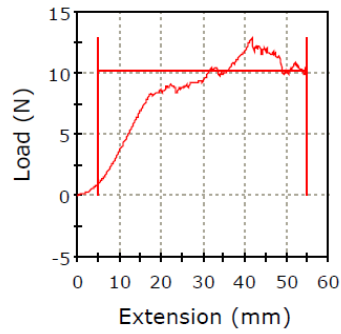
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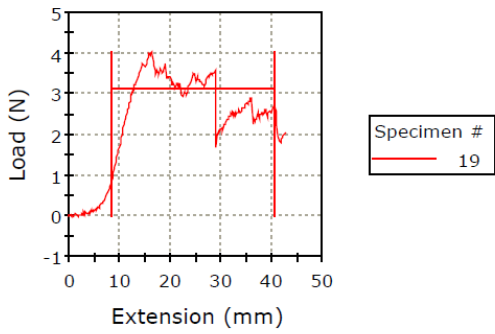
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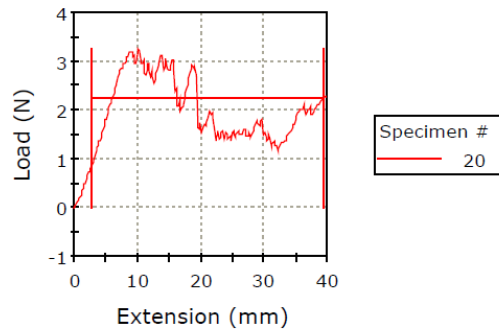


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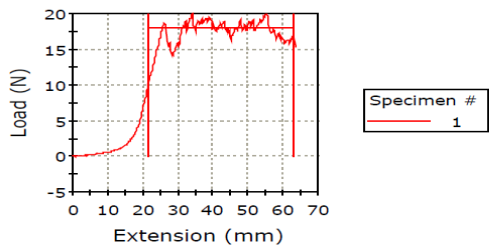
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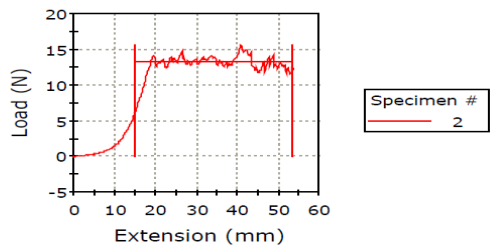
ii) Graphical representation of finish adhesion (wet method) by sole bond test for pigment binder combinations described in table 4.31b.

ii) Graphical representation of finish adhesion (dry) by sole bond test for pigment binder combinations described in table 4.31c

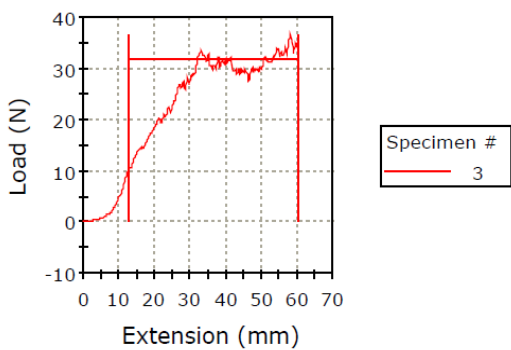
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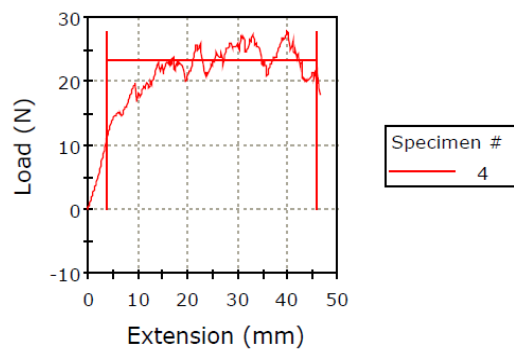
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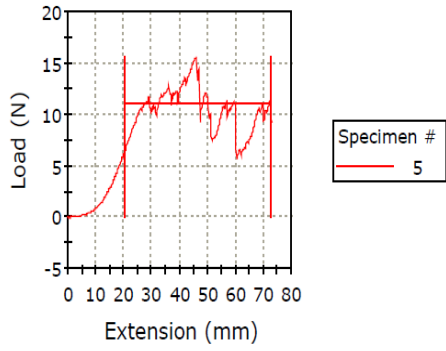
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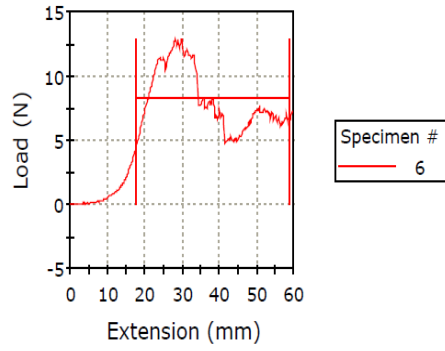
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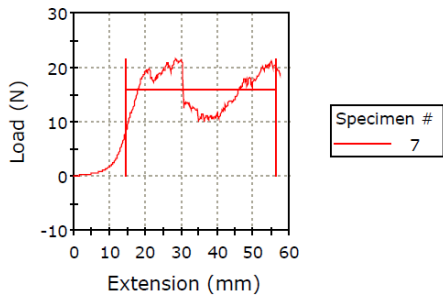
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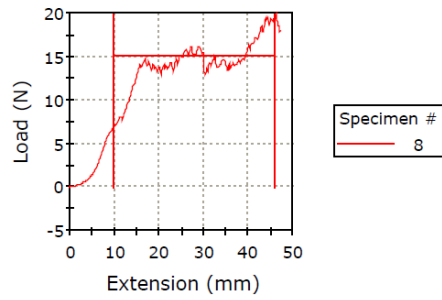
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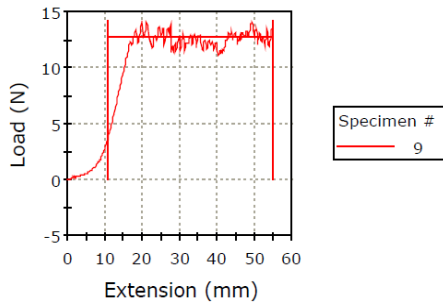
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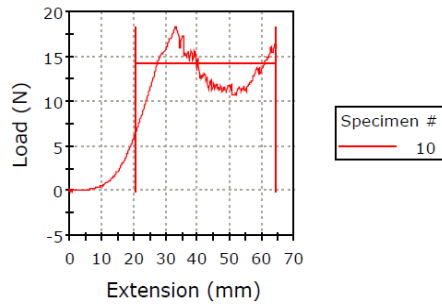
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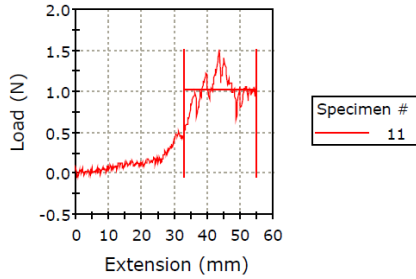
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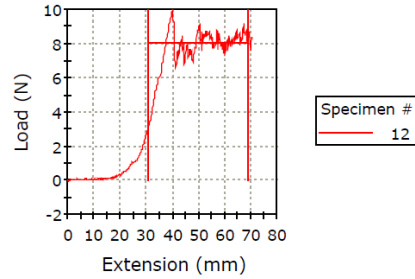
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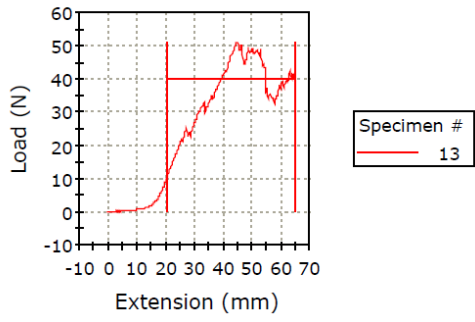
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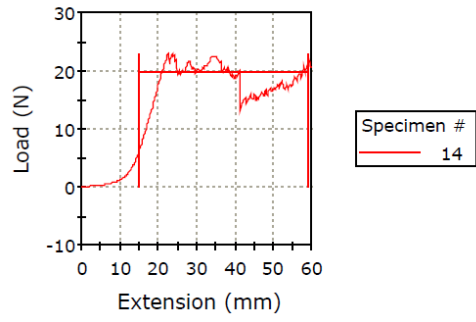
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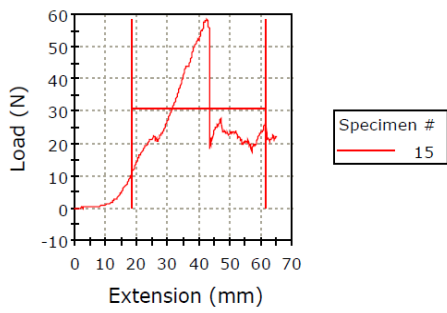
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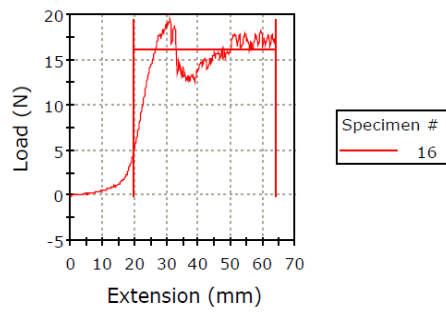
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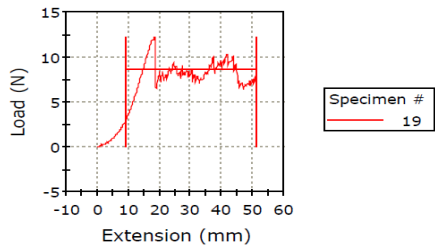
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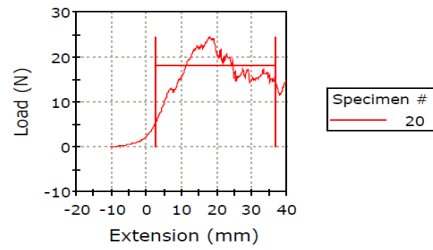
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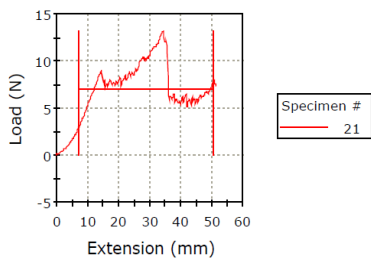
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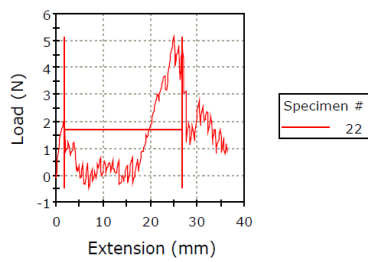
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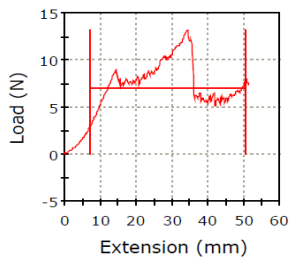
SOLE BOND TEST



SOLE BOND TEST

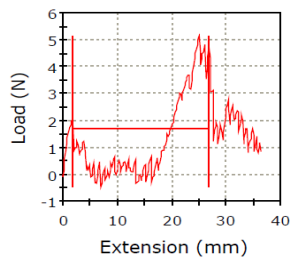


SOLE BOND TEST



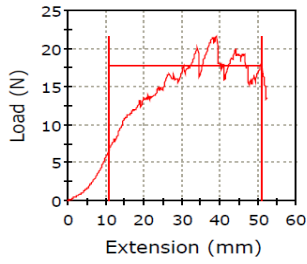
Specimen #
21

SOLE BOND TEST



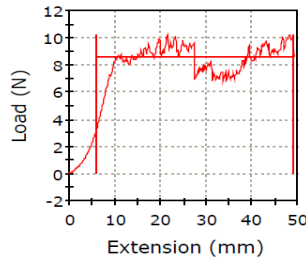
Specimen #
22

SOLE BOND TEST



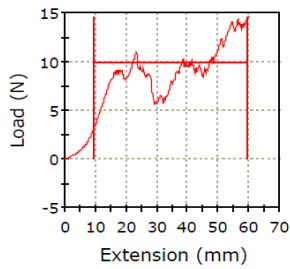
Specimen #
23

SOLE BOND TEST



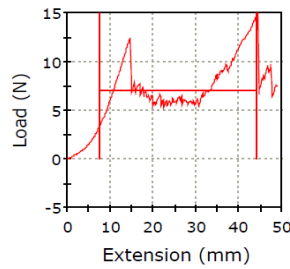
Specimen #
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SOLE BOND TEST



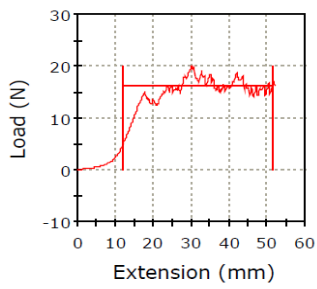
Specimen #
25

SOLE BOND TEST



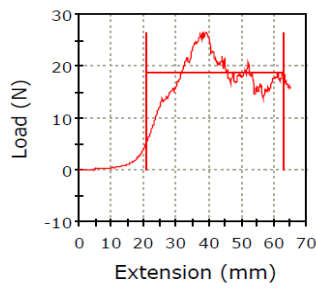
Specimen #
26

SOLE BOND TEST



Specimen #
27

SOLE BOND TEST



Specimen #
28

