

**EFFECT OF ACRYLIC POLYMER DISPERSIONS ON WATER VAPOUR
PERMEABILITY AND SOME OTHER PHYSICAL PROPERTIES OF FINISHED
LEATHERS**

BY

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ZARIA, NIGERIA**

NOVEMBER, 2015

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LEATHERS**

BY

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**DEPARTMENT OF CHEMISTRY,
FACULTY OF SCIENCE,
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA**

NOVEMBER, 2015

Declaration

I declare that the work in this Dissertation entitled **Effect of Acrylic Polymer Dispersions on the Water Vapour Permeability and Some Other Physical Properties of Finished Leathers** has been carried out by me in the Department of Chemistry, Ahmadu Bello University, Zaria. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this Thesis was previously presented for another degree or diploma at this or any other institution.

Michael Ifeanyichukwu UGBAJA
(M.Sc/Sci/14220/2011-2012)

Signature

Date

Certification

This project Dissertation entitled EFFECT OF ACRYLIC POLYMER DISPERSIONS ON THE WATER VAPOUR PERMEABILITY AND SOME OTHER PHYSICAL PROPERTIES OF FINISHED LEATHERS by **MICHAEL IFEANYICHUKWU UGBAJA**, meets the regulations governing the award of the degree of Masters in Polymer Science and Technology of the Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

Dr. P.A.P. Mamza Chairman Supervisory Committee Signature Date
Dr. A. Ejila Member, Supervisory Committee Signature Date
Prof. V.O. Ajibola Head of Department Signature Date
Prof. K. Bala Dean, School of Postgraduate Studies Signature Date

Acknowledgement

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Abstract

The effect of acrylic polymer dispersions on the water vapour permeability and some other properties of finished leathers have been studied. An acrylic based commercial binder AE 558 Nycil has been characterized and its effect when applied in a finish formulation on some of the physical properties of originally retanned leathers was investigated. The binder was found to have an intrinsic viscosity of 227 dL/g, and a viscosity molecular weight (M_v) of 4.03×10^5 . This was obtained by conducting a solution viscosity measurement of the solid polymer in toluene at 25 °C. The melting temperature of the solid binder has been found to be in the range 361.7 °C - 370 °C. The results of these physical properties suggest that this is a very high molecular weight polymer with high thermal stability. Formulations for leather finishing was prepared containing the binder at varied proportions of 125 g, 150 g, 175 g, 200 g and 250 g and was applied on the leather substrates corresponding to samples A1, A2, A3, A4, and A5 respectively. Tests on some of the physical properties of these coated samples were conducted. The water vapour permeability of the originally retanned (uncoated) leathers was reduced significantly after the finish was applied. A1 has the lowest permeability at 125 g of the binder in the formulation, while A5 has the highest permeability at 250 g of the binder in the formulation. Generally, the water vapour permeability of the coated leathers increases as the factor varied in this experiment was increased. A3 had the highest Shore A value at 175 g of the binder in the formulation while A5 has the lowest Shore A value at 250 g of the binder in the formulation. Distension and Bursting strength of the uncoated leathers was improved after the leathers were coated. However, there was no particular trend in effect as the quantity of the binder in the finish formulation increased. The fastness of the coated samples generally increased as the quantity of the binder in the finish formulations was increased with sample A5 having the best resistance to wet rub action.

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Abbreviations/Symbols

FT-IR – Fourier Transform Infrared-Spectroscopy

SLTC – Society of Leather Technologists and Chemists

W_{vp} -- Water Vapour Permeability

A1-A5 – Codes representing five samples of coated leathers

B1-B5 – Codes representing five samples of uncoated leathers

CHAPTER ONE

1.0 INTRODUCTION

Acrylics are esters of acrylic acids, which are the products formed by the reaction of an acrylic acid and alcohol. The esters of acrylic acid polymerise readily to form exceptionally clear plastics. These are widely used in applications requiring clear durable surfaces, e.g. in the aircraft and automobile industries. In more common use are surface coatings involving acrylics. The physical properties of acrylics (such as gloss, hardness, adhesion and flexibility) can be modified by altering the composition of the monomer mixture used in the polymerisation process. Acrylics are used in a wide range of industries, and the list below is simply a selection of some of the more common examples: Adhesives, textile industry (e.g. making sponge fill used in padded jackets), paper coatings, paint industry particularly in paints used for road markings.

The polymerisation process proceeds readily in the presence of catalysts and may be carried out in any one of four different ways: emulsion, bulk, solution or in suspension.

Emulsion polymerisation occurs in a water/monomer emulsion using a water-soluble catalyst.

Emulsion polymerisation is the main process used in the production of acrylic polymers.

Bulk polymerisation is carried out in the absence of any solvent. The catalyst is mixed in with the monomer and the polymerisation is then left to occur with time. This is the method commonly used to manufacture acrylic sheets.

Solution polymerisation is carried out in a solvent in which both the monomer and subsequent polymer are soluble. Only low molecular weight polymers can be manufactured by this process, as high molecular weight polymers cause very high viscosities.

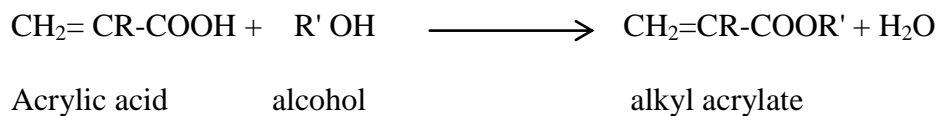
Suspension polymerisation is carried out in the presence of a solvent usually water, in which the monomer is insoluble, and in which it is suspended by agitation. To prevent the droplets of

monomer from coalescing and also to prevent the polymer from coagulating, protective colloids are added. Suitable colloids include bentonite, starch, polyvinyl alcohol and magnesium silicate. In contrast to emulsion polymerisation the catalyst is monomer-soluble and is dissolved in the suspended droplets. The polymers are manufactured from monomers that are formed from the reactions of acrylic acids with alcohols. These are then polymerised using a radical initiator in a water emulsion.

The following components are needed for the emulsion polymerisation reaction:

Monomer

Monomers are prepared by a reversible reaction between an acrylic acid and an alcohol:



The major monomers used are ethyl acrylate, methyl methacrylate and butyl acrylate, as well as non-acrylic monomers such as vinyl acetate and styrene which behave similarly.

Surfactant

A surfactant is a substance composed of mutually repellent polar and non-polar ends. The surfactant surrounds each monomer droplet with a layer of surfactant with the polar tails oriented towards the surrounding water thus forming a micelle.

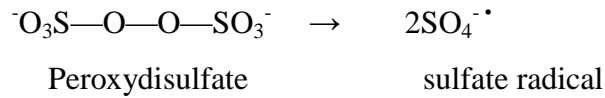
Water

Water is used as the medium to disperse these micelles. During the process the water acts as a solvent for the surfactants and initiators, as well as a heat transfer medium.

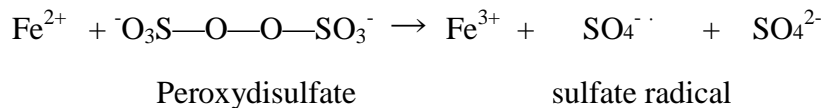
Initiator

The initiators (catalysts) usually used are water soluble peroxidic salts such as ammonium or sodium peroxydisulfate. The reaction can be initiated either by thermal or redox initiation.

In thermal initiation the peroxydisulfate dissociates to give two SO_4 radicals.

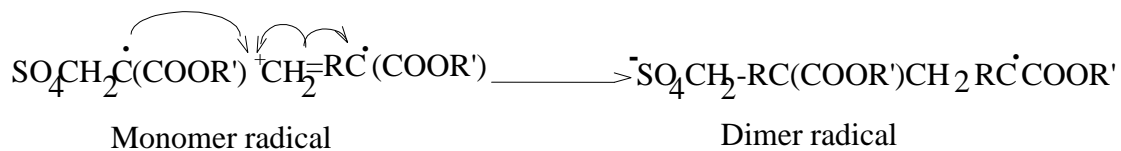
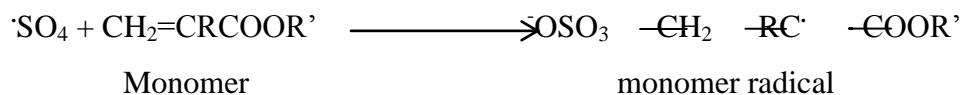


In redox initiation a reducing agent (usually Fe^{2+} or Ag^+) is used to provide one electron, causing the peroxydisulfate to dissociate into a sulfate radical and a sulfate ion:



The emulsion polymerisation process can be carried out in a reaction kettle, which is fitted with a jacket for heating and cooling to allow control of temperature during the reaction.

Surfactant and water are first charged into the kettle. The monomer emulsion and initiator solution (containing redox agents to split the persulphate into sulphate radicals) is then transferred from the monomer feed tank into the kettle at a controlled rate. The mixture in the kettle is constantly agitated while the monomer is being added. During this time the monomer polymerises in accordance with the reactions given below:



Once the reaction has proceeded far enough to use up all the available polymerisation sites, the contents of the kettle are transferred to the stainless steel blend tank. The batch is then cooled, adjusted and transferred to holding tanks for storage and subsequent packing. The quality of the final product depends on the control exercised during the production process. Routine quality control checks of the following properties are carried out throughout the manufacturing process:

- a) Solids content
- b) pH
- c) Viscosity
- d) Gel levels
- e) Residual monomer
- f) Mechanical stability
- g) Freeze/thaw stability
- h) Compatibility

One of the most important tests of the finished polymer is determining its 'glass transition temperature', which is a measure of its toughness. This is done by heating the polymer at a constant rate and measuring its temperature. When a graph of time against polymer temperature is plotted, there will be points where the graph is flat, i.e. the polymer is being heated but it is not getting hotter. At these points the plastic is undergoing some sort of phase change between two different solid phases, and the heat energy is being used to rearrange the structure of the material rather than to simply heat it. Where these transitions occur and how many there are affects the toughness of the plastic.

Leather is made from hides and skins of animals. Large animals such as cattle have hides, small animals such as sheep have skins. The skin of any animal is largely composed of protein referred to as collagen, so it is the chemistry of this fibrous protein and the properties it confers to the

skin with which the tanner is most concerned. Leather making is a traditional industry, which has been in existence since time immemorial, certainly over 5000 years, because the industry was established at the time of the Hammurabi Code (1795- 1750 BC) when Article 274 laid down the wages for tanners and curriers (Reed, 1972). Indeed, the use of animal skins is one of man's older technologies, perhaps only predated by tool making. In the modern world, the global leather industry exists because meat eating exists. Hence, most leather made around the world comes from cattle, sheep, pigs and goats. One of the byproducts of the meat industry is the hides and skins: considering that the annual kill of cattle alone is of the order of 300 million, such a byproduct, amounting to 10-20 million tonnes in weight, would pose a significant environmental impact if it were not used by tanners.

Skin is primarily composed of the protein collagen and it is the properties and potential for chemical modification of this protein that offer the tanner the opportunity to make a desirable product from an unappealing starting material, allowing it to be converted into a product that is both desirable and useful in modern life.

Collagen is a generic name for a family of at least 28 distinct collagen types, each serving different functions in animals, importantly as connective tissues (Bailey and Paul, 1998; Comper, 1996; Kichy *et al.*, 1993; and Kadler, *et al.*, 2007). The major component of skin is type I collagen. Unless otherwise specified, the term 'collagen' will always refer to type I collagen.

Collagens are proteins, i.e. they are made up of amino acids. They can be separated into alpha amino acids and beta amino acids. Each one features a terminal amino group and a terminal carboxyl group, which become involved in the peptide link, and a side chain attached to the methylene group in the centre of the molecule.

In terms of the leather making, some amino acids are more important than others, since they play defined roles: the roles of importance are either in creating fibrous structure or involvement in the processing reactions for protein modification. Amino acids create macromolecules, proteins such as collagen by reacting via a condensation process.

An important part of the structure of collagen is the role of water, which is an integral part of the structure of collagen and hence their chemically modified derivatives (Bienkiewicz, 1990). Privalov, (1982) believed that the hydrogen bonding by water at hydroxyproline is important in stabilizing collagen but thought that the Ramachandran model (Ramachandran and Ramakrishnan, 1976) could not solely explain the high denaturation energy- rather the stabilization probably included wider layers of water. Privalov stated that having in mind the tendency of water molecules to cooperate with their neighbours; it does not seem improbable that the hydroxypropyl can serve as an initiator to an extensive network of hydrogen bonds. This envelops the collagen molecule and might be responsible for the exceptional thermodynamic properties of collagen.

Leather is used for various purposes including clothing, bookbinding, leather wallpaper, and as a furniture covering. It is produced in a wide variety of types and styles and is decorated by a wide range of techniques. Several tanning processes transform hides and skins into leather:

a) Vegetable tannage:

Vegetable-tanned leather is tanned using tannins and other ingredients found in different vegetable matter, such as tree bark prepared in bark mills, wood, leaves, fruits and roots and other similar sources. It is supple and brown in color, with the exact shade depending on the mix of chemicals and the color of the skin. It is the only form of leather suitable

for use in leather carving or stamping. Vegetable-tanned leather is not stable in water; it tends to discolor, so if left to soak and then dry it will shrink and become less supple, and harder. In hot water, it will shrink drastically and partly gelatinize, becoming rigid and eventually brittle. Boiled leather is an example of this, where the leather has been hardened by being immersed in hot water, or in boiled wax or similar substances. Historically, it was occasionally used as armor after hardening, and it has also been used for book binding.

b) Chrome tanning:

Chrome-tanned leather, invented in 1858, is tanned using chromium sulfate and other salts of chromium. It is more supple and pliable than vegetable-tanned leather and does not discolor or lose shape as drastically in water as vegetable-tanned. It is also known as wet-blue for its color derived from the chromium. More esoteric colors are possible using chrome tanning.

c) Aldehyde tannage:

Aldehyde-tanned leather is tanned using glutaraldehyde or oxazolidine compounds. This is the leather that most tanners refer to as wet-white leather due to its pale cream or white color. It is the main type of "chrome-free" leather, often seen in automobiles and shoes for infants. Formaldehyde tanning (being phased out due to its danger to workers and the sensitivity of many people to formaldehyde) is another method of aldehyde tanning. Brain-tanned leathers fall into this category and are exceptionally water absorbent.

d) Oil tannage:

Brain tanned leathers are made by a labor-intensive process which uses emulsified oils, often those of animal brains. They are known for their exceptional softness and their ability to be washed. Chamois leather also falls into the category of aldehyde tanning and,

like brain tanning, produces highly water-absorbent leather. Chamois leather is made by using oils (traditionally cod oil) that oxidize easily to produce the aldehydes that tan the leather to make the fabric the color it is. Rose tanned leather is a variation of vegetable oil tanning and brain tanning, where pure rose otto replaces the vegetable oil and emulsified oils. It has been called the most valuable leather on earth, but this is mostly due to the high cost of rose otto and its labor-intensive tanning process.

e) Syntans:

Synthetic-tanned leather is tanned using aromatic polymers such as the Novolac or Neradol types (syntans, contraction for *synthetic tannins*). This leather is white in color and was invented when vegetable tannins were in short supply during the Second World War. Melamine and other amino-functional resins fall into this category as well, and they provide the filling that modern leathers often require. Urea-formaldehyde resins were also used in this tanning method until dissatisfaction about the formation of free formaldehyde was realized.

f) Aluminium tannage:

Alum-tanned leather is transformed using aluminium salts mixed with a variety of binders and protein sources, such as flour and egg yolk. Alum-tawed leather is technically not tanned, as tannic acid is not used, and the resulting material will revert to rawhide if soaked in water long enough to remove the alum salts.

Tanning by strict definition is the conversion of a putrescible organic material into a stable material that resists putrefaction by spoilage bacteria. Some of the features of tanning expected include the following:

- a) Appearance: dried raw pelt is translucent but dry tanned leather is opaque and/or may change in colour e.g. chrome tanning;
- b) Handle: some degree of softness in comparison to dried raw pelt.
- c) Smell: some tanning agents will introduce smell, e.g. cod oil for chamois leather, extracts of plant materials for vegetable tanned leather or aldehyde compounds;
- d) Rise in denaturation temperature;
- e) Resistance to putrefaction by microorganisms;
- f) A degree of performance to the changes.

The traditional way of thinking about tanning is based on the idea that the tanning agent confers stability to the collagen by changing the structure through crosslinking and thereby preventing the helices from unraveling: here is the first indication that a new concept of tanning is required, in which the function of the tanning agent is to prevent shrinking occurring by altering the thermodynamics of the process. The basis of the chrome tanning reaction is the matching of the reactivity of the chromium (III) salt with the reactivity of the collagen. The availability of ionized carboxyls varies over the range pH 2-6. This the reactivity ranges of collagen, since the metal salt only reacts with ionized carboxyls: the rate of reaction between chromium (III) and unionized carboxyls is so slow it can be neglected (Geher-Glucklich and Beck, 1971).

Chromium (III) salts are stable in the range pH 2-4, where the basicity changes, but at higher values they will precipitate. The development of modern chrome tanning went through three distinct phases:

- a) Single bath process: the original process used chrome alum, $\text{Cr}(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, applied as the acidic salt, typically giving $\text{pH} \approx 2$ in solution. Following penetration at

that pH, when the collagen is unreactive, the system is basified to $\text{pH} \approx 4$, with alkalis such as sodium hydroxide or sodium carbonate to fix the chrome to the collagen.

- b) Two bath process: in this process which was an alternative approach to the single bath process, the technology of making chromium (III) tanning salts was conducted in situ to achieve a more astringent and efficient tannage. This means that the process is conducted in two steps. The pelt is saturated by chromic acid in the first bath, and then it is removed, usually to stand overnight. At this time, there is no reaction, because Cr (VI) salts do not complex with protein. The pelt is then immersed in a second bath, containing a solution of a reducing agent and enough alkali to ensure the final pH reaches at least 4. At the same time, processes were also devised that combined both valencies of chromium, exemplified by the Ochs' process (Ochs et al., 1953). However the dangers of using chromium (VI) drove change back to the single bath process. Not least of these considerations was the incidence of damage to workers by chromium (VI) compounds: the highly oxidizing nature of the reagents typically caused ulceration to the nasal septum.
- c) Single bath process: with the development of masking to modify the reactivity of the chromium (III) salt and hence its reactivity in tanning, the global industry universally reverted to versions of the single bath process.

Chromium is a $3d^44s^2$ element, so chromium (III) compounds have the electronic configuration $3d^3$, forming octahedral compounds. The hexaquo ion is acidic, ionizing as a weak acid or may be made basic by adding alkali. The hydroxyl species is unstable and dimerises, by creating bridging hydroxyl compounds because the oxygen of the hydroxyl confirm a dative bond via a lone pair. This process is called olation. It is a rapid, but not immediate reaction.

The work of Bjerrum, 1910, tells us how we can know that there are hydroxyl bridges in these complex molecules.

Irving 1974 reviewed the chemistry of chromium (III) complexes from the point of view of the leather industry. Some of his more important observations can be summarized as follows:

- a) The half-life of water exchange in the Cr (III) ligand field determined by isotopic exchange of ^{18}O is 54hrs at 27°C : this is an associative interaction. This can be compared to other metals, including Al (III), which have half-lives of the order of 10^{-2}s : these are dissociative interactions. This difference between associative and dissociative complexation has implications not only for the stability of Cr (III) complexes, but also for the role of Al(III) in tanning technology.
- b) The diol complex constructed from the two hydroxyl bridges was assumed to be the preferred form of the chromium dimer. It was also argued that the trimer is the linear version of the bridged structure:
- c) The stability of transition metal complexes can be discussed in terms of thermodynamic stability and kinetic stability. Chromium (III) complexes with carboxylates are thermodynamically less stable than some other complexes, such as amines, but they are kinetically more stable.
- d) The mechanism of exchange between ligands into an octahedral complex depends on the stability of the intermediate crystal field; either five- coordinate square pyramidal ($\text{S}_{\text{N}}1$ mechanism) or seven- coordinate pentagonal bipyramid ($\text{S}_{\text{N}}2$ mechanism). From the calculation of the crystal field activation energies, both mechanisms exhibit high values, with a higher value for the mechanism involving seven- coordination. Whichever is the

actual dominating mechanism, the high activation energies explain the complexes are kinetically stable.

- e) The stability of complexes between Cr (III) and carboxylates is inversely proportional to the dissociation constant of the carboxylic acid. This was first proposed by Shuttleworth (1954). A plot of $\log K_{\text{ChL}}$ against $\log K_{\text{LH}}$ does indicate a good correlation (Chemical Society Special Publication, 1964; Tsuchiya, et al., 1964 & 1965).
- f) The formation of chelate complexes is favoured compared to complexes with monobasic carboxylates.
- g) Olation occurs at the trans positions because the rate of ionization of the aquo ligand is faster (Irving and Williams, 1953).

Although the modern process is conventionally referred to as ‘chrome tanning’, the reaction is most commonly conducted with basic chromium (III) sulfate, as the commonest reagent used in the global leather industry. The importance of that caveat lies in understanding the roles of every component of the salt and in reviewing the alternative options.

The reasons for the popularity of the process are clear, when the features of the process are compared with vegetable tanning:

- a) The process time for the chrome tanning reaction itself is typically less than 24 hrs: the vegetable tanning reaction takes several weeks, even in a modern process.
- b) Chrome tanning confers high hydrothermal stability: a shrinkage temperature of 110°C is easily attainable. This opens up new applications, compared with vegetable tanned leather, where the maximum achievable shrinkage temperature is 85 °C, depending on which vegetable tannin type is used.

- c) Chrome tanning alters the structure of the collagen in only a small way: the usual chrome content of fully tanned leather may contain up to 30 % tannin and hence the handle and physical properties are inevitably modified, restricting applications of the leather.
- d) Vegetable tanning creates hydrophilic leather, because of the chemical nature of the plant polyphenols that constitute the tanning materials, but chrome tanning makes collagen more hydrophobic, so the tannage allows water resistance to be built into the leather.
- e) Chromium (III) can act as a mordant (fixing agent for dyes) and its pale colour allows bright deep and pastel shades (even though the base colour of the leather is pale blue). Tanning with plant polyphenols has the effect of making the dyeing effect dull, which ever vegetable tannin or dye types are used- the leather becomes dull (Irving and Williams, 1953).
- f) Vegetable tanned leather may exhibit poor light fastness, depending on the type of vegetable tannin, but chrome tanned leather will retain its colour better.

Chrome tanning in summary, is faster, better in all sorts of ways and offers more versatility to the tanner, with regard to the leather that can be made from wet blue, the name given to leather after the chrome tanning reaction is complete.

In essence, the chrome tanning reaction is the creation of covalent complexes between collagen carboxyl groups, specifically the ionized carboxylate groups and the chromium (III) molecular ions. In this way, the reaction is no different to making any other carboxylate complex, such as acetate or oxalate, although tanners tend to think of the reaction as fixation of chrome onto collagen. The one difference between simple complexation, such as acetate and chromium (III), and the typical tanning reaction is the ability of the reactants to come together. For a simple reaction, the reactants are in solution and can come together without hindrances, limited only by

diffusion. In the case of the tanning reaction, the substrate has finite thickness, so the additional parameter of penetration through the cross-section comes into play.

The term 'post tanning' refers to the wet processing steps that follow the primary tanning reaction. This might refer to following tannage with chromium (III), as is usually the case in industry, but equally it applies to vegetable tanning or indeed any other tannage used to confer the primary stabilization to pelt. The combination of post tanning processes may not always be the same for all tannages: the choice of post tanning processes depends on the primary tannage and the type of leather the tanner is attempting to make. In all cases, post tanning can be separated into generic processes:

- a) **Neutralisation:** The process of deacidification of the excess of free or easily liberated strong acid in leather, prior to dyeing, retanning and fatliquoring is called neutralization. Especially from chrome and other mineral tanned leathers this process is of great importance if consistently satisfactory results are to be achieved in leather manufacture. Collagen bound acids from the surface of the skins and the major part of the acid associated with unfixed or the loosely fixed chrome may be removed by relatively prolonged but simple washing before neutralization. Their removal by washing before neutralization prevents interferences in dyeing, fatliquoring or retanning and may be regarded as a part of the process of neutralization, effecting economy of alkaline salts and time required for neutralization.
- b) **Retanning:** This may be a single chemical process or may be a combination of reactions applied together or more usually consecutively. The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. The effects are dependent on both the primary tanning chemistry and the retanning reactions. Retanning can involve many different types of

chemical reactions. These include mineral tanning with metal salts (including chromium (III) applied to chrome tanned leather), aldehydic reagents, hydrogen bondable polymers, electrostatic reactions with polymers or resins or any other type of synthetic tanning agent (syntan).

- c) Dyeing: This is the colouring step. Almost any colour can be struck on any type of leather despite the background colour, although the final effect is influenced by the previous processes. Colouring almost invariably means dyeing. Applying dye in solution or pigment, to confer dense, opaque colour, can be performed in the drum or colouring agents may be sprayed or spread by hand (padding) onto the surface of the leather.
- d) Fatliquoring: This step is primarily applied to prevent fibre sticking when the leather is dried after completion of the wet processes. A secondary effect is to control the degree of softness conferred to the leather. One of the consequences of lubrication is an effect on the strength of the leather. Fatliquoring is usually conducted with self-emulsifying partially, sulfated or sulfonated (sulfited) oils, which might be animal, vegetable, mineral or synthetic. This step might also include processing to confer to the leather a required degree of water resistance.

Finished leather reflects all the operations and processes which have taken place from the stage of flaying the carcass to the final finishing operations before sorting. It is difficult and in some cases impossible to correct faults which have occurred in process prior to leather 'finishing'. The term 'leather finishing' relates to those operations which give the leather its final appearance and make it useful, attractive and appealing to its users. Finishes on leather also serve as a protective coating.

Formerly leather finishing was done by coating varying mixtures of natural dye-woods, mucilages, oxblood, milk and white eggs on the leather surface. This gave an even and pleasing

appearance to the finished leather. This method of finishing continued for a long time until the period 1916-1918 when American Leather manufacturers introduced first pigment finished leathers in the market. The introduction of pigment finishing created a revolution in the technology of leather finishing and has thus made it possible to produce leather of uniform appearance even from raw materials with defective grain.

While in use, leathers are subjected to various mechanical stress and strain. In order that the finishing coats on leather can also stand the severe mechanical handling, they should satisfy the following physico-chemical requirements (Eliseyeva, 1959):

- a) An elongation adequate to maintain the coating when the leather is stretched to the maximum permissible degree.
- b) A modulus of elasticity in line with the hardness of the coating.
- c) Stability against repeated tensile and compressive strains and bending.
- d) Elasticity, ensuring the coating will return to its original condition when the deforming forces no longer act.
- e) Durability against weathering and ageing
- f) Durability against rubbing on dry and wet leather
- g) High adhesion
- h) Permeability to water vapour and air, ensuring the hygienic properties of leather.

Finishing is one of the main processes for the preparation of leather. The application results of the aqueous polymer dispersions are affected not only by the properties of the polymer dispersions, but also by the coating conditions. Tanners usually care very much about the properties of the coating on the surface of leather, such as softness, touch, toughness, covering

grain damage and mending properties, adhesive force to leather, wet fastness, solvent resistance, flex resistance(Zhu, 1998; and Price, 2001). This study mainly focuses on the study of acrylic based finishing formulations suitable for application in leather finishing.

1.1 The Chemistry and Development of Finished Leathers

Leather is a collagen- mineral or vegetable tannin substrate possessing either positive or negative ionic charges respectively. Control of these surface charges is necessary for retanning, fatliquoring and dyeing purposes but necessarily the case in their surface coatings. Leather finishes are used as surface coats to enhance their aesthetics, comfort, softness, stiffness, flexibility, etc. leather “dressing” as finishing used to be called was an art, but presently it is a technology that uses guided procedures for leather surface coatings. It is the duty of “coating specialist” to apply a well-defined blend of materials that makes up a coating which best accomplishes the desired effect on the surface in question. Blends or formulations of surface coatings of synthetic polymers, polyacrylates, polybutadiene and polyurethanes all in dispersion forms are used as film forming materials. The superiority of polyurethane dispersions over polyacrylate dispersions is principally shown, in many cases, in their considerably improved physical fastness properties. For example, they can be used virtually alone for finishing high quality leather splits as well as in the manufacture of extremely soft leathers (Walther, 1988). The dispersed solutions of polyacrylates, polybutadienes and polyurethanes are used for providing a base for the top coat, top coatings of leathers and binding colouring materials to the leather surface. Acrylic resins are dispersions of polyacrylates such as ethyl acrylate, methyl methacrylate, and methyl acrylate. These dispersed particles form surface films that tends to allow water gain access to the interstices, because the hydrophilic group (COOH) accumulates

on the surface of the particles. In order to reduce this draw back to the bearest minimum, crosslinkers or waxes are usually added to the formulation.

There are three different types of leather finishes which are commonly used by leather finishers.

They are:

- a) Water- type Finishes: these may be based on pigments, protein binders, such as casein, shellac, gelatin, egg and blood albumen, waxes and mucilaginous substances like decoction of linseed. The finishes are mainly used for glazed-finish leathers which are required to be glazed by glazing machine. The binders in the finish are intended to hold the pigments or dyes in suspension and be bound firmly on the leather surface. Softness, glazing properties and handle are contributed by water-soluble plasticisers, waxes and mucilaginous matters. Water-type finishes based on pigments, dyes and resin dispersions including urethane are increasingly used to achieve special effects on the finished leather. The use of such finishes has produced many improvements over the conventional protein based finishes such as better adhesion and flexibility of the finish, improved filling and sealing properties and greater uniformity of the finish.
- b) Solvent-type Finishes: In contrast to water-type finishes solvent based finishes contain as a binder either polyurethane or colloid cotton (nitro-cellulose). These finishes are dissolved in organic solvents such as butyl acetate, cyclohexanone, etc. these finishes are widely used for finishing upholstery leather, bag and case leather etc. solvent finishes based on vinyl resin instead of nitrocellulose have shown improved resistance to flexing and better flexibility at low temperature . They (Shaw, 1952) have been successfully used on upholstery leather, case leather and certain military leathers where low temperature flexibility is necessary.

c) Emulsion-type Finishes: Emulsion-type finishes consists of emulsion of nitrocelluloses or resins. Such emulsions are being widely used to confer ‘combining properties of water and lacquer finish’. Lacquer/emulsion topcoats for upper, garment and glove leather are gaining wide acceptance (Shaw, 1952).

In leather finishing the three types of finishes mentioned above can either be used alone or in combination with one another. The choice depends on the specific effects desired on the finished leather.

The suitability of leather for shoe manufacture is based upon the twin abilities of being able to exclude water, but allow air and water vapour to pass through the cross-section of the upper. This is the basis of foot comfort when shod. The properties are so important that attempts have been made to mimic them in synthetic materials, by the so-called poromerics of which to date, none has been successful. One typical example is the failure of Corfam in the 1960s (Kanigel, 2007). The properties of leather depend on the origin of the raw materials, how the pelt is prepared for chemical modification, how that modification is conferred chemically, how the leather is lubricated and finally how the surfaces are prepared. Leather can be made as stiff and as tough as wood, as soft and flexible as cloth and anything in between. It is the traditional art and craft of the leather technologist to control the parameters and variables of processing to make leathers with defined desired or required properties. It is from the creativity of the leather scientists that the range of leathers that can be made is continually widening.

1.2 Statement of the Research Problem

The interest on this study stemmed from the increasing incidence of worn shoe complaints involving lack of finish fastness, and other performance defects thus leading to investigation of the influence of finish components, and impregnating resins. It would be impossible to investigate a comprehensive range of resin dispersions, thus simple formulations of acrylic based binder have been selected.

1.3 Research Aim and Objectives

This research is aimed at preparing a formulation of acrylic polymer dispersions suitable for application in leather finishing.

1.3.1 Objectives

The aim of this research was achieved through the following objectives:-

- 1 Preparation of acrylic polymer formulations.
- 2 Retannage of chrome tanned leather.
- 3 Application of the prepared formulation on the retanned leather.
- 4 Testing of the finished leathers to determine the water vapour permeability, and other physical properties of the leathers.

1.4 Justification

Among various leather finishing materials, acrylic resin finishing agents are popular in leather industry due to its good film-forming performance, good adherence, simple production process and low production cost, large market share in both product kinds and yields, and has a bright market prospect and application prospect. The suitability of leather for shoe manufacture is based upon its twin ability of being able to exclude water and allow air and water vapour to pass through the cross-section of the upper. This is the basis of foot comfort when shod (Kanigel, 2007). Therefore the testing for the water vapour permeability of the finished leathers is necessary.

CHAPTER TWO

2.0 LITERATURE REVIEW

Polymer binders are the main components of aqueous finishing preparations. Three chemically different synthetic types of binders are widely used in leather finishing: acrylates, butadiene, and polyurethanes. They all have specific properties depending on their chemical basis. In order to find out which is the right synthetic binder for a certain application, the typical attributes for these binders have to be established. Typical attributes of acrylates include: good light fastness, good heat stability, good hydrolytic stability, good drying properties, good wet properties, good adhesion, poor embossing properties, poor cold flex properties, poor covering properties, low price range. In order to ascertain which type of polymer fulfils best the necessary properties of a finish, the key attributes which make up for the quality of finished leather have to be demonstrated. For the choice of polymers not only the expected character and properties of the leather are of importance but also the behavior of the binder during the finishing operations. These include stability, compatibility with solvents, flow out properties, penetration properties, drying properties, stackability of the leather, ironing- and embossing properties of the finished leather, and smell of the binder. Binders with small particles size have better penetration properties. These are good for impregnation, but less suitable for covering grain defects and not good for embossing. The acrylic binders are very useful for tightening the grain. The harder a product based on the same chemistry, the better it tightens the grain. That means an acrylic with a Shore A hardness 45° would be better than one with 25°. On the other hand the leather becomes slightly firmer. Ever since its acceptance as a binder in leather finishing, the acrylic polymer resins have been enjoying a deserving preference rather as 'filler-binders' for excellent impregnating and grain-sealing properties. As film-forming binders they are also acknowledged

for their performance on base coats by virtue of their film-adhesion, grain tightening and sealing effects.

Acrylic polymers have found extensive use in leather finishing. The basic properties that these polymers offer are softness, heat and light stability, and favourable economics. Acrylic polymers have been the choice of basecoats for all types of leathers. The softness of acrylic resins, penetration and adhesion, lightfastness, good molding under the embossing press, and their low cost have contributed to the success of acrylic resins for decades. However, traditional acrylic polymers have been regarded as having high tack, modest fill and coverage, poor embossing plate release, cut-through under harsh conditions (sharp plate and high temperature), and moderate to poor flexibility. These shortcomings were usually remedied by the addition of other resins such as butadienes or polyurethanes or processing additives such as fillers, waxes and crosslinkers. The challenge for acrylic polymers has been to offer soft polymers with reduced tack, improved embossing properties, and physical properties that improve performance of acrylic leather finishes (Campbell and Choi, 1997).

Campbell and Choi (1997) have developed the SB (soft binder) line of polymers in order to close the performance gap and thus extend the performance of soft acrylic polymers. The new technology employed by SB polymers was able to obtain a soft hand with improved embossing, plate release and print retention, higher flexibility, and better rub resistance. These polymers represent a new generation of acrylics that are alternatives to polyurethane and butadiene systems typically used in performance oriented applications. The SB (soft binder) resins represent a new line of acrylic emulsion polymers for leather finishing. The SB family raises the level of performance of acrylic polymers so that soft acrylic resins can be used as sole binders in basecoat formulations. Because of its large contributions in the total finish, the aesthetic and physical properties of the finish rely heavily on the basecoat, which in turn is governed by the

resin properties. The rub resistance test was carried out using the Crockmeter tests, the VESLIC test, and the Taber abrasion test. Crock and VESLIC type tests contain two independent factors that need to be considered. One is the ability to prevent discolouration or transfer of colour onto the cloth or felt pad, and the other is the ability of the finish to resist damage. Polymers that form a good film and are hydrophobic give good performance in preventing discolouration. However, when it comes to resisting finish damage, harder or higher T_g polymers perform better than soft polymers in acrylic and polyurethanes. These factors are important in achieving a good rub resistance and were considered in the design of SB polymers. The SB polymers are all soft polymers but each represents a different level of hydrophobicity, softness, and toughness in order to achieve a balance of properties such as adhesion, fill, and flexibility to the coating. The softest SB-100 was a slight improvement over traditional acrylic resins. The tougher SB-150 showed an improvement over SB-100 in dry VESLIC test but similar performance in the wet VESLIC test. The new technology SB-200 showed even better rub resistance in both dry and wet VESLIC tests. In this study anyway, the factor varied has been the amount of the binder in the finish formulation which was applied three times on the leather. The SATRA method was used to test the rub resistance of the finish. The finishes showed excellent dry rub resistance, while the wet rub resistance of the finish was improved as the binder in the formulation was increased.

Leather finishers have at their disposal an exciting range of film forming polymeric synthetic resin dispersion binders based on acrylic, methacrylic, butadiene and acrylonitriles (synthetic rubber lattices for finishing splits and deep buffed leathers), and polyurethanes which despite their relatively higher price than the natural binders are increasingly used in view of their strong filling, covering, adhesion, elasticity, fastness and pull-up properties. Self-crosslinking epoxy resin emulsions are also finding their way in leather finishing.

Richard *et al.*, 2005 synthesized acrylate-based block copolymers by atom transfer radical polymerization (ATRP) processes. The polymers were multiblock copolymers consisting of poly(butyl acrylate) or poly(lauryl acrylate) soft blocks and hard blocks composed of poly(methyl methacrylate), poly(isobornyl acrylate), or poly(styrene) homo- or copolymers. These polymers were evaluated as drug delivery matrices for the controlled release of paclitaxel from coronary stents. Depending on the ratio of hard to soft blocks in the copolymers, coating formulations were produced that possessed variable elastomeric properties, resulting in stent coatings that maintained their integrity when assessed by scanning electron microscopy (SEM) imaging of over expanded stents. In vitro paclitaxel release kinetics from coronary stents coated with these copolymers typically showed an early burst followed by sustained release behavior, which permitted the elution of the majority of the paclitaxel over a 10-day time period. It was determined that neither the nature of the polyacrylate (n-butyl or lauryl) nor that of the hard block appeared to affect the release kinetics of paclitaxel at a loading of 25 % drug by weight, whereas some effects were observed at lower drug loading levels. Differential scanning calorimetry (DSC) analysis indicated that the paclitaxel was at least partially miscible with the poly(n-butyl acrylate) phase of those block copolymers. The copolymers were also evaluated for sterilization stability by exposing both the copolymer alone and copolymer/paclitaxel coated stents to e-beam radiation at doses of 1-3 times the nominal dose used for medical device sterilization (25 kGy). It was found that the copolymers containing blocks bearing quaternary carbons within the polymer backbone were less stable to the radiation and showed a decrease in molecular weight as determined by gel-permeation chromatography. Conversely, those without quaternary carbons showed no significant change in molecular weight when exposed to 3 times the standard radiation dose. There was no significant change in drug release profile from any of

the acrylate-based copolymers after exposure to 75 kGy of e-beam radiation, and this was attributed to the inherent radiation stability of the poly (n-butyl acrylate) center block.

Acrylic polymer emulsions (PA) have been widely used for leather coatings, with interest in polyurethane dispersions (PU) increasing in the last decades because they are environmentally friendly materials (Chan and Chen, 1988; Martin *et al.*, 2000; and Biemond *et al.*, 2008). A blend of the two systems and synthesis of the polyurethane/polyacrylate (PUA) composite latex particles has also been reported (Wu *et al.*, 2002). These systems can be tailored to form a unique core shell and interpenetrating network structures, a technique which has been widely practiced in recent years (Zhang *et al.*, 2001; Shi *et al.*, 2003; Barrere and Landfester, 2003; Anzlover and Zingir, 2005).

Wei *et al.*, (2006) had in their study attributed the unique role cationic acrylic polymers play in leather and some other industries to their special molecular structures. Cationic acrylic polymers are polymers or copolymers made from cationic surfactants or acrylic monomers with positive charge, their basic characteristic is having positive charge on their surface or on themselves. With positive charge, cationic polymers can not only neutralize negative charge, adsorb and collect objects with negative charge on surfaces, but also can control bacteria, resist dust, and static effect, so they have been widely used as surface conditioning agents for super absorbent resins, silk fabrics and paper, antistatic agents for polymer materials, coagulants for sewage treatment, a kind of necessary and effective additive in solid free oil drilling fluid system, and a kind of electrodeposition coating, etc (Qiang *et al.*, 2005). In leather industry, besides special retanning agent and new finishing agent, cationic acrylic resin has also been widely used as a sewage treatment agent. Therefore, the preparation and application of cationic acrylic resins are

of high interest in the research of acrylic resin polymers (Fan and Shi, 2001; Zang *et al.*, 2006; Hu and Ma, 2007).

The synthesis of acrylic polymer dispersions is obtained by free radical polymerization. A free-radical polymerization has three principal steps:

- a) Initiation of the active monomer
- b) Propagation or growth of the active (free-radical) chain by sequential addition of monomers, and
- c) Termination of the active chain to give the final polymer product.

Many free-radical reactions are conducted in solution. Important water-soluble polymers that can be synthesized in aqueous solution include poly (acrylic acid), polyacrylamide, poly (vinyl alcohol) but poly (methyl methacrylate) can also be polymerized in organic solvents. Another technique that utilizes water as a heat-transfer agent is emulsion polymerization. In addition to water and monomer, a typical reactor-charge for an emulsion polymerization consists of a water-soluble initiator, a chain-transfer agent, and a surfactant such as the sodium salt of a long-chain fatty acid. An example of a commonly-used water-soluble initiator is the persulphate–ferrous redox initiator, which yields a radical sulphate anion through the reaction.

Various analytical techniques have been developed to study structural changes in complex composite biomaterials such as leather. Fourier transform Infrared (FTIR) is particularly one of the most adaptable analytical methods for molecular structural elucidation especially of organic based compounds, particularly in the analysis of raw materials (Ibrahim *et al.*, 2011 and El-Nahass *et al.*, 2013). Rashid *et al.*, 2014 has been able to elucidate the molecular structure of sulfonated melamine glycoxylated based resin using the FT-IR and Nuclear magnetic resonance spectroscopic analysis, a technique which has also been reported in the past by the following

researchers (Ibrahim and Gawad 2012; and Nashy *et al.*, 2012). Infrared spectra of commercial polymers in substance or film provide information on the main constituents of the polymer, i.e., the monomers from which it was synthesized, the plasticiser, and the inorganic additives, such as pigments or dulling agents, provided they are present in sufficiently high concentrations (Nursten and Selby, 1966). The technique however, do not normally yield information about the degree of polymerization, antioxidants, initiators, chain transfer agents, the type of polymer, i.e., whether block or graft copolymer, or mixture, and the nature of other constituents present in small quantities. Additional difficulties can occur through overlap of the absorption bands due to the individual components. The versatility of the technique can be greatly increased by combination with chemical methods of analysis but advantage has not been taken of this here. Spectra of films of reference polymers: poly (methyl acrylate) (PMA), poly (ethyl acrylate) (PEA), and Poly (butyl methacrylate) (PBMA), has been reported not to differ greatly from those of the corresponding monomers (see Table 2.1) Nursten and Selby (1966).

Table 2.1: Absorption Bands of Acrylate Monomers, Acrylate Polymers, and their Assignments (Nursten and Selby, 1966)

Monomers (cm ⁻¹)	Polymers (cm ⁻¹)	Assignments
-	3440	C=O overtone
2870	2875	CH ₂ stretching
1725	1730	C=O stretching
1455	1470	CH ₂ bending
1365	1380	CH ₂ bending
1270	1270	CO stretching
-	1240	CO stretching
1190	1165	CO stretching

In the study, the spectra of commercially available finishing materials: The Primal range (Charles Lennig, Ltd.), The Eukanol range (Farbenfabriken Bayer, A.G., Leverkusen), The Encryl range (Earnshaws Ltd., Northalerton), The Breon range (British Geon, Ltd., Barry), The boston range (Bostik Ltd., Leicester), mostly showed peaks characteristic to that of PEA.

Methods to determine molecular weight averages and distributions of polymeric and oligomeric materials have been devised and developed over many decades. Most of the early classical techniques were primary methods which usually yield only a single molecular weight average, based on theory and measurable constants. Of the classical methods only ultracentrifugation can determine a molecular weight distribution. Secondary methods, which depend on the availability of calibration materials, have largely supplanted the older classical techniques. Methods based on fractionation, with molecular weight characterisation of the fractions, or chromatography, with

continuous determination of molecular weight, is currently used to generate molecular weight distributions. Newer methods based on dynamic light scattering and viscoelastic measurements are available to determine the molecular weight distribution of difficult soluble materials. Development of methods to describe the molecular weight and compositional distribution of multimer polymers continues to be a vibrant research area (Cooper, 2004). However, in this study, the molecular weight of the polymer was determined by calculation from the intrinsic viscosity of the polymer binder using the famous Huggin's equation. The high value of the intrinsic viscosity was also reflected on the calculated molecular weight of the binder indicating clearly that the material is suitable for leather finishing.

Many methods are available for measuring viscosity of polymer solution. The Ostwald method is a simple method for the measurement of viscosity, in which viscosity of liquid is measured by comparing the flow times of two liquids of equal volumes using same viscometer. Mamza and Folaranmi, (1996) successfully determined the molecular weight of polymer blend systems by comparing their viscosities using the solution viscometric method. The resultant plots of relative viscosity with compositions are of the S-type, indicating two-phase formation with reversal of phases at intermediate composition. Comparison of the calculated and observed intrinsic viscosities shows higher calculated values. Data obtained using all solvents are similar, implying that polymer-polymer interactions are dominant over polymer-solvent interactions. Their results confirmed that the versatility of viscometric techniques and density measurements is not affected by the choice of solvent.

Type and ratio of the vinyl polymer have effect on properties of retanned leather; in fact fastness, heat stability, softness and tannage distribution depend not only from tanning agent concentration but also by distribution of molecular weight and comonomers ratio: then it is very important to choose the retanning agents on the basis on these factors. By modifying the

backbone composition, molecular weight and branched functional group polymers can be designed to give a specific performance. Acrylic acid is usually used in combination with acrylonitrile, acrylamide, and acrylate (esters). The acrylamide have a remarkable effect on the fullness, as the presence of amido groups gives to tanning agent compatibility with collagen fibres, resulting in better penetration and combination ability.

A comonomer that contains polar groups, such as $-\text{CN}$, CONH_2 , COOH , can increase the strength of collagen fibres. At proper ratio, it can also increase the stability to wet heat. For example the introduction of acrylonitrile into the molecule of the tanning agent can increase the tensile strength of retanned leather as it increase the combination of the tanning agent with collagen and produce more hydrogen bonds. However the introduction of polar groups harms the softness of the leather. The introduction of acrylic ester co-monomer (i.e. methyl acrylate) into tanning agents can improve the flexibility of collagen fibres of retanned leather and the extent of the improvement depends on the length of the carbon chain in the ester group. The copolymer with a methyl group inside the main chain, such as methylacrylic acid or methyl methacrylate, can produce a low tanning effect as it increases the distance between the molecules of the tanning agents and the collagen. For this reason, the side methyl group in the tanning agent does also harm to the strength, softness, fullness of retanned leather and the flexibility of the collagen fibres.

Wolfgang, (1993), had studied and gave a report of how glass transition temperature of polymer binders can affect the finish film properties such as hardness, flexibility, cold flex, etc. The glass transition temperature is another phase transition which occurs at a temperature at which the polymer changes from a hard, brittle, glassy substance to soft, flexible one. The glass transition is associated with amorphous regions and is interpreted in terms of the ability of regions or segments of the segments of the chains to move. These segments consist of a number of

repeating units. Below T_g , the internal energy is insufficient to allow them to move and they are frozen into position like the atoms or ions in glass. Above T_g the segments can move under the influence of thermal energy like the molecules in a liquid but with some constraint because they are attached to other segments in the chain. It follows that if T_g is below room temperature the polymer will be soft and flexible. If it is above room temperature the polymer will be hard and rigid. The value of T_g depends on interchain forces and chain flexibility, the greater the interchain attraction and chain stiffness the greater the value of T_g . Crosslinking increases T_g but the incorporation of liquids into the polymer may reduce it considerably. The glass transition point, T_g is responsible for the cold flex properties of the finish. All acrylic binders have a higher glass transition point than butadienes and polyurethanes in the same range of hardness. Therefore, acrylic binders are not appropriate for leather with high cold flex requirements. The T_g is related to the film hardness only as long as the same chemistry is involved. In this instance, the harder film should have the higher T_g . Basically; the T_g of the film is related to the T_g of the homopolymers of the used monomers. According to this theory, it is possible to produce acrylic binders which lead to films with low T_g , but, unfortunately, these films are very tacky especially during embossing or plating.

Melting temperature, T_m , is the temperature at which the crystallites of a polymer melt and the polymer becomes a viscous liquid. The process of melting involves separation of chains in crystalline regions so that melting points will inevitably depend on interchain forces. The melting point of linear polyethylene, with only dispersion forces between the chains, is only 135 °C but that of 6.6 nylon, with additional interchain attraction due to hydrogen bonding between >NH and >CO groups, is 280 °C. The melting point of polyacrylonitrile is 300 °C but the reduction of interchain attraction by introduction of methyl groups reduces the melting point of

methacrylonitrile to 115 °C (Moore, 1965). The melting point obtained in this study is similar to these reported values.

Moore, (1993) has reported that binders with small particle size have better penetration properties. These are good for impregnation, but less suitable for covering grain defects and not good for embossing. The acrylic binders are very useful for tightening the grain. The harder a product based on the same chemistry, the better it tightens the grain. That means an acrylic with a shore A hardness 45 ° would be better than one with 25 °. On the other hand the leather becomes slightly firmer. The Shore A hardness recorded in this paper is much higher than the reported ones.

Properties improved by increasing particle size include: Since larger particle size emulsions penetrate less into the substrate, or rather sit on the surface, the overall fill of the finish on the leather is increased. The ease of application generally increases with increasing particle size. There is less drag under the pad and a more uniform film is laid down improving the overall film continuity and ultimately the final aesthetic properties of the leather is improve. Cover and spreading rate are a function of penetration into the substrate, since this depends on particular size. It is apparent that these properties will improve with increasing particle size. Drying of finishes and films prepared from films of larger particle size emulsions are far quicker than the opposing smaller particle size emulsions. Gloss of NC lacquer emulsions increases with increasing particle size. This is ascribed to the nature of the drying mechanism of these products as opposed to the drying or coalescence of emulsion polymers.

Many of the properties and problems mentioned above are also influenced by many other factors, such as polymer constitution, molecular size, ionic character, torsional modulus, etc. Although particle size is very important for many of the reasons cited, actual polymer composition is by far

the most important factor controlling film properties. Generally, all emulsions prepared and available today consists of a range of particle sizes optimizing many of the final desired characteristics of the dried film. Thus in the final choice of an emulsion, for any particular end use or requirement, all factors influencing the desired properties should be considered.

Generally, it is important for the finisher to know what he can expect from certain binders. Depending on the leather, he should be able to adjust finishing formulations to the needs of his leather and machines available, with emphasis given to the base-coat formulation. Most physical properties of the finished leather are determined by the base-coat which represents a layer 3-5 times thicker than the top-coat. It has been reported by Moore (1993) that only acrylates and particularly polyurethanes are suitable for base-coat and top-coat applications. In this study, the finish formulation has been applied as a base-coat and therefore provides an adequate parameter that can influence the physical properties of the finished leathers under study even without applying any top-coat

Chrome tannage is still the most widely used method in the tanning industry. Hexavalent chromium has been determined in mixture of Cr (III) and Cr (VI) in some Egyptian tanneries in wet finishing bath (Eid and Nashy, 2002). Retanning process is one step of wet-finishing operations and is very important operation which overcomes the disadvantages of chrome tan.

Retanning agents can be inorganic mineral substances (chrome, aluminium, zirconium salts) or organic substances (aldehydes, vegetable tannins and syntans, resins). Retannage and choice of retanning materials is crucial to the physical binding and other surface coating properties of the finished leather compared with values in some literatures, the water vapour, the actual temperature reached by the leather, the amount of moisture present in the leather and how easily it can escape under the conditions of the application of heat (Landmann and Sofia, 1970). This is

important because new processes to speed the production of shoes, involve the action of heat and moisture on the leather. Many retanning agents have been developed to improve the chrome tanned leather properties. In general, the most retanning agents are vegetable tan and phenolic synthetic/organic tanning materials. In addition, many trials of acrylate polymers derivatives to be used as retanning agents (Anton, 1998), which are suitable for filling, softening, and even water proofing (El-A'mma, *et al.*, 1991), air permeability, (Jing *et al.*, 2008) or which combine all these properties. Many researches focused on grafting of different monomers onto the leather such as styrene, (Mohamed *et al.*, 2009) and acrylate derivatives (Abd El-Ghaffar *et al.*, 2003; Klasek *et al.*, 2003 and Klasek *et al.*, 2003). Two different nano-emulsions of styrene/acrylate copolymers have been prepared to be used as retanning agents (El-Shahat *et al.*, 2010). The main difference and characters of the two nano -copolymers were studied. The particle size of the two prepared co-polymers was proved by transmission electron microscope (TEM). The influence of the two prepared copolymers on chrome tanned leather as retanning agents was also studied. The properties of the retanned leather, namely, tensile strength and elongation at break were measured. The retanned leather was achieved with an improvement of mechanical properties, enhancement of thermal stability, uniform dyestuff, softness and firmness grain. Retannage and choice of retanning materials is crucial to the physical binding and other surface coating properties of the finished leather compared with values in some literatures, the water vapour, the actual temperature reached by the leather, the amount of moisture present in the leather and how easily it can escape under the conditions of the application of heat. Landmann and Sofia, (1970). Polyacrylic acid (PAA) retanning agents are an important class of leather filling materials, which can significantly change the softness, fullness, flexibility, thermoplastic and other physical and mechanical properties of leather. Researchers have investigated the relationship between structure and properties of PAA according to molecular weight (Liao, 1993 and Yang *et al.*,

1999), monomer composition (Ma *et al.*, 2001; Ma *et al.*, 2002 and Jin *et al.*, 2004), molecular architecture (Wang *et al.*, 2009 and Chai *et al.*, 2010) and other aspects, and have established certain empirical principles. According to the toughening and reinforcing theoretical aspects of the polymer, the mechanical properties are an important factor for filling properties (Phatak *et al.*, 2006 and Yong *et al.*, 2008). Chemical composition as well as the aggregating environment of a polymer is an important factor influencing mechanical properties of finished leathers (Zhang *et al.*, 2008).

Water vapour permeability of the finish on leather substrate controls the escape of moisture and is responsible for foot comfort when shod. It is one of the most precious physical properties of leathers, which may greatly affect the breathability and the comfortable feelings of leather goods (Kellert, 2004). There are plenty of capillaries among collagen fibres in leathers as well as lots of hydrophilic groups on the collagen chains. They may endow leathers with good water vapour permeability, compared with other synthetic clothing materials (Kyoji, 2000). Researchers have reported different methods of measuring the water vapour permeability of leathers. Keyong *et al.*, (2013), studied the water vapour permeability of leathers using the Grey System Theory (GST). The Grey relation analysis was employed to analyse the main affecting factors, and the contributions of each factor to the water vapour permeability of leathers were investigated and compared. The results indicated that GST can be used to investigate and calculate the water vapour permeability of leathers, and the techniques have been reported to be effective and convenient. The Grey System Theory (GST) is a mathematic method. Different ‘colours’ were used to describe whether the information is clear or not. “Black” indicates unknown or uncertain information, “white” indicates exact (or clear) information, and ‘grey’ indicates partially clear and partially uncertain information. Since the emergence of Grey System Theory (GST), in only

about 20 years, the GST has been improved rapidly and greatly. In the meantime, it has also been applied extensively and deeply in plenty of such fields as society, economy, science and technology, agriculture, industry, ecology, weather, petroleum, geology, hydrology, water resources, medicine, hygiene, securities, finance, and law, by systematic analysis, model establishing, and results predicting with great achievements (Hu *et al.*, 2002; Zhang *et al.*, 2004; Tang and Liu 2005). However, few studies have been reported on the application of Grey System Theory in the field of leathers as at when the writers did their study. The Grey System Model is made up from the physical structure parameters, chemical property parameters (i.e. groups on the collagen chains) and the water vapour permeability of leathers. The information is partially unknown and partially clear. At the same time, because the structure characteristic parameters and water vapour permeability may vary with different leathers, this system may be regarded as a Dynamic Grey System (Chen and Tien, 1996 and Wu *et al.*, 2012). According to this theory, a Grey Model (GM) may be set up. Using the ‘white’ information (clear or exact information) in the Grey System, the water vapour permeability of different leathers may be calculated immediately, conveniently and effectively. It may also be helpful to know more about the water vapour permeability mechanism of leathers. In this paper, the water vapour permeability cup method has been employed to determine the water vapour permeability of both the finished and unfinished leathers. The water vapour permeability cup is a popular method to determine the water vapour permeability. Ideal results may usually be obtained for the materials with a good humidity resistance. Marcinkowska and Ewa (2000 and 2001) used the water vapour permeability cup method and prototype-measuring instrument (Hy-tester) to study the moisture transporting in leather and leather-like materials for clothing and shoes. It was reported that the standard error, as well as total and partial uncertainties, was successfully discussed by the statistical and mathematical analysis.

There are many factors that may affect the water vapour permeability of leathers. For example, the thickness, density, water-absorbing ability, and aperture ratio of the samples may contribute to the water vapour permeability of leathers. Besides, the water vapour permeability of leathers may vary greatly with changing the temperature and relative humidity of the environment when the experiment is conducted. Because of the complexity of leathers and the uncertainty of affecting factors on the water vapour permeability of leathers, it is difficult to study the water vapour permeability of leathers and few studies are reported in the field.

Tang *et al.*, (2002) have studied the water vapour permeability of unfinished leather, polyurethane finished leather, filmed leather and synthetic leather. The results showed that finishing play an important role in affecting the water vapour permeability of leathers. According to their results, the water vapour permeability of unfinished leather is far better than those of the other three samples. It was also found that the water vapour pressure difference between the two sides of the sample and the transferring action of hydrophilic groups on collagen chains are two main factors affecting the water vapour permeability for unfinished leathers. In cases of finished leather, filmed and synthetic leather, however, the mechanism of water vapour permeability is only the transporting of water molecules through capillaries in leathers, driven by the water vapour pressure difference between the two sides of the leather samples. It was also found that the traditional processes of tanning, retanning, and fatliquoring may greatly affect the water vapour permeability of leathers according to the following researchers (Bosch *et al.*, 1999 and Fan *et al.*, 2005).

Williams-Wynn (1969) had reported that acrylates are known to have water vapour permeability of $0.9 \text{ mg/cm}^3/\text{hr}$ that correlates to 71.5 % set. The factors which affect the water vapour

permeability of the finish are the chemical nature of resin, amount applied and film integration achieved on the particular substrate

In all that has been done, acrylics are used in top coats, mostly in admixture with urethanes, indicating an on-going interest for their further development as a versatile resin binder. There are a number of aqueous dispersed resin binders based on acrylics, polyurethanes, synthetic rubbers available in the market. After selection of the proper binders the formulation of the finish is worked out according to requirements, which in essence is the focus of this study.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Experimental equipments

- i. BS- U Viscometer,
- ii. Hand Pump,
- iii. Lastometer (Muver, Model 5077-ET),
- iv. Thermometer,
- v. Thermostat,
- vi. Water vapour permeabilimeter (Muver Model 5011),

3.1.2 Finishing consumables

- i. Resin Binder (Nycil, AE 558),
- ii. Wax (Lepton-Wax A, Basf),
- iii. Penetrating agent (EE 8044, Pixel Colour),
- iv. Liquid Syntan (Syntan-Re, Smit-zoom),
- v. Powdered Syntan (Syntan-SA, Smit Zoom),
- vi. Bagaruwa (Vegetable Tannin),
- vii. Wet Blue sheep skins,
- viii. Toluene.

3.2 Methodology

3.2.1 Viscosity measurement of the resin binder

The solution viscosity measurement of the Binder was carried out at 25 °C using toluene as the solvent. 1 g of the solid polymer was dissolved in 50ml of the solvent to give a stock solution of 0.02 g/dl. The stock solution was divided into four portions, one was left that way while the other three were diluted by adding the solvent in the order 5 ml, 10 ml, and 15 ml. 10 ml of the pure solvent was introduced into the viscometer and the elution time, t_0 was obtained. This was repeated for each solution and the corresponding elution time was obtained and recorded as t_1 , t_2 , t_3 , and t_4 respectively.

3.2.2 Melting point determination of the resin binder

A melting point capillary was used. A tiny sample of the resin Binder was placed on a piece of weighing paper. The samples were placed into three melting point capillaries which have been previously sealed at one end. The capillaries containing the samples were then inserted into sample compartment of the melting point apparatus Barnstead Electrothermal A9100 (UK), and the instrument was switched on with a set temperature of 0-400 °C. The capillaries containing the samples were heated slowly and the temperatures at which melting occurred was observed and read out from the scale of the instrument.

3.2.3 Preparation of leather substrate

Five (5) pieces of sheep skins in the blue state was weighed (4.5 Kg) and then soaked in 9 Kg of water (i.e. 200 % of the sheep skins) at 50 °C for 15 minutes. The leather samples were then neutralized under this condition with 1 % NaHCO_3 for 45 minutes and the resulting pH of the bath was determined at the end of the operation. The samples were then rinsed with 200 % water at 50 °C for 15 minutes. The leather samples were then retanned using the following retanning

agents: liquid syntan (4 %) for 20 minutes, powdered syntan (6 %) for 10 minutes, and bagaruwa (6 %) for 60 minutes sequentially in accordance with established procedures in 200 % water at 60 °C. Finally, 6 % of fatliqour was added in 80 % water at 60 °C for 30 minutes. The leathers were then horsed up overnight, hanged to dry at room temperature for 45 minutes. The samples were then conditioned and hand staked before finishing. The leathers were cut into two groups of five leathers each in order to finish them according to one with the finish labeled A1, A2, A3, A4, A5 and the other without a finish labeled B1, B2, B3, B4 and B5 respectively.

3.2.4 Preparation of the finish formulations

The ingredients for the preparation of the finish formulations were weighed in grams (g) using an electronic weighing balance and were introduced into five containers and was stirred vigorously for proper mixture. Five different quantities of the resin binder were incorporated as shown in Table 3.1.

Table 3.1: Finish Formulations

Additives/Ingredients	Formulations				
	(g)	A1	A2	A3	A4
Acrylic Resin	125	150	175	200	250
Pigment	6.25	6.25	6.25	6.25	6.25
Water	50	50	50	50	50
Penetrator	6.25	6.25	6.25	6.25	6.25
Wax dispersions	8.75	8.75	8.75	8.75	8.75

3.2.5 Application of the finish formulations on the prepared leather substrate

A spray gun was used to apply the finish on the prepared leathers at room temperature under a fume hood. The finish formulations were applied on the retanned leathers three times in order to obtain adequate cover and were allowed to dry at normal temperature and after which it was plated using a hot electric pressing iron.

3.2.6 Water vapour permeability test

This test is used to determine the effect of the surface coat on porosity of the leathers. Weighed coated leather samples were placed inside thermostated sample holders containing 20 cm³ of water in water vapour permeabilimeter (Muver Model 5011) for 1 hr. The test sample capsules together with the leathers were weighed again to take the difference in accordance with IUP 15. Water vapour permeability (P_{wv}) is calculated as: $P_{wv} \text{ (mg/cm}^2\text{/hr)} = 7640 M/d^2xt$, where, M= mass gain between weighings in milligrams; d² = area of diameter of sample in cm², t = time in minutes between first and second weighing.

3.2.7 Lastometer test

Circular samples of the coated and uncoated leathers were cut and placed on an electronic lastometer (Muver, Model 5077-ET) respectively and were tested for distension and grain burst strength in accordance with official methods (SLTC, 1996). The forces (Kg) and displacement (mm) at burst was obtained from the corresponding digital print-out. Distension as a good index of film strength is a measure of the extent to which the film will extend before film breaks. The film strength in Kg/mm is established as the product of the force at break per unit area of the net distensions, i.e., grain film strength (Kg/mm) = Force (Kg)/ Distension (mm).

3.2.8 Shore A (°) hardness test

The grain side of the leather was placed on the Shore A Hardness Tester/Durometer (Muvier Model: 5019/5023-1/5023-A) to measure the degree of hardness.

3.2.9 Wet rub fastness test

A rectangular piece of the leather samples was cut, and for each track 20 mm wide. The grain side of the leather to be tested was rubbed with pieces of standard wool felt under pressure with a given number of forward and backward motions. The SATRA machine was used, the samples were examined after 32, 64, 128, 256, 512 and 1024 revolutions of the dry and wetted pad and given scores of 0, 1, ½, 2,2/3, 3, ¾, 4, 4/5, and 5 when compared with a standard grey scales. A score of 1 is given to a sample with very poor resistance to rubbing effect while a score of 5 is ascribed to a sample with excellent resistance to rubbing effect. 0 is applicable to samples that were damaged due to the rubbing effect.

CHAPTER FOUR

4.0 RESULTS

4.1. Examination of the Resin Binder

4.1.1 Viscosity and molecular weight measurement of the resin binder

Viscosity is an integral property of a fluid that offers resistance to flow. It is due to the internal friction of molecules and mainly depends on the nature and temperature of the liquid/solution. Results of solution viscometry of the polymer are presented in table 4.1 below. The elution time measured in seconds of the varied concentrations was transformed into relative viscosity, specific viscosity, and reduced viscosity. The plot (fig 4.1) of reduced viscosity against concentration was extrapolated to the intercept which correlates the intrinsic viscosity of the polymer. The intrinsic viscosity was found to be 227 dL/g, and the calculated average molecular weight of the polymer was 4.03×10^5 (see appendix II).

Table 4.1: Solution Viscosity Measurement of the Resin Binder

Dilution factor	Conc.	Time	Relative viscosity	Specific viscosity	Reduced viscosity
(cm ³)	(g/dl)	(sec)	η_{rel}	η_{sp}	η_{red} (dl/g)
+5	0.040	155	131.6	5.62	140.5
+10	0.020	92	68.6	2.93	146.5
+15	0.013	74	50.6	2.16	166.2
+20	0.010	60	57.6	2.46	246.0

t_0 (secs) = 23.42

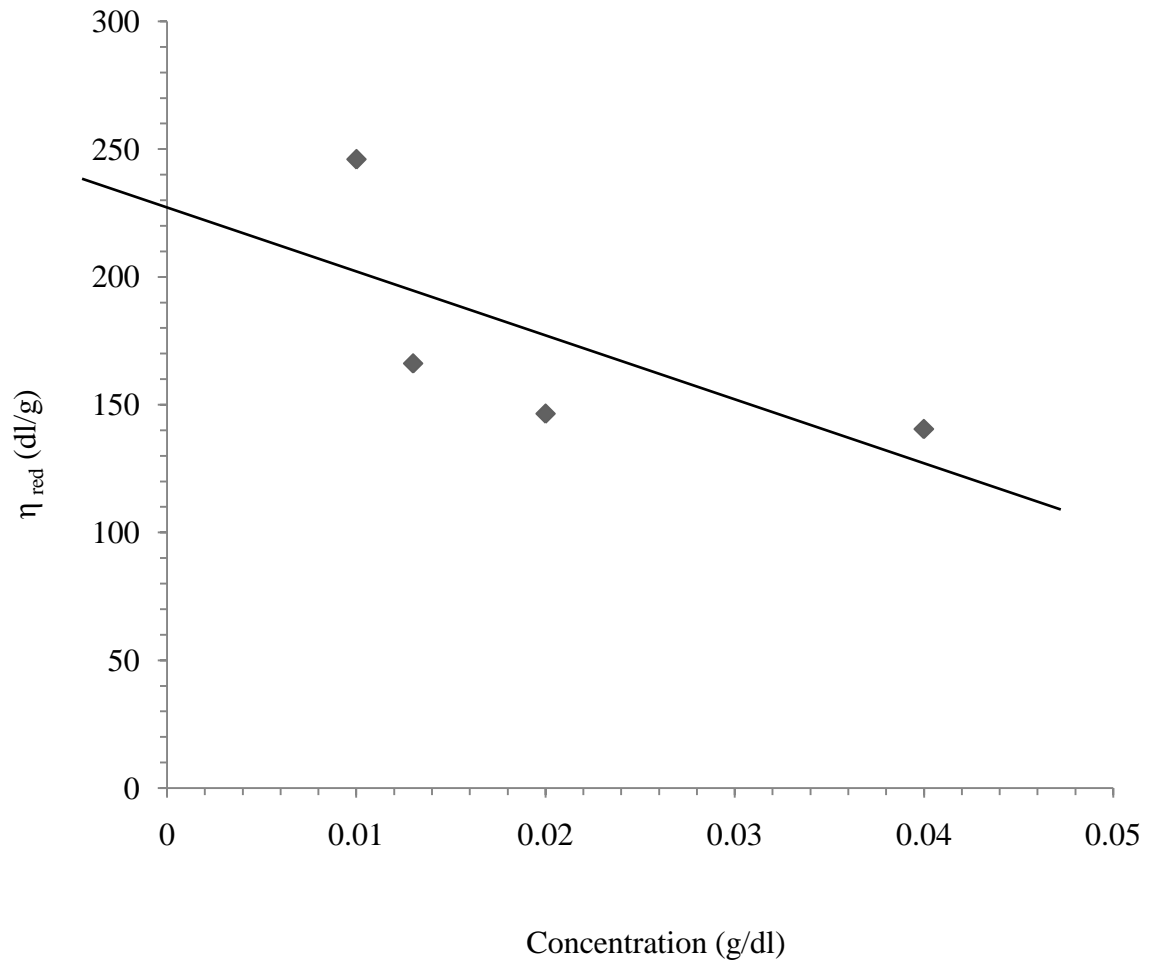


Figure 4.1: Plot of Reduced Viscosity versus Concentration

4.2 Physical Testing of the Finished Leather

4.2.1 Water Vapour Permeability of Leather

Water vapour permeability tests on the coated and uncoated acrylic resin finished leathers were conducted and the results are shown in Table 4.3, and the graphical plot of the water vapour permeability against the acrylic offer is shown in Figure 4.3.

Table 4.2: Effect of Acrylic Dispersion on Water Vapour Permeability of Leather

Sample Code	Resin Offer	Mean mass	Mean Wvp	WVP per unit
(Coated)	(g)	(g)	(mg/cm ² /hr)	thickness (mg/cm ² /hr/mm)
A1	125	0.18	18.71	11.62
A2	150	0.28	29.10	23.28
A3	175	-	-	-
A4	200	0.62	64.45	43.54
A5	250	1.10	114.34	47.84
<hr/>				
(Uncoated)				
B1	-	3.20	332.6	220.26
B2	-	4.08	424.1	350.49
B3	-	3.18	330.54	277.76
B4	-	4.00	415.78	349.39
B5	-	3.25	337.82	268.11

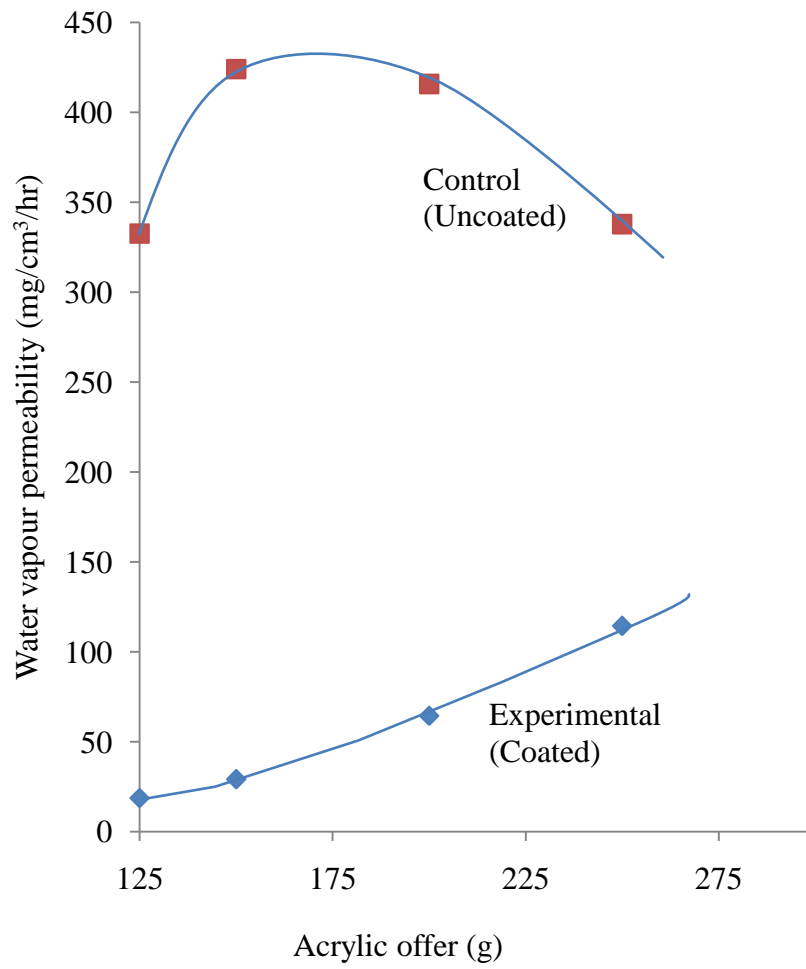


Figure 4.2: Water Vapour Permeability of Finished (Coated) and Unfinished (Control) Leathers

4.2.2 Distension and bursting strength

The distension and bursting strengths of coated and uncoated acrylic resin finished leathers were carried out, and the results are shown in Table 4.4, and the corresponding plot is shown in Figure 4.4.

Table 4.3: Lastometer Tests on Leather Samples

Sample Code (Coated)	Resin Offer (g)	Distension (mm)	Bursting Load (kg)	Bursting Strength (Kg/mm)
A1	125	8.60	42.65	4.959
A2	150	8.30	31.24	3.763
A3	175	7.30	30.74	4.210
A4	200	6.86	40.91	5.960
A5	250	9.80	56.16	5.730
<hr/>				
(Uncoated)				
B1	-	6.9	27.82	4.03
B2	-	7.7	35.29	4.58
B3	-	6.5	32.21	4.96
B4	-	6.9	37.87	5.49
B5	-	7.0	39.81	5.68

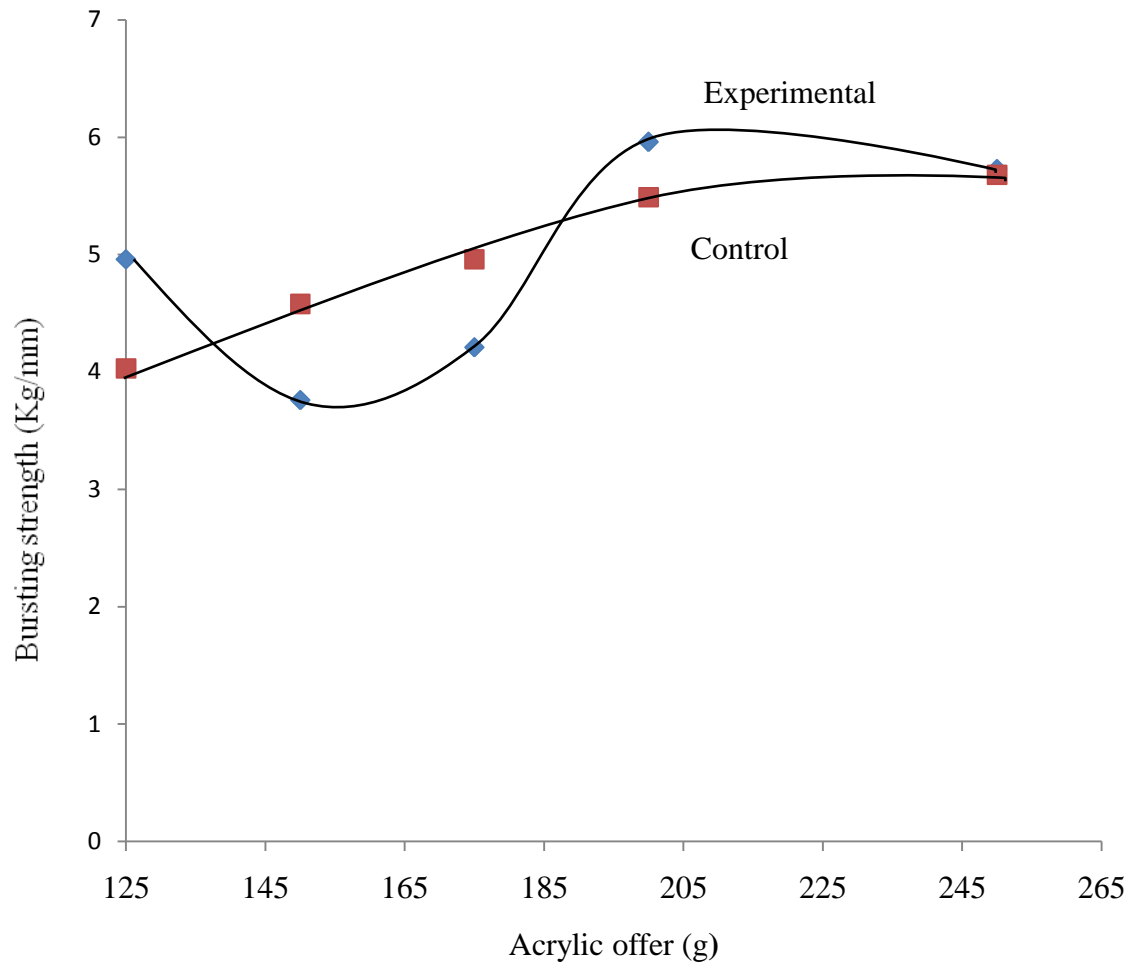


Figure 4.3: Bursting Strength of Finished (Experimental) and Unfinished (Control) Leathers

4.2.3 Shore A (°) hardness of finished leather and melting point of binder

Film hardness of the acrylic resin coated leathers and the melting point of the binder was carried out on the acrylic resin coated leathers and the results are presented in Table 4.5 below.

Table 4.4: Determination of Shore A (°) of Finish Film and Melting Point of Resin Binder

Tests	Values
1. Shore A (°)	
A1	77.7
A2	77.3
A3	80.0
A4	73.7
A5	70.7
2. Melting range (° C)	361.7-370

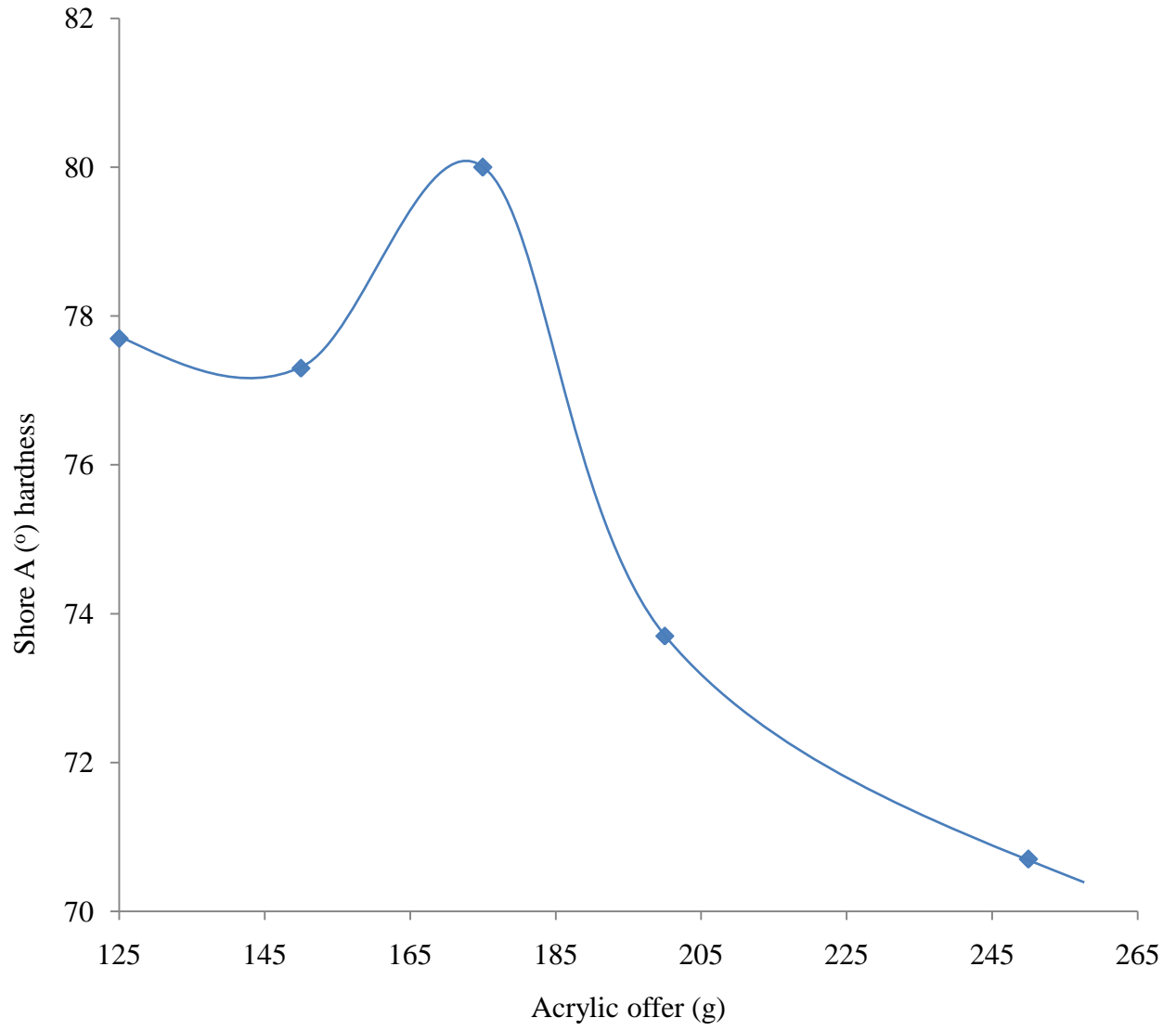


Figure 4.4: Shore A Hardness (°) of Finished Leathers

4.2.4 Wet rub fastness

Wet rub fastness tests were carried out on the acrylic resin coated leathers and the results of counts in seconds and the corresponding Grey Scale ratings are presented in Table 4.6.

Table 4.5: Effect of Finish Formulations on Wet Rub Fastness of the Coated Leathers

Sample	Acrylic Offer (g)	32	64	128	256	512	>512<1024
A1	125	2	0	-	-	-	-
A2	150	3	½ or 2	3	1/2	0	-
A3	175	3	3	3	0	-	-
A4	200	4 or 4/5	4	4	3	0	-
A5	250	4 or 4/5	3 or 3/4	3 or ¾	2	1 or 1/2	0

CHAPTER FIVE

5.0 DISCUSSION

Results of solution viscometry of the resin binder are presented in Table 4.1. Viscosity is a measure of the resistance of a fluid to flow. Anderson and Dea, (1967) stated that viscosity is one of the most important analytical and commercial parameters in polymers because it is affected by the size and shape of macromolecules. Viscosity of the resin binder in toluene was found to depend on binder concentration. In this study, the elution time measured in seconds of the varied concentration was transformed into relative viscosity (η_{rel}), specific viscosity (η_{sp}) and reduced viscosity (η_{red} (dl/g)). The plot of the reduced viscosity (η_{red} (dl/g)) against the concentration (g/dl) was used to obtain the value of intrinsic viscosity $[\eta]$. This plot is shown in Figure 4.1 whereby the value of the intrinsic viscosity (227 dl/g) was obtained from the intercept of the reduced viscosity at zero concentration. This is the measure of the inherent property of the binder. The intrinsic viscosity was used to determine the molecular weight of the binder using the famous Huggins equation: $[\eta] = KM^a$. The calculated viscosity average molecular weight is 403,000, and the details of the calculations are shown in Appendix II. This result showed that the binder is a high molecular weight polymer suitable for use in leather finishing. It has been reported that for a material to qualify as a binder in leather finishing the material must have an average molecular weight in the range 300,000 to 1,000,000. The physical observation of the resin showed that it is a hard, flexible and stretchy binder. These properties are important in leather finishing whereby it is required that protective colloids should provide inherent internal stability. The synthetic production of acrylic resins in modern time uses emulsion polymerisation techniques which aims at producing very fine particle size emulsions, due to the higher concentration of total surfactant in the emulsion (Braithwaite, 1977).

Intrinsic viscosity of the acrylic binder is for determining the average molecular weight of the polymer binders. The inherent viscosity (IV) in figure 4.1 affords a convenient basis for determining the molecular weight of the resin. The higher the inherent viscosity, the higher the molecular weight. The calculated molecular weight of 403,000 is less than the molecular weight of Elvacite acrylic resins of 450,000, but is still higher than most other commercial acrylic resins. These high molecular weight resins have generally better toughness and abrasion resistance and are less readily attacked by solvents than lower molecular weight resins of similar composition. The Weight profile could correlate with the film hardness (shore A) property and in fact whether it is soft, medium or hard binder. The knowledge could lead to further development of much improved binding polymer or copolymer for leather finishing. Hence value of the molar mass is important.

Methylmethacrylate resins form harder films than the ethyl or butyl methacrylate resins and have higher softening points as indicated by glass transition temperature values. The copolymer resins are intermediate in hardness and tack temperature between the methylmethacrylate and softer butylmethacrylate resins. A good balance between film flexibility and hardness can often been achieved with a properly selected copolymer. Some grades contain carboxylic acid groups to enhance pigment wetting and gloss, and to improve adhesion to metallic and cementitious substrates.

Permeability to water vapour is a property of major importance in garment leather, upper leather, and articles of clothing in general. It is this property which permits escape of perspiration from the body, and thus contributes to the comfort of the wearer. Table 4.2 shows the effect of the acrylic finish on the water vapour permeability of the original retanned leathers. It also tries to demonstrate the effect variations in the quantity of the acrylic offer (g) in the formulations had

on the water vapour permeability of the finished leathers. First it is worthy to point out that the water vapour permeability of leathers especially for upper shoe determines the level of foot comfort obtainable when shod. For this particular test, the general average of these results is surprisingly high. This is partly due to the method of measurement (see Tests Applied in methodology) and partly by the fact that the quantities of the finish applied are not large enough in order to obtain adequate cover, or probably the pores were not properly closed (contributions from the retannage). However, the permeability of the uncoated samples was significantly reduced by the application of the finish formulations when compared to that of the coated leathers (Figure 4.2). Sample A1, which has the lowest quantity of the resin binder in the formulation, was unexpectedly the least permeable with a water vapour permeability of 11.2 mg/cm³/hr. Sample A5 with a water vapour permeability value of 47.84 mg/cm³/hr was the most permeable. These results, which are the reverse of what was expected with the thought that increasing the quantity of the binder in the finish were supposed to close up more available pores in the substrate, may be attributed to the hydrophilic nature of the acrylic resin binder. For the coated samples increase in the amount of the acrylic offer in the formulation produced a corresponding increase in the water vapour permeability of the finished leathers, except for A3 which has a permeability of 22.39 mg/cm³/hr which was slightly lower than that of A2 which has a permeability of 23.28 mg/cm³/hr. The reason for this behavior could not be ascertained at this point of the work. The uncoated samples generally as expected produced a much larger water vapour permeability of the originally retanned leathers when compared with their finished counterpart. The values obtained in this work are typical for uncrosslinked acrylates when used as basecoats. When crosslinked and used as topcoats on the other hand, the water vapour permeability could be as low as 0.9mg/cm²/hr (Williams-Wynn, 1969). However, the uncoated samples gave values that are consistent for uncoated shoe upper and lining leathers (BASF,

1982). By scientific fitting, the calculated water vapour permeability of the leather samples may serve as a reference in leather-making and leather goods making to get leather goods with good water vapour permeability. The factors that affect the water vapour permeability of leathers may be classified into two fields. One is the structure parameters, including thickness, density and so on. The other is the feature parameters of leathers such as the kinds of leathers (including hydrophilic groups on the collagen chains in the samples, the kind of leathers, and the leather chemicals used in leather making). Because many factors may affect the water vapour permeability of leathers, some questions may arise and need to be solved in order to improve the water vapour permeability of leathers: which are the main factors and which are less important? Which contribute more to the water vapour permeability and which contribute less? Which need to be strengthened and which need to be weakened to get leathers with reasonable water vapour permeability? By putting the research into use, leathers can be produced with ideal water vapour permeability by appropriately controlling the factors in leather-making. According to study, water-absorbing capacity is the most important factor affecting the water vapour permeability of leathers. In other words, among the four factors studied, water-absorbing capacity affects the water vapour permeability of leathers the most. The next is the thickness of the samples. Comparatively speaking, the contributions to the water vapour permeability from the real density and aperture ratio are really less (Keyong et al., 2013). Therefore, in order to improve the water vapour permeability of leathers, the most efficient way is trying to increase the water-absorbing capacity of leathers. This is demonstrated according to the result in figure 4.2 where the water vapour permeability of the experimental increases as the acrylic offer in the formulation increases which in effect contributes to the water-absorbing capacity of the leathers. The hydrophilic nature of the binder was able to contribute to boost the water absorbing capacity of the leathers and as the quantity of the offer in the formulation increases, the water vapour

permeability of the leathers was also increasing. Therefore, it is better to choose leather chemicals with polar group to increase the water affinity of the collagen fibres in leather-making. The results could also be guidance in choosing leather materials (such as shoe or garment with good water vapour permeability). The second contributing factor to the water vapour permeability of leathers is the thickness of the leather samples. From figure 4.2, the effect thickness of the control samples is obvious having observed that the water vapour permeability of the samples is not the same. Thinner leathers usually have advantages of providing high water vapour permeability.

The result of the distension and bursting strength both for the coated sample and for the uncoated is depicted in Table 4.3. The distension (mm) values of the coated acrylic binders generally were above the minimum standards. This may be attributed to the resistance of the stress on the acrylic film formed on the grain surface of the leather. However, the uncoated leathers have lower distension (mm) values. Also from the table, the bursting load (Kg) of the coated leather samples were generally enhanced by the application of the acrylic resin binder, the finished leathers (A1 to A5) generally requires more load to cause failure when compared to their corresponding unfinished samples (B1 to B5), however the quantity of the resin in the formulation of the finished samples, i.e., the factor varied in this experiment had no effect on the lastometer load as no consistent trend. Similarly, the bursting strengths of the coated leathers were also enhanced by the application of the acrylic resin surface basecoats (Figure 4.4). A1 which has the lowest resin offer (125 g) with 42.65 kg had a higher load at failure than A2 (150 g resin offer) 31.24 kg which was followed closely by A3 (175 g resin offer) with a value of 30.74 kg. This decreasing trend with increasing resin offer altered, and started to increase with A4 (200 g resin offer) having a value of 40.91 kg, and A5 (250 g resin offer) having the highest with a value of 56.16

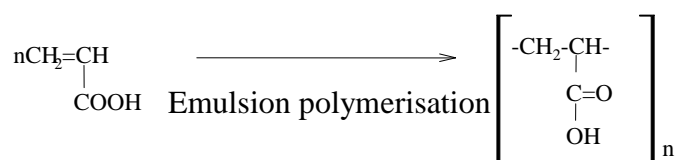
kg. The lastometer extensions were not very much influenced by the factors varied in this experiment. The finished samples (A1 to A5) increased the extension when compared to that of the unfinished samples (B1 to B5) which serves as the control (see table 4.3). As a way of comparison, A1 when compared to B1, significantly increased the distension from 6.90 mm to 8.60 mm and this follows accordingly for A3 and A5 which increased from 6.50 mm and 7.00 mm respectively to 7.30 mm and 9.80 mm. Another significant parameter is the bursting (failure) strength of the finished samples when compared with that of the unfinished samples. There was an increase from 4.03 kg/mm to 4.96 kg/mm as we compare B1 with A1. The bursting strength of sample A4 and A5 also increases from 5.49 kg/mm and 5.68 kg/mm to 5.96 kg/mm and 5.73 kg/mm respectively. In general, the finish has provided adequate strength to the leathers without compromise to its extensibility. However, the effect of the acrylic offer in the finish did not follow any consistent order (i.e. increasing or decreasing). This behavior can be attributed to the differences in the sample thickness. Generally, this evidently showed that while there was no order of effect with respect to acrylic offer in the finish formulation, there was an increase in the lastometer behavior of the coated samples when compared to that of the uncoated samples. Table 4.4 shows the lastometer distension at finish failure (mm) and the lastometer load at finish failure (kg). It can be noted that the distension averages and bursting strength of the original retanned samples were lower than that of the finished leathers (figure 4.3).

Shore A Hardness ($^{\circ}$) of the acrylic coated leathers was determined, and the melting point of the resin binder were carried out and their results are presented in Table 4.4. The Shore A values ranged between 70.7 $^{\circ}$ to 80.0 $^{\circ}$. These Shore A Hardness ($^{\circ}$) properties of the leathers were well above the thresholds for impregnated acrylic soft binders. Wenzel (1993) has shown that the Shore A Hardness of impregnated binder was 25 $^{\circ}$. The above results therefore show that the resin

binder under study was most probably a hard binder. The property of acrylic finish film is assisted by a combination of a penetrator to increase its penetration power, because excessive deposition on the grain results in an inferior appearance. The factors that influence this are, a) the dependence of the penetration power of an impregnate on its contents of wetting agents and solvents, b) the influence of molecular weight of the polymer and, c) the influence of film hardness on the handle of the leather. Breugel (1969) had explained some basis of acrylic resin grain impregnation with the emphasis on the effects of addition of wetting agents and solvents on surface tension, viscosity and rate of penetration of leather grounds, noting that the penetration rates is dependent on the molecular weight of the acrylic polymer, the thermoplastic properties of the polymers was dependent on the molecular weight, and that the influence of film hardness on the handle of leather is only of minor importance, but leathers become increasingly firmer with increasing depth of penetration of the polymer into the leather. A5 with a shore A value of 70.7 demonstrated the lowest shore A hardness value, and was followed just above it by sample A4 with 73.7 Shore A ($^{\circ}$) value. The highest shore A harness of 80 $^{\circ}$ was demonstrated by A3, and was followed by A1 and A2 in that order with average Shore A ($^{\circ}$) hardness values of 77.7 and 77.3 respectively. Generally, there was a decrease in the shore A ($^{\circ}$) hardness values of the samples as the quantity of the resin offer in the formulation increases (Figure 4.4). The hardness of surface coating films is determined by the glass transition temperature (T_g). The T_g occurs at a temperature where polymers changes from hard, brittle, glassy substance to soft, and flexible one. Below T_g , the internal energy is insufficient to allow them to move and they are frozen into position like the atoms or ions in glass. Above T_g , the segments can move under the influence of thermal energy like the molecules in a liquid but with some constraints because they are attached to other segments in the chain. It follows therefore that if T_g is below room temperature, the polymer will be soft and flexible, but if it is above room temperature, the polymers will be hard

and rigid. Acrylic binders are known to have higher T_g than other binders, e.g. polyurethane and polubutadienes (Wolfgang, 1993). Because T_g relates to higher film hardness, the harder film should have the higher T_g . In leather finishing, where the binder is of the soft type with low T_g , during hot-plating these films are very tacky, and the finish formulation would require a plate release agent.

The Melting Point (T_m), of a polymer is the temperature at which the crystallite melts and the polymer becomes a viscous liquid (Moore, 1966). Melting Point is obviously one that can only be applied to a crystalline polymer and the melting point (T_m) of the acrylic resin was in the range of 346-371 °C (Table 4.4). This is an indication of good thermal stability due to the high molecular weight and polydispersity of the resin. The process of melting involves separation of chains in crystalline regions so that melting points will inevitably depend on interchain forces.



Scheme 5.1: Synthesis of Polyacrylate

Interchain forces leads to high cohesive energy. Many properties of polymer such as melting and softening points depend on this and therefore on interchain forces. A high cohesive energy is associated with a high softening or melting point (T_m). From Scheme 5.1, it could be deduced that the interchain forces in polyacrylate polymer resin would result from the attraction of the carbonyl ($-\text{C}^+=\text{O}^-$) and the corresponding hydroxyl ($-\text{O}^--\text{H}^+$) of the atoms.

Dry rub had no effect on the fastness of the finished samples in all the factors varied in this experiment. The overall fastness to wet rub was excellent with high mean value of 4 or 4/5. The

Sample A1 finish gave the poorest fastness with a score of (2) after 32 rubs, and was damaged beyond 32 rubs. The sample A4 gave the best fastness with a score of 4, equivalent to no damage after 128 rubs. All the finish formulations of the samples were damaged beyond 256 rubs. Table 4.5 shows the result of the wet rub action on the finished leathers. The samples were subjected under number of revolutions as indicated in table 4.5. Sample A1 had the least score (2 'poor') when examined after 32 rubs. The sample was damaged even before the 64 rubs could be completed. At 32 rubs, A2 demonstrated 'fair' resistance with a score of 3, 'poor' resistance with a score of $\frac{1}{2}$ or 2 after 64 rubs, the sample offered good resistance with a score of 3 after 128 rubs and then $\frac{1}{2}$ (very poor) again after 256 rubs, but was damaged beyond 256 rubs but less than 512 rubs. Sample A3 had 'good' (3) resistance to the rubbing action after 32, 64, and 128 revolutions, but was badly damaged beyond the 128 revolutions. Samples A4 and A5 demonstrated much better resistance to wet rub action with scores of 4 (which implies 'very good') and 3 or $\frac{3}{4}$ (implying 'very good') respectively after 128 revolutions of the rubbing action. Sample A4 still offered 'good', (with a score of 3), resistance after 256 rubs but was damaged beyond the 256 rubs. While sample A5 had scores of 2 'poor' and 1 or $\frac{1}{2}$ 'poor' after 256 and 512 rubbing actions, but was damaged beyond the 512 rubs. Generally, the resistance of the finished leathers to wet rubbing increases as the quantity of the binder in the formulation increases from A1 to A5. A score of 1 indicates very poor resistance to wet rubbing, whereas a score of 5 shows that the finish was not affected after 512 rubs with a wet felt pad. The performance requirements of a finish depend on the type of leather used, the application, and the final product. For, example, the performance requirements are different between full-grain for sports shoes and full-grain for upholstery leather. Polymers that form a good film and are hydrophobic give good performance in preventing discolouration. However, when it comes to resisting finish damage, harder or

higher T_g polymers perform better than soft polymers in acrylic and polyurethanes (Alexander and Chol-Yoo, 1997).

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The acrylic resin binder is a hard binder with a very large molecular weight, and has a melting temperature in the range 361-370 °C. This shows that the binder is a high polymer and possesses the properties suitable for application in leather finishing. The effect of the resin formulations on some physical properties of the originally retanned leathers have been studied and it is obvious that the finish had significant effect on such properties as water vapour permeability, lastometer, Shore A hardness, and wet rub fastness. The results showed that the finished leathers were better than their unfinished counterpart. Increasing the quantity of the acrylic resin in the formulations also increased the water vapour permeability and wet rub fastness of the finished leathers except for the lastometer tests and shoreA hardness where there was no specific trend in behaviour. All the formulations showed better and adequate response to all the properties tested when compared to that of the unretanned leathers. Sample A1 (125 g resin offer), however would not be suitable for use in leather finish formulations where wet rub fastness is a priority. Aesthetic properties are very important, but finishes must be durable and standards for upper leathers and must include an assessment of finish properties. This has been highlighted in literatures because of the increasing incidence of worn shoe complaints involving lack of finish fastness, and this report has shown that the quantity of components in finish formulations play an important part in determining wet rub resistance. The effect is probably from the resin binder dispersions.

6.2 Recommendations

It is suggested that future development should be aimed at producing components for leather finishes more resistant to water, or means must be found for inactivating the wetting agents present in the finish. While a comprehensive assessment of the effect of all finish components is impossible it is likely that a limited number are of interest to individual tanners who should ensure that new formulations are adequately tested before applying them to bulk production.

As finishing plays an important role in water vapour permeability in order to improve the water vapour permeability of leathers, studies should be done on how to improve the water-absorbing capacity of finishing agent. On the other hand, if the water absorbing capacity of finishing agent is too high, the wet rubbing resistance may be decreased. So the work should be done to find a balance to improve the water absorbing capacity without decreasing the wet rubbing resistance of leathers.

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APPENDICES

Appendix I: Retanning Process

All percentages were calculated based on the shaved blue weight of 4.5Kg.

Washing:

200% water at 50°C, for 15 minutes.

Neutralisation:

200% water at 50°C.

1% Sodium bicarbonate, for 45 minutes, pH 5.5

Rinsing:

200% water at 50°C, for 15 minutes.

Retannage:

200% water at 60°C.

+ 4% Liquid syntan, for 20 minutes.

+ 6% Powdered syntan, for 10 minutes.

+ 6% Bagaruwa, for 60 minutes.

Fat liquoring:

80% water at 60°C.

6% fatliquor, for 30 minutes.

Rinsed, horsed up overnight, hanged to dry, conditioned, and toggled.

Appendix II: Calculation of the Viscosity Molecular Weight of the Polymer from the Determined Intrinsic Viscosity

The intrinsic viscosity of the acrylic dispersion was $[\eta] = 22.7 \times 10^{-1}$.

Mark-Houwinks equation is $[\eta] = K \times M^a$.

The value of K can be obtained from the slope of the graph using the Huggin's Equation:

$sp/C = [\eta] + K[\eta]^2c$. Where the slope S is $K[\eta]^2$ is equivalent to the slope. The slope, S is given as:

$$S = \frac{\Delta y}{\Delta x} = \frac{200-130}{0.01-0.04} = -2333.33.$$

Therefore, $K[\eta]^2 = -2333.33$ and $K = \frac{-2333.33}{[\eta]^2} = -0.04528$

Then $[\eta] = KM^a$ (Mark-Houwink Equation), where M is the molecular weight of the polymer, and a = 0.660 is the solvent – solute parameter.

Taking log of both sides, $\ln [\eta] = \ln K + a \ln M$ and

$$\ln \frac{[\eta]}{K} = a \ln M$$

$$\ln \frac{227}{0.04528} = 0.660 \ln M$$

$$8.519839863 = 0.660 \ln M$$

$$\ln M = \frac{8.519839863}{0.660} = 12.90884828$$

$M = \text{Antiln} 12.90884828 = 403869.9813$; $M \cong 4.03869 \times 10^5$