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With best regards,

Ahammod Hossain July, 2007

#### AIM OF THE PROJECT WORK

Bangladesh is a developing country. It has only a few items for export i.e. garments jute, tea, crust and finished leather and finished leather goods etc. In these, Bangladesh earns a good amount of foreign currency by exporting leather and leather goods.

The aesthetic look creates great market demand of high quality finished leather today. So leather industries of Bangladesh are in a changing and challenging phase since a decade, to meet the market demand. The export turn over of Bangladesh from the leather industries has increased several hundred times presently after the banned of wet-blue leather export. At present, finished leather export is increasing more rapidly. After few years crust leather may be banned, so leather finishing technology is a present day requirement of leather industry. For this reason, time proved the finishing technology very much propitious to be learnt and practices sincerely to enable the leather technologist fit for coming future.

Leather is one of our indigenous raw materials based principle export items. A good number of shoe manufacturing industries and fancy leather goods industries have been already set up in Bangladesh. More industries are expected to be set up in near future. Currently leather is a fashion item, beyond the reach of average people's pocket. A wide variety of synthetics are coming up to replace leather but natural leather is superior to synthetic due to its natural look, feel and inherent properties. So, this is very right time to concentrate our mind on this much promised field building up our knowledge about them. The leather industry must be prepared to fight the leather substitute. In the overseas market glazed finished leather are price worthy. Glaze kid leather is one of the highest quality and most elegant upper leather, used mainly for the manufacture of fancy ladies and gents shoes and also fancy

leather goods. Besides, as people wants variety, so there the technology invents the two other types of glaze kid leather-they are: Wet-look glaze kid and Imitation glaze kid. The Bangladesh goat skins are usually considered the best. Nothing can compare with glaze-kid leather which can meet the requirements of absolute water proof ness, water resistance, flexibility and

wet rub-fastness etc. which are required to meet the demands of glazed -kid upper leather can be produced using protein binder.

The principle aim of this project work is to assess the film forming properties of Bangladesh goat skin and commercial process for the production of wet-look glaze kid leather. Taking in mind, all these above factors I have picked up my topic to achieve a successful result.

## CHAPTER ONE

## 1.1 HIDES, SKINS AND LEATHER

#### Hides

Heavy weighed skins of larger animals of more than 1m2 and a respective thickness of at leather several mm are termed as hides. According to weight, more then 30 lbs weighted greed salted cattle hide is called a 'Hide'. Example- cattle's, camels, elephants, horse, steers, etc.

#### Skins

The term skin used for the integument of smaller animals or immature outer covering of larger kind.

According to weight, cattle hide less than 15 lbs in the green salted state is called calfskin. Example- goat, sheep, calf, deer, pig, lizard, snakes, full frogs, turtles etc, and many fish skins like sharks, rays, scalps, different dolphins, cod, Pollack, haddock sales etc.

This classification has some exception in the case of outer covering of wild animals. For example, tiger and crocodile skin is as big as or sometimes bigger than cowhide but they are called skins.

#### Leather

Leather is a product made by stabilizing the protein of animal skins, which is found by chemical and mechanical treatment to give it new properties are called leather. To convert the raw hides and skins to leather the epidermis layer is first removed (except fur tanning) and before tanning appreciable amount of hypodermis layer is also removed during fleshing. Leather is therefore made from derma only.

Leather has definite physical chemical and biological properties, which can be used in our daily life and industries. It is a non-uniform material containing collagen fiber network, tanning materials, fat, dyestuff, finishing materials and moisture.

## **1.2 COMPOSITION OF HIDES AND SKINS**

Raw hides and skins are composed of protein, fats, carbohydrates, mineral matter and water. The relative proportions of these constituents vary depending upon the species, age, feeding and other habits of the animals. The composition of animal skin can be stated to be approximately as follows:

Composition	On the green weight
(a) Water:	60-70%
(b) Protein:	33%
(c) Fats:	3%
(d) Minerals:	0.5%
(e) Coloring:	Very little.

## **1.3 PROPERTIES OF LEATHER**

Leather is a not-uniform material consisting of a collagen fiber network, tanning material, fat, dyestuff etc. and water, compared with other substances such as plastics, the water content is very high and may fluctuate considerably depending on the relative air humidity. The greatest flotation in the water content as function of the relative air humidity is observed in chrome leather. Water repellent agents, which have a so-called 'Open' waterproofing effect, do not influence this property. On the other hand, the effect of the relative air humidity on the water content is noticeably reduced by strong fat-liquoring such as is given, for example, to classical waterproof leathers. One property, which depends on the porosity and is therefore very much dependent on the moisture and fat-contents, is the heat transfer coefficient (heat conductivity). The heat transfer co-efficient is linked directly to the specific gravity (as a measure of the porosity), which is changed, for example, by the uptake of moisture, rolling or the incorporation of hat tic substances.

## 1.4 GLAZED KID LEATHER

The glaze kid also called glace kid is highly glazed fancy leather manufactured from special quality goatskin and is for the manufacture of fancy ladies and gents shoes and also fancy leather goods.

The gloss of glaze kid has some specially and differ from the gloss of other types of upper leather like box, corrected grain chrome retained upper leather etc. when glaze after finish, reflect light in the same was in done by a big piece of mirror. On the other hand, if we look to the surface of a glaze kid through a microscope against reflected like it will appear like the night sky or winter- a cloudless sky with millions of shining stars in it. Skin indicated that the glace kid surface consists of hundreds and thousands of tiny mirrors like plane surface.

## **1.5 PROPERTIES OF GLACE KID LEATHER**

- 1) The glace kid leather should have special types of gloss.
- 2) This type of leather should have degree of roundness when folded with grain side out, resiliency and must not be papery.
- 3) It must posses' sufficient strengths like tensile, bursting, tear etc. good feel and resistance to grain creakiness.
- 4) This type of leather should be non-stretchy and only that much of stretchiness is allowed which is absolutely necessary for wearing comfort.
- 5) It should have open, silky, flat, smooth and clear grain.
- 6) It should have sufficient water resistance and wet rub fastness.
- 7) Drop and wet friction resistance.
- 8) Non- thermo plasticity of finish film that ensures excellent gloss and brilliance of the finish film under ironing machine at maximum temperature.
- 9) Pleasing hand smooth and natural touches and looks on the finish film.

10) Good coverage at the bottom and base coat with ideally helpful for polishing and glazing as well in case of crust leather with defects like pinholes, scratches vein marks and roughness of grain.

## Chapter Two

### 2.1 GOATSKIN

Goats are hardy animals that can live on a side variety of food and can supply meat and milk. They are adaptable to difficult climates and are popular in Asia, Africa, and South America. The original sources many of the goatskins are villages of widely diversified areas, so the quality varies greatly. Also important in determining the qualities of the goatskins are the type of animal, the method of slaughter, the method of cure, and the marketing practices of the area of origin. Between the villages and the world market there is a system of collectors and dealers. The practices of handling skins and the business methods of each area have long been established by custom and tradition. These factors, different in each part of the works, are important in determining the quality, characteristics, and price of the skins. The skins are identified by the area of origin and are sold either on a size specification or by the pound.

## 2.2 PROPERPERTIES OF GOATSKIN

The characteristics property of goatskin is following below:

(a) The grain layer of goatskin usually occupies approximately 24 to 25% of the total thickness of the skin.

(b) The tight-natured fiber of goatskin is recognized.

(c) In the grain layer the collagen of goatskin fibers are compactly woven.

(d) There are more elastin fibers in goatskin than in sheepskin, and a relatively greater amount is present in the neck and backbone regions.

(e) In goatskin a very low angle of weave is usually found even in the butt area.

(f) A considerable amount of reticular tissue is present in goatskin.(g) The goatskin has a wider pattern of hairs and a denser structure of skin.

(h) The goatskin has straight hair follicles, and consequently straight hairs. The hair follicles in goatskin are quite deeply rooted and dip down roughly 0.8 to 2.9 mm. below the skin surface.

(i) The glands and fat cells are very much less in number of goatskin.

## 2.3 SOURCES OF GOATSKIN

These are tougher and more tightly fibred than sheep, and have a very hard-wearing grain. There are no domestic supplies in the U. K. and tanners have to import them from Bangladesh, India, Pakistan, East and West Africa, Ethiopia, Yemen, South Africa, Southern Europe and Central and South America. Large supplies are also available from the Far East. The raw skins are dry-salted, wet-salted or simply dried, and then baled for shipment to the tanneries.

#### **Bangladesh:**

Bangladesh skins of direct interest to upper leather tanners are confined to Dhaka, Dinajpur and Kushtia.

'Wet blue' goatskins in an unhaired, chrome-tanned condition have become a major export commodity from India and Bangladesh.

#### India:

Raw goatskins obtained from India, usually from the Kolkata districts, are invariably of a miscellaneous quality and size.

#### Africa:

East Africans often suffer frain damage due to disease and drying faults and the majorities are used for the production of suede. These are usually suspension-dried on a frame. From Nigeria the skin of the red goat of 'Sokoto' is one of the finest obtainable, 'kanos' too are popular, as they are uniform in size and shape and are spared the many hazards of the nomad herds. These skins are used for all types of kid upper leather.

### 2.4 STRUCTURE OF GOATSKIN

In many respects the skin of the goat may be regarded as having a structure intermediate between those of calf and sheep. The epidermis is thicker than in sheep skin and covers approximately 1.5 to 1.8% of the thickness of the skin. Unlike in sheep, hair follicles a goat are straight and less deeply rooted. The glands and fat cells, which are responsible for the sponginess of sheep leather, are very much less in number in goat skins and the glands are rather smaller in size. Hair muscle is well developed and longer in goat skin than in sheep skin.

The thermostat layer covers approximately 24 to 54% of the total thickness of the skin and is relatively thicker in the neck. A dense network of elastin is found in the goat skin covering approximately two-thirds of its thermostat layer. As in sheep skin, a relatively greater amount of elastin is present in the neck in the goat.

The corium proper in goat skin covers approximately 45 to75% of the total thickness of the skin, the percentage varying considerably over the entire area. The collagen fibres in this layer are fuller and firmer than those of sheep but are hardly equal to those of the calf. Unlike in sheep skin, fat cells and fat droplets are rarely found in this layer of the skin.

## 2.5 GRAIN PATTERN OF GOATSKIN

In many respects the skin of the goat may be regarded as having a structure intermediate between those of calf and sheep. The epidermis is thicker than in sheepskin and covers approximately 1.5 to 8% of the total thickness of the skin. Unlike in sheep, hair follicles a goat are straight and less deeply rooted. The glands and fat cells, which are responsible for the sponginess of sheep leather, are very much less in number in goatskins and the glands are rather smaller in size. Hair muscle is well developed and longer in goatskin than in sheepskin.

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The corium proper in goatskin covers approximately 45 to 75% of the total thickness of the skin, the percentage varying considerably over the entire area. The collagen fibers in this layer are fuller and firmer than those of the sheep but are hardly equal to those of the calf unlike in sheepskin, fat cells and fat droplets are rarely found in this layer of goatskin.

## Chapter Three

## **3.1 LEATHER FINISHING**

The term finishing refers to the further processing of the leather after crusting. The aim is to adapt the leather to suit the fashion demands of the consumer with regard to color surface effect etc.

The reason for this is probably that finishing of the leather had long been more of an art that science.

The grain far surface of the leather must be provided with coating which protects the leather from injuries caused by rubbing and scratching and from penetration of excessive moisture and dirt. This protective coating should impart to the leather a level appearance and wear a suitable at fain-high utility value and quality.

Leather finishes should not be affected by rubbing or peeling during the processing of leather end products should be resistant to heat, cold and moisture should not crack on extension or fixing and should be fast to staining and light.

Leather finishing may be expressed as the treatment of the fur face off the leather and/ or top section of the leather with materials, which will exchange the appearance of the leather and improve its properties for the purpose to which it is to be used.

## **3.2 OBJECT OF FINISHING**

- 1. Levelness of color on the leather.
- 2. Uniformity of shade from skin to skin and pack to pack.
- 3. Changing the color to that, which is required.
- 4. Imparting color or pattern to undid leather.
- 5. Giving a surface to the leather varying from matt to gloss.
- 6. Adding a transparent film through which the natural appearance of the leather may be viewed.
- 7. Adding a transparent colored film to the leather.
- 8. Covering the leather with and opaque film in order to obliterate all defects.
- 9. Alter the surface of the material, i.e. splits.
- 10. Improve the water resistance of the leather, i.e. the finish should not discolor or swell and hence protect the leather and retain its good appearance.
- 11. By filling the surface of loose leather improve the break of the grain.
- 12. Give a leather of optimum cutting value.
- 13.Seal the leather surface so that it remains clean.
- 14.Render the leather light fast; heat fast, fast to alkalis, fast to acids.
- 15.Render the leather resistant to a light pull up on lasting.
- 16.Improved the scuff resistance of the leather.

# 3.3 CHARCTERISTICS OF AN IDEAL FINISH FILM

#### **3.3.1 Flexibility and stretchiness:**

Leather is a flexible material with certain degree of stretchiness. If the film to the leather surface does not possess these properties to the same extent as leather, it will make the leather hard and the film crack in course of time.

#### 3.3.2 Adhesion:

The film should be firmly fixed to the leather surface so that the formal does not come out during use. The film should also adhere to the pigment particles and others very firmly.

#### 3.3.3 Holding power:

The film should have sufficient capacity to hold in it other substances like pigment, plasticizer etc. During drying or film formation no ingredient of the finish should precipitate out. The ideal film will never allow the plasticizer to migrate into the leather.

#### 3.3.4 Gloss:

The film should glaze by itself or should acquire this quality after glazing under glazing machine or hot plating or brushing.

#### 3.3.5 Abrasive Resistance and fastness:

The film should have sufficient resistance to abrasion for longer life and at the same time, it should hold the coloring materials so tightly that it does not come out when rubbed will a dry or wet cloth.

#### **3.3.6** Water proof ness and water vapor permeability:

The film should repeal water so that it does not spoil the leathery appearance of the finished leather at all but at the same nine, the film should hide all the defects in the leather.

#### 3.3.7 Thickness:

The film should be as thin as possible so that it does not spoil the leathery appearance of the finished leather at all but at the same time, the film should hide all the defects in the leather.

#### 3.3.8 Resistance to acid, Alkali and chemicals:

During use the leather comes on contact with dirt, mud, acid and alkaline fumes, sweat etc. this is especially true for leathers used by army in the field. The film on the leather should have therefore, sufficient capacity to protect the leather from these.

## **3.4 CLASSIFICATION OF LEATHER FINISHING**

Medium Based Non-aqueous 1. Varnish (linseed oil) 2.N.C 3. CAB 4. Alkyd 5. Vinyl 6. P.U Resin Emulsion 1. N.C. Lacquer Emulsion

- 2. CAB
- 3. Alkylic
- 4. Styrene-Butadiene
- 5. Polyurethane
- 6. Epoxy Co-polymer

#### 3.4 CLASSIFICATION OF LEATHER FINISHING











## **3.5 FINISHING MATERIAL**

#### 3.5.1 Pigments:

A pigment is any particulate matter that is insoluble in and essentially physically and chemically unaffected by the media into winch it is dispersed, three types of pigments are used in leather finishing:

1. Inorganic pigments (e.g. Iron, Oxide, Lead, Chromates, Titenium Oxide, Carbon black, Cadmium Sulfide, Ultramarine blue etc.)

2. Color lakes

3. Organic pigments (e.g.Monoazo, Disazo, Toners, Lakes, Phthalocyanine and metal complex and vat pigments).

Inorganic pigments are insoluble colored materials and have high opacity. These pigments are either prepared pigments or earth colors have the most body, covering power and permanency, hewing least affected by chemicals, but they lack brilliancy. On the other band, the prepared pigments have less body and covering power than the earth colors.

Color lakes, another group of pigments, are precipitated coal tar dyes and available in many shades and various degrees of brilliancy. And some fade on long exposure to light.

The organic pigments are normally insoluble dyestuffs available m different color ranges with different chemical and physical properties. Some new types of micro pigments are also transparent and soluble in some organic solvents.

The organic pigments give better brilliancy, but they have less covering power, less body, less setting, less light fastness and tendency to cause bleeding in comparison to inorganic pigments. Moreover, the organic pigments are expensive and are used in finishing high quality better grade upper leathers.

#### 3.5.2 Dyestuffs:

Soluble concentrated dyes are used for staining, brightening and enriching the color in water pigment finish. Soluble acid dyes of the same color as the pigment should be selected carefully as otherwise there may be bleeding of dyes; poor light fastness and poor dry and wet rub fastness. The use of brilliant dyes is very important for making aniline and semi-aniline finishes. Properly selected metal complex dyes may also be used for better light fastness and rub fastness.

#### 3.5.3 Film-Forming Materials:

These are the most important materials in leather finishing. The film forming materials may be classified according to their general chemical composition as follows:

#### (a) Protein:

All glazed finishing is done by the use of protein binders. The one specific advantage of this is capacity to retain the original grain characteristics of the leather as different from that finished by synthetic binders. Casein, gelatin, albumen etc. fall under this group and are used for aqueous glazed finishes.

#### **Casein:**

Casein is the most important protein binder and is widely used in finishing of leather.

#### Albumen:

Egg albumen and blood albumen used in finishing produce high gloss when leathers are friction glazed. Egg albumen is considered better than blood albumen.

#### Glue and gelatin:

Both glue and gelatin is produce from hide cuttings, fleshing, bones of animals etc. by extracting them by heat treatment. When the breaking of collagen molecule is slight, gelatin is produced and heavy breaking at higher temperature results in glue formation. The molecular weight gelatin is higher than that of glue.

#### (b) Shellac:

Shellac is a natural resin obtained from lac-a resinous exudation of insect " Lacier lace". Aqueous solution of shellac in Borax or Ammonia is used in leather finishing for glazed leather. Shellac is a good film forming material for leather finishes and it imparts waterproof ness, good luster, hardness and strength, fastness to wet rubbing and to light. The main disadvantage with this natural resin is that it is brittle and cannot retain the politicizes for long. Due to its inadequate fixing properties and brittleness it should only be added in small amounts.

#### (c) Synthetic resin binder:

The proteinious materials and shellac are used mainly for glazed leather and to some extent in making plated finish in combination with synthetic resins. For full grain, glazed finished leathers only first grade raw hides, with no or little grain defects, are needed, which are very scarce in our country. Moreover, the protein finishes can not meet the requirements of absolute waterproof ness, water resistance, flexibility, wet rub-fastness etc. which are required to meet the demands of modern leather and shoe manufactures as well as to fight the competition of leather substitutes. The development of synthetic resins has made greater utilization of raw materials, particularly of low grade stocks, possible by manufacturing corrected grain leathers of upgraded quality and greater cutting value for shoe and leather goods manufactures. The synthetic resins, which are used for leather finishing, can be broadly classified into two groups:

a) Synthetic resins for aqueous leather finishes and

b) Synthetic resins for non-aqueous leather finish.

The properties resins for bottom coat season are different from those required for pigment coat season and the resins for pigment coat and top coat seasons differ considerably. But there are certain properties, which are more or less common for resins of all the three coats. There are-

1. Softness and elongation

2. Glass transition temperature (Tg)

All resins for leather finishing should be soft and extensible so that the film formed may stretch with the leather without cracking the softness, of course, differing from coat to coat. A resin to be suitable for leather finishing must have stretchiness between 300 to 1000 p.c.

#### 3.5.4 Plasticizers:

A plasticizer is a material that increases the plasticity of mass. The function of the plasticizer is to keep the finfish film soft and flexible and it does> not crack both no solvent and types of politicize are in use.

#### a) Non solvent type:

Raw and blown castor oil, Specially treated linseed and tong and many other non-drying oils, glycerin, high quality sulphated oils come under non -solvent type are uses to plasticize the films of casein, shellac, albumen, gelatin etc. in the aqueous finishes.

#### b) Solvent type:

High boiling point solvents such as dibutyl phthalate, trictesyl phosphate, triphenol phosphate, dimethyloxy tetra glycol, benzophenone etc. are used to plasticizer nitrocellulose films.

#### 3.5.5 Wax emulsion:

Aqueous wax emulsion prepared by adding wax to soap solution, preferably Trietholamine soap with constant stirring are added to water pigment finishes to impart of smooth fell, waterproof ness and good gloss. The waxes, which are generally used for leather finishing, are: carnauba wax, paraffin wax, shellac wax, sisal wax etc. a 10 p. c. wax emulsion is commonly used in leather finishing.

Wax emulsions prepared from various waxes are for various purposes. Some wax emulsions from a perfect sealing coat with resin binders used in the bottom coat, some are glazable and can be used in the top coat. Certain wax emulsions reduced the tackiness of resin binders and prevent the leather from adhering to the hot hydraulic plate; others can give a slight waxy feel to the finished leather surface.

#### **3.5.6 Preservatives:**

As protein binders used in the preparation of leather finishes are liable to putrefaction, it is necessary to add preservatives after prevent decomposition. Many types of chemicals used as preservatives are:

- 1. para-Nitrophenol
- 2. para-Chloro-Meta-Cresol
- 3. para-Chloro-Metaxylenol
- 4. Sodium salt of Ortho-Phyenyl Phenol
- 5. Sodium salts of Di-Chloro, Tri-Chloro and Penta-Chloro Phenates.

#### 3.5.7 Modifiers:

These products give the leather the desired surfaced handled. A variety of finishes can be achieved such as smooth, blunt, slippery, supple, dry and waxy greasy or fatty. They are added to the topcoats or mostly applied as separate topcoat.

#### 3.5.8 Malting agents:

The heavily covered and coated leathers topped with lacquers tend to appear unnatural and unappealing in look. Therefore the gloss of the leather needs to be reduced without affecting other characteristics. For this purpose matting agents, either aqueous or solvent based, are recommended for incorporation in lacquer emulsion in certain proportion for top spraying, the amount depending on the extent of dullness desired. Besides the desired matt effect these products provide fullness, settled surface appearance, smooth handle and reduced thickness of the finish coat.

#### 3.5.9 Penetrator:

Mainly used for grain impregnation and base coating to achieve deeper penetration of the finishing agents below the grain layer. These products are water-miscible organic solvents and/or capillary active substance.

#### 3.5.10 Cross-linking agents and hardeners:

Poly isocyanates are used to harden polyurethane's. The film is formed by across linking reaction. The products based on poly functional aziridine compounds have a cross linking effect on dispersion binders.

#### 3.5.11 Fixing agents:

Formaldehyde is the must popular type of fixing agent to fix protein binders and a mixture of Formaldehyde and Acetic Acid is generally used as the maximum fixing capacity of Formaldehyde is found at acidic pH.

#### 3.5.12 Organic solvents and diluents:

A product based on Nitrocellulose, cellulose aceto buryrate and polyurethane requires the use of organic solvents. In addition, nondissolving thinners are used as low price extenders and also to regulate the rate of evaporation this does not apply to reactive lacquer components, as these must be used only with free solvents, which are from hydroxyl or amino groups.

Correct adjustment of the rate of evaporation is essential for these solutions. The rate of evaporation must not be too high and not too low because this will impair proper film formation, gloss, adhesion or flow out. The mixture of solvents with diluents should be carefully matched.

#### (a) Solvent:

Esters- ethyl acetate, propyl acetate, butyl and iso-butil acetate etc. Ketones- methyl ethyl ketone, cyclohexanone etc. Ether alcohols- ethoxy ethanol, ethylene glycole etc. Ether alcohol ester- ethoxyethal acetate, butoxyethal acetate etc.

#### (b) Diluents:

Alcohols- ethanol, n-butanol, di-acetone alchol, benzyl alchol etc. Aromatic- hydrocarbons-Toluene, xylene, white spirit, decalin, tetralin etc.

## 3.6 THEORY OF FINISH FILM

Season, containing film forming materials with other ingredients is applied on the leather surface in the liquid state and its dilution is so adjusted that sufficient time is available of uniform spreading of the season on the leather surface by hand or machine evaporation. As evaporation of volatile matters (solvent) continues, the solid content of the season increases with gradual decrease in film thickness till a constant thickness, which again depends on the concentration of nonvolatile matters in the season is reached and after which no decrease in thickness is noticed event though evaporation conditions. The molecules of the film forming materials present thus approach each other and since the inter molecular forces, called vender walls is forces are inversely proportional to the sixty powder of the distances between molecules, the force of attraction increases very rapidly with the decrease of molecular distance.

Many practical tanners have the wrong impression that as these molecules comes close to the nearest approach they chemically react (polymerize) and from the film. But this is true when polyurethane linseed mucilage etc. are used for parent leather finishing but which other materials like casein, shellac, acrylic or met acrylic resin, synthetic rubbers based on butadiene, vinyl resins, nitrocellulose lacquers etc. no such chemical reactions take place during film formation. The molecules in such films remain together due to vender walls force of attraction, which is also called residual valence or secondary valence forces. In the liquid or solid state the term internal pressure is also applied. The tensile strength flexibility, water resistance and practically all other physical properties of film naturally depend to a large extent on the strength of this secondary valance force. What is secondary valance force then? This is the force, which keeps the molecules in matters together just like the atoms in molecules remain together by the influence of primary valance force? The forces due to ionic, covalent, co-ordinate, metallic bonds and resonance in the molecules are the primary valance forces or inter known as Vender Waals forces are the secondary valance force Hydrogen bonding is a so kind of secondary valance.

The secondary valance forces are actually due to residual fields left about the molecules as a how after two or more atoms have combined together to a form a molecule through primary valance force. When electrons are transferred from one atom to another, as is in round in ionic bonds to forma molecule, the latter becomes a dipole with permanent dipole moment. Similarly when a molecule with dissimilar atoms is formed through co- violent bonds the canters of actions negative charges. The whole system thus will show a dipole moment. The same rule can be attributed when molecules are formed from atomic stages through other types of bonds.

In a molecule there may be several diploes but the overall dipole moment of the molecules is the resultant of 11 the dipole moments is it. For simplicity let us consider two different arrangements of equal and opposite charges at the corners of a square as shown in figure (a) and (b)



In fig (a) the canters of action of both the positive and negative charges are at the point 'O' and therefore the dipole moment in zero. But in fig (b) the centers of action of positive and negative charge are L and M respectively. The whole system electrically is thus a rod LM of length S. One end of which is negatively charge which an intensity 2e and the other end positively which the same intensity. The molecules with definite dipole moments are called polar molecules where as no polar molecules have no dipole moments.

Of course, dipole moments can be induced on many no polar molecules are separated from each other; the leathers become no polar again. This is called induction effect.

There is another effect called the dispersion effect by which no polar molecules may gain polarity. This type of secondary valence force Aries from the temporary relative displacements of the nuclei and electrons during the vibration of several parts of molecule with repeat to one another.

During film formation the dipoles rotate. If necessary and finally arrange themselves in ant parallel arrangements as shown below:

Polar molecule Intermolecular space This is called orientation effect.

Thermal agitation always tends to upset these alignments, so that this type of secondary valance force is highly dependent upon temperature. In a film, both attractive forces between dissimilar poles and repulsive forces between similar poles play their roles side by side, no doubt but due to orientation effect the average distances between similar poles and therefore overall resultant force is the attractive force, if, on the other hand the resultant force was repulsive, the molecules would behave like a perfect of forming any film.

## 4.1 PRINCIPLES OF GLAZED KID LEATHER

Glaze kid is light fine high-class shoe upper leather. Principle of glaze kid leather is designed depending its. Cartelistic like, full in substance, tine, smooth, lightly, glossy soft to feel, resilient, and non-stretchy etc, and also from, its physical quality requirements. On the whole its principle can. Be summarized in the following way.

Goatskins having length 70-90 cm without any defects and disease may be chosen for glaze kid leather. Soaking is done in as a usual manner, prolonged soaking is avoided as far as possible, because it may loose hide substance though, bacterial attack.

Liming is sharp and not very prolonged. Unhearing by painting is usually done because it keeps the goat hair unaffected, which is an important by product of glaze kid leather. After pointing pelts are also impedes in fresh lime liquor with certain quality of sharpening agent. After liming, sharp declining and bedding is done. After deliming and bating pelt should be flaccid, silky grain, clean and should lie in any position in which it is kept.

Cr-attaining can be done following both single and double bath process, but best known process according to the practice of Dr. Belaveky's is the skins are treated with chrome alum and dichromate in the same bath to which, after some time, hypo and acid are added. Liquor of tanning should not mask. Neutralization should do with mild alkalis and pH should be near scout 4.8. It will be better if we can avoid neutralizing syntax. Retaining is carried out in a way that there in no surface deposition. Direct dyes have been found to have good affinity for chrome leather, acid dyes are also need. Basic dyes are used to increase brilliancy in the topping. It must note contain any kind fat or oil to its surface and fact contain should not exceed 6-8%. Mainly used synthetic and semi-synthetic fat because sulphited fats are highly penetrative and make leather too soft and natural bats have very poor fixing power. So may come out on pressure. Finishing is very vital in glaze kid leather. It is essential to use smallest possible quality of pigment finish to preserve the natural grain of goatskins and to impart smooth and soft feel. It should be resistant to dry and wet rubbing and also key test should not break the finish film until the it is cracked by key test, in season coats, now-a-days caseins based water pigment finishes employed, some cases polyurethane finish is used. Stone polishing provides smooth grain. Top coat, protein binders, poly amide etc, used. Fixing is done by HCHO.

## 4.2 ASSORTMENT FOR GLAZED KID LEATHER

It is advisable to do assortment at least at three stages for the full utilization of goatskin for the manufactures of different types of leather. The selections are:

- a) Raw selection
- b) Lime selection
- c) Blue selection

They are briefly described below

(a)Raw selection: -In this assortment the skins are to be graded in different sizes and quality and may be processed for different types of leather

(1) Skins below 70cm length may be processed for hair -on kid for toy manufacture,

(2) Prime quality skins of 70-90 cm may be chosen for glazed kid leather,

(3) Large average sizes 90-105cm may be selected for shrunken kid, E.I tanning, chamois, book binding, etc.

(4) Skins above 105cm may be chosen for making vegetable chrome tan fancy leather etc.

(b) Lime selection: - After liming operation, the skins should be assorted as follows: the fine and tight grain skins without any grain defects may be chosen for glazed kid, those skins that suffer from raised grain, loose structure, poor structure, and defective grain may be rejected from glazed kid lot and processed for E. I chamois leather etc

(c) Blue selection: - after chrome tanning and shaving the skins of glazed kid lot may be assorted as follow: the fine, tight and smooth grained pieces may be chosen for glazed kid finish and the pieces with drawn grain and thin substance may be processed for chrome/vegetable crushed kid.

## 4.3 IMMITATION GLACE KID

Imitation glace kid leather is one of the highest quality and most elegant leather and is used for the manufacture of fancy ladies and gent's shoes and also fancy leather goods. The classic glazing finish of the earlier years had typical transparent, fine and high luster appearance with a smooth natural handle: finished look of this nature is still in demand for high class shoe upper. For this reason, goat, sheep, and light calf skins (cow and buffalo calves) are often platefinished to look as though they have been glaze-finished.

For full-grain, glazed finished leathers only first grade raw hides with no or little grain defects, are needed, which are very scarce in our country. On the other hand, medium quality raw stocks may be used for the production of artificial glaze upper leather. Even, corrected grain leathers may be finished with a glazed look appearance.

As natural glazed kid leathers are protein finished, they can not meet the requirements of absolute water proof ness, water resistance, flexibility, wet rub-fastness etc. which are required to meet the demands of modern leather and shoe manufactures as well as to fight the competition of leather substitutes. Generally, imitation glaze upper leather is free from these disadvantages of natural glaze kid leather. For the production of artificial glaze upper leather, synthetic resin binder is used alone or in combination with protein binder. As result, imitation glaze upper leather can meet the requirements of absolute waterproof ness, water resistance, flexibility, wet rub fastness etc.

## 4.4 PROPERTIES OF IMITATION GLAZE -KID

1) The synthetics glaze upper leather should have special type of gloss.

2) This type of leather should be non-stretchy and only that much of stretchiness is allowed which is absolutely necessary for wearing comfort.

3) This type of leather should have some degree of roundness when folded with grain side out, resiliency and must not be papery.

4) It must posses sufficient strengths like tensile, bursting, tear etc. good feel and resistence to grain crackiness.

5) It must not posses any looseness because looseness is aserious defect in glaze upper leather.

6) It should have open, silky, flat, smooth and clear grain.

7) It should have sufficient water resistence and wet rub fastness.

# 4.5 OPERATIONS IN GLAZED KID MANUFACTURE

The operations involved are (1) soaking,(2)limmg, (3) deliming and bating, (4) pickling, (5) tanning, (6)neutralizing, (7) dyeing, (8) fatliquoring and (9) finishing. Each of these operations produces its characteristic effect on the skins by its chemecal, physical and biochemical action on them. In most operations alternative materials may be used. The nature of the materials and the concentration of their solutions or imulsions used for treating the skins, the temperature and the duration for which skins are treated all these influence the quality of the final leather. Good quality of the leather is the result of skilful balancing of all these operations.

#### 4.5.1 SOAKING

The object of this operation is to restore to the cured skins the water lost by dehydration in the curing process. The duration of soaking naturally depends upon the speed with which the skins absorb the water to regain that percentage of moisture content, which they had in their green condition. For wet salted skins 3to 4 hours or at the most, over night soaking is enough, but for dry and dry salted skins which soak slowly the soaking period has to be extended, sometimes to 48-50 hours depending on the hardness and degree of drying of the cured skins. Adding to the soaking bath "soaking agents" can substantially accelerate the soaking of dry and dry salted skins. Since a long time sodium sulphide and caustic soda have been used to facilitate soaking of dried stock. IOOg. caustic soda or 150g. sodium sulphide is generally used per 100 liters soak water. More recently surface active agents known as "wetting agents"-usually sulphated fatty alcohols-have been introduced to aid the soaking operations.

It is not advisable to prolong the soaking to a great extent, because long period of soaking sets up bacterial action, which dissolves the skins substance and affect leather quality. If on account of the nature of the dry cured skin, the soaking period is to be lengthened, antiseptics, such as chlorine, carbolic acid, P naphthol, trichlorophenol, preventol liquids, are to be added in small quantities to the soak liquor.

When the skins are sufficiently soft they are washed either in a drum or in a paddle by two or three changes of water to cleanse them.

If the skins are received in the tannery in green condition, which is seldom the case, soaking is reduced to mere washing of the skin in a few changes in water with the sole purpose of removing the adhering dirt, dung, etc. from the skin.

Adequately soaked skins are ready for liming.

#### 4.5.2 LIMING

The objects of liming in the case of glazed kid manufacture are the same as in the case of manufacture of the other types of leather.

(1) Removal of hair by the dissolution of hair roots and the epidermal layer.

(2) Saponification of all fats goat skins usually content high percentage of natural fats. These fats are to be removed, as otherwise they will interfere with getting a uniformly high gloss in finishing, which glazed kid must have. The lime used in liming acts upon the fats and converts them into lime soap which is mechanically removed from the limed skins by scudding.

(3) Removal of certain amount of the interfibrillary substance which is mainly glycoprotein. This is soluble in lime liquor on account of which it is removed to a very large extent in liming process. This removal is necessary to facilitate subsequent tanning and also to make the final leather soft.

(4) Splitting the fibre bundles into fibres and fibres into fibrils. This is effected by the swelling action of lime on collagen fibres. This splitting caused by liming is essential for satisfactory tannage and for getting a finished leather of full substance, soft feel, and open febre structure, the individual fibres and fibrils of the skins are made accessible to the chrome tanning salt during the subsequent chrome tanning process.

In the manufacture of glazed kid the skins are often unhaired by painting their flesh side with a paste of lime and sodium sulphide and piling the painted skins over night. Next morning, the hair is found to be sufficiently loosened for removal by working them on the unhairing beam with an unhairing knife or as is done in the large tanneries by passing the skins through the unhairing machine. The advantage of unhairing by painting is its speed and also the fact that it keeps the goat hair in good condition, unaffected by the alkaline lime and sodium sulphide. Goat hair is an important by-product of a glazed kid tannery and it has a market. Those tanneries which unhair by painting, give the unhaired skins a subsequent liming in a fresh lime liquor made of lime and certain quantity of sodium sulfide, to plump up the skins and thereby split the fibre bundles and fibres. There are also tanneries which loosen the hair by putting the skins into a lime liquor sharpened by sodium sulphide or sodium hydrosulphide or dimethylamine. Formerly, arsenic sulphide or red arsenic used to be employed as a lime sharpening agent but this practice has become less common on account of the poisonous nature of the compound and the subsequent risk to lime yard workmen. Arsenic sulphide was used because it did not cause as much swelling of skin as sodium sulphide and thus helped to produce on the finished glazed kid, a fine and silky grain that is very much prized. The recent introduction and use of sodium hydrosulphide and dimethylamine has removed the disadvantage pertaining to sodium sulphide.

An enzyme process known as 'Arazym' process is also employed for unhairing goatskins for glazed kid.

## **4.5.3DELIMING AND BATING**

The limed skins are delimed and bated. The object of this operation is: (1) Deliming;

(2) Pulling down the swollen pelt, making it fallen, flaccid and slippery in feel. Well-bated skins area so slippery that it is said that they can be drawn through a wedding ring.

(3) The opening up of the skin pores so that enclosed lime can be squeezed out through the pelt.

(4) Loosening of natural dirt, remnants of hair roots and hair follicles, fat gland sheaths and insoluble lime soaps, produced by saponification of the natural fats of skins by lime. All these are technically called scud. This scud is loosened by the bating process and removed by the subsequent mechanical scudding and through washing done after bating.

(5) Removal of the interfibrillary protein, which is glycoprotein or skin mucoid.

When the above objects of the bating process are achieved the skins are thoroughly cleansed and brought to the proper condition which facilitates the subsequent process of tanning and finishing to produce a brightly glazed, soft, full and resilient leather having not much stretch.
Bating is one of the most important operations in glazed kid manufacture on which the final quality of the leather largely depends. The exact stage when the bating can be regarded to have been satisfactorily completed is generally judged by the following indications:

(1) The skin should be thoroughly delimed and phenolphthalein applied to the edge of act piece of bated pelt should not show a red colouration.

(2) The bated skin should be absolutely fallen and flaccid and should lie in any position in which it is kept. It should not show any tendency to spring back. The absence of the tendency to spring back is generally tested by pressing the grain of the skin by thumb, and thumb impression should remain.

(3) When bated skins are scratched on the grain by thumb nail the scud consisting of broken hair roots, other epidermal remnants, dirt etc. should easily come out showing that it has been thoroughly loosened and rendered easily removal.

(4) When the flesh side is scratched by the thumb nail, the adhering flesh should be removal when some pressure is applied, but the flesh should not be too easily removable, as in the case of over bating.

The bates are mixtures of proteolytic enzymes like trypsin and ammonium salts like ammonium chloride or sulphate. The enzymes were originally obtained from animal pancreas, but recently are derived from microbial sources like bacteria, moulds etc.

After bating the skins are ready for subsequent processes of pickling and tanning.

#### 4.5.4 PICKLING

Pickling may be defined as the conditioning of the pelts for subsequent chrome tannage and is done by treating them with a mixed solution of acid and salt. Pickling completing delimes the pelts, should this still be necessary and acidifies them. This acidification is conducive to a mellow initial tannage. It also opens up the fibres. This opening is imperative for a thorough and uniform fixation of the basic chromium sulfate. If pickling is conducted the subsequent tanning agent will penetrate very quickly, thoroughly and uniformly, producing a leather of round, soft and smooth feel and fine grain. But usually glazed kid tanners do not pickle the skins when double bath tanning is followed, since some sort of pickling effect is obtained in the first bath, which is definitely of acidation.

Pickling is essential if single bath tannage is employed. If pickling is omitted in single bath tannage, the pelts would be exposed to the astringent action of the basic chrome salt at the initial stage of tanning and would thereby become case hardened and coarse grained. These surface being rapidly tanned, the chrome liquor would not penetrated into the inner layers of the pelt and the completion of the tanning would be delayed. Pickling makes the pelt acid and consequently the basic chrome salt of the single bath liquor meets an acid pelt and thereby becomes less astringent and mellow in action. The case hardening action is prevented and the penetration of the tanning agent into the inner layers of the pelt continues unimpeded promoting quick and uniform tannage. Non material difference has been found in the final leathers obtained from pickled skins tanned by single bath tannage and unpickled skins tanned by the double bath process. Of course, the acid to be added to the first bath in case the skins are pickled is adjusted earlier.

#### 4.5.5 TANNING

Glazed kid was first introduced into the leather trade by tanning goat skins prepared according to the pertaining operations described above, by the double bath process of chrome tanning discovered and patented by Schultz in 1884.

The first bath is prepared with 5% by chromate of soda or potash, 2.5% hydrochloric acid and 200% water-on bated pelt weight. When bated pelt is introduced into this bath the pelt which terms yellow in colour absorbs the chromic acid produced in the bath. When the yellow colour has penetrated through and through, the action of the bath is completed. The skins are taken out from the first bath and piled up over night covered by gunny bags protecting them from light. In the presence of light the absorbed chromic acid is apt to oxidize the substance of the skin and thereby exert an injurious effect on the skin. The piled skins are them struck out by a putting out machine to remove the excess of chromic acid and also the creases and fold marks on the skin. The struck out skins are then passed quickly through a dip bath one by one. The dip bath may be a used second bath or afresh bath prepared with 2.5kg hypo, 2.5kg hydrochloric acid, 5kg. Salt and 50kg. water. Many tanners, however, omit the dip bath and put the struck out skins into the second bath.

The second bath is composed 20% hypo, 10% commercial hydrochloric acid and 300-400% water on bated pelt weight.

The difference between double bath and single bath processes is that in the former the basic chrome tanning salt, namely the basic chrome sulphate, is produced in situ on the fibres of the skins by the reduction of chromic acid by acidified hypo in the second bath while in the latter, this basic chromium sulfate is prepared separately by various ways but principally by reducing acidified bichromate wit an organic substance like sugar or molasses. It is quite possible that the differences observed between single bath and two bath-tanned leathers may be due to the differences in the chrome complexes formed in these processes.

#### 4.5.6 NEUTRALISATION

On completion of the chrome tannage the leather must be properly prepared for the subsequent processes of dyeing and fatliquoring. This preparatory operation is termed 'neutralizing'. It consists of the removal by washing of any uncombined chrome liquor or neutral salts remaining in the tanned leather, followed by neutralization with mild alkali of any free acid left in the washed leather and finally washing the neutralized leather free of the neutral salts form in neutralizing. For, if any appreciable amount of uncombined chrome or neutral salts is left in the leather or if it contains free acid, their presence will affect the dyeing, fatliquoring and the appearance and quality of the finished leather. In neutralising, a strong alkali like NaOH is not employed because it reacts too rapidly with the acid present in the out side layer of the leather, greatly increasing its basicity and producing surface overtanning and consequent case hardening. Milder alkalis like borax and sodium bicarbonate, which react slowly and more uniformally are used. These weak alkalis form more stable chromium complexes which have a beneficial effect upon the subsequent processes of dyeing and fatliquoring.

#### 4.5.7 DYEING

Aniline dyes are generally used for dyeing glazed kid leather. They were formarlly classified as acid, direct and basic dyes. The acid dyes are sodium salts of color acids of the general formula RSO<sub>3</sub>Na. Direct dyes are similar in chemical constitution to acid dyes but are mostly manufactured from benzidine. They are called direct colours because they dye cotton directly without the mordanting required in the case of dyeing with either acid or basic dyes. The direct dyes have been found to have good affinity for chrome leather. Hence they are much used for this purpose. As the matter of fact, direct black is mostly used for dyeing glazed kid into black colour. To produce brown shades, both acid and direct dyes are used, as they produce very level shade without exaggerating grain defects. In dyeing with acid dyes, it is necessary to use a strong acid like formic acid in order to liberate

the colour acid, which had got the greater tinctorial property and not the salt. After dyeing the leathers have to be thoroughly washed to remove any uncombined acid.

Basic dyes on the other hand are usually hydrochlorides of the colour bases, of the general formula RNH<sub>2</sub>HCl. They have no affinity for chrome leather and so are not used for glazed kid dyeing. The basic colours have the disadvantage of producing on leather what is known as 'bronzing' or a metallic sheen. Sometimes they are used for top dyeing if the leather is mordanted.

#### **4.5.8 FATLIQUORING**

After the skins have been neutralized and dyed to the required shade they are fatliquored. It is well know that unlike vegetable tanned leather chrome tanned leather cannot be dried to a crust state after tanning, because once dried it cant be wetted back for the subsequent operation of dyeing. Even if the leather is dyed immediately after tanning and then dried, the leather can't be adequately softened. On account of this, the process of fatliquoring had been introduced chrome leather manufacture. The object of fatliquoring is to incorporate adequate amount of oil into the leather, so that is dry out soft and supply instead of hard and horny. Apart from this main object, the introduction of oil into the leather also makes the leather desirably resilient and increases its tensile strength and stitch tear resistance. These properties are desirable in all chrome tanned shoe upper leathers and also in other types of chrome leather. They are indispensable in the case of glazed kid.

The incorporation of oil is effected by treating the leather with a hot emulsion of oil known as fat liquor. The process is called fatliquoring. The usual emulsifying agents for making fat liquor for chrome leather in general and for glazed kid also, are soap and sulphated oils. Of the two types of fat liquor, namely (1) oil and soap and (2) sulphated oil, and oil, the latter is most convenient and generally used by chrome tanners. The glazed kid manufacturers, however, prefer to use soap and oil fat liquor. All oils are not suitable for making fat liquor. Animal oils like neat's-foot oil, cod oil and sperm oil, are considered to be better than vegetable oil. The soap and oil fat liquor the leather less then the sulphated oil fat liquor. The sulphated oil fat liquor makes the leather too soft and raggy whereas a good glazed kid should be somewhat firm and resilient so that the shoes may maintain their form.

#### **4.5.9 FINISHING**

In glazed kid leather manufacture, as in the manufacture of other chrome tanned leathers, all peeresses carried out after the skins have been taken out on the completion of fatliquoring, are included ion finishing. The fatliquored skins are then passed through some mechanical operations, viz. sammying, setting, staking, buffing and ironing etc. and made ready for seasoning.

#### Seasons:

Black season is usually made of logwood extract, blood and nigrosine. Sometimes milk and egg albumin are added. For brown, pigment, egg albumin, milk, and an acid dye are generally used but nowadays, casein based water pigment finishes are employed.

Some important points to be observed in the finishing of glazed kid.

1. In making colored glazed kid careful attention should be paid to dyeing. The shade of the dyed leather should be as far as possible very close to the shade of the finished leather, which would depend upon the pigment finish to be applied. If the bottom dyed colour is lighter then the pigment finish colour, the leather will pull up light when it is stretched in lasting the shoe. This is objectionable.

2. Grease in the leather whether coming from the fat liquor or from oiling up or from the natural grease of the skins sometimes, makes it difficult to get a smooth level finish. This is to be avoided and minimized by clearing the grain by brushing with 10% solution of commercial ammonia or a mixture of ammonia and methylated spirit.

3. Sometimes the dyed skins show light coloured patches, especially at their center. This too can be remedied by clearing the skin before seasoning, with a weak solution of ammonia.

4. If a finished leather is turned grain inwards and vigorously rubbed between the thumb and finger, sometimes the finish film crumbles down and the pigment comes off from the grain surface as a fine powder, and if this occurs rapidly it's an indication that the film is dry and brittle. The condition can usually be corrected by the addition of plasticizer to the finfish or by replacing certain inherently brittle materials in the finish such as shellac or albumin by softer mucilage. Sometimes the film may come off the grain in soft rolls on account of the use of excessive plasticizer.

5. if the grain surface of the lather before applying the finish is very acid, there is a possibility of the medium (casein) precipitating in case a water pigment finish is being used, giving the effect of an under bound film. Padding with a weak solution of ammonia should be tried in such a case.

6. The presence of lime soaps and chrome soaps will give rise to areas on which no finish will adhere. Although the actual quantity of soap present may be extremely small, it's almost impossible to overcome its effect in the finishing process. The chromium soaps are extremely sticky and resist all attempts at emulsification, while the lime soaps are practically insoluble in the usual solvents.

7. A finish which is stable at pH 6 shows less binding and may draw up the grain preventing a smooth finish. The finish, therefore, should be stabilized at about pH 7-8.

8. A colorless topping is apt to give a grayish break and it's usual to tint it with a little dye or season solution.

9. 'Fixing' i.e., rendering the colour fast to stripping by water and to dry rubbing may be achieved by spraying the leather with commercial formaldehyde solution diluted with 3-6 parts of water. This fixing slightly dulls the gloss, but this is recovered when the skins are subsequently ironed or plated. The most rapid fixing action of formaldehyde is obtained at pH values less than 4.5. It's therefore now a common practice to add to the formaldehyde small amount of chromium sulphate of chloride or acetic acid for lowering the pH in

order to induce the casein-formaldehyde resin formation which produces the fixing effect.

10.To preserve the natural grain of goatskins and to impart a smooth and soft feel to the surface it's essential to use the smallest possible quantity of pigment finish, so that a very thin film is produce.

11. Resistance to dry rubbing is tested by rubbing the finished surface with a soft cloth, usually a handkerchief. Dry rubbing should not occur with inorganic pigments unless the film is badly underbound, but brilliant organic lakes are difficult to fasten, principally because of their immense staining power. The usual method of avoiding dry rubbing trouble is to apply a coat of clear nitrocellulose finish over the pigmented surface to provide a protective film.

Sometimes finished skins are oiled with mineral oil to make the finish more waterproof. Key test should not break the finished film until the grain itself is cracked by the test.

#### 4.6 PUTTING A GLOSS ON FASHION

Fashion rules and has its own rules. Shiny patent is to be seen everywhere as are imitation wildlife prints. Sometimes, the art of the tanner is such that one has to look twice to check whether the crocodile is for real and that the patent is not a plastic. Now-a-days, the industry can delight in a multi-faceted approach to what's in and what's out.

In the paste, producing patent leather based on using linseed oil was a long and tedious process ( see technology this issue). And it was not all that long ago when creating patent leather was a well-guarded secret known only to a handful of tanners who were able to transform the oily finish into a strong, resistant film. There was a midnightmysticism about the preparation of the lacquer. What was done at night took a long time to dry in sunshine in a UV- and-siccative, accelerated process. It was easy to identify those tanneries who at the secret they were the once with large 'gardens' where the leathers were exposed to the sun, nailed to wooden frames and taken quickly under cover when rain threatened. Those where the days: today's air-pollution would make it debatable whether one would end up with the expected high gloss finish or dull, smooth sandpaper.

Fortunately for fashion followers, all this has changed dramatically with the invention and development of polyurethane finishes and there is no shortage of companies, which can supply the system needed. Among purists there will always be a debate as to whether it makes sense to use real leather as a support for a rather heavy film, which lacks porosity or breathability, although they will concede that, for shoes, the leather is an essential support in terms of comfort.

#### **4.7 GLOSS AND GLOSS RETENTION**

A surface can give gloss only if it can reflect maximum amount of light and for which smoothness of the surface and its opacity are mainly important. Mirror reflects light because it is smooth and highly opaque. The object of glazing, plating or brushing in tanneries is to impart smoothness to the leather surface.

By glazing, plating or brushing also the leather surface can not be made glossy unless the particle sized of the pigment and other ingredients in it are micro fine. As far as opacity is concerned, it is the inherent property of the pigments. The films produced by the film forming materials are generally transparent and they are made opaque by pigments. All the pigments are not equally opaque and therefore selection of pigment for the manufacture of pigment paste of a particular shade is a skillful task. The brilliancies of organic pigments are generally better but these are transparent in comparison to in organic pigments. The gloss of a film is reduced by anything that causes drying to wrinkled film. If the rate of drying is too rapid due to low humidity of air, shrinkage starts with the formation of wrinkles on the film surface. For high gloss, the drying of season coat on the leather should therefore be slow and uniform.

If a pigmented film dries in such a manner that a layer of clear vehicle forms on the surface, a film of high gloss results. Glazing materials like egg albumen, blood albumen etc. can function best when added to the top coat mainly for this reason.

Anything, which causes scattering of light, reduces gloss. In sufficient plasticizer in the film is one of the reasons or hair cracks to the film and in such leathers, gloss is impaired. For high gloss the melting points of the ingredients used in the season, should also be considered. When leather is glazed under glazing machine high temperature is raised at the point of friction between leather and glazing glass. If the melting point of any ingredient in the film is lower than this temperature that melts and reduces the gloss.

When the leather is finished with thermoplastics like acrylic and met acrylic resins the gloss is imparted by hot plating. If the melting point of the plastic used is much lower than the hot plate, it melts and flows causing uneven distribution, as a result of which gloss is highly reduced.

For good gloss it is wanted that the thermoplastic in the film should become soft due to the temperature of the hot place and be uniformly distributed the formation of a coherent smooth uniform film throughout the leather surface but in no case the plastic should melt to the liquid state.

#### 4.8 ENVIRONMENT AND HEALTH

#### Health, safety and welfare:

With attention to health and safety, all chemicals are kept in a purpose-built store outside the factory. All weighing of materials takes places in departments adjacent to manufacturing areas and protective equipment has to be used in handling these chemicals.

The company runs two shifts of eight hours, and operates a six-day week. Approximately a third of the 250 people employed are women. All are covered by an insurance-linked health assurance plan, covering not only employees for both accidents and ill health at work, but their also their families.

The company also owns two factories producing shoe uppers and shoes in its Presidency Kid Leather Shoe Division. These use 15-20% of the output of the tannery, and are located about 10 km from the parent company.

#### **Environmental Concerns:**

Concern for environmental matters has always been a priority, the tannery being situated in 90 acres of picturesque farmland next to lake and surrounded by hills. Initially, treatment was by discharge into a series of linked lagoons for settling. The large size of these lagoons, coupled with a high evaporation of the effluent! The logistics of an increased output, however, called for further developments and, today, treatment is fully comprehensive. Effluents are balanced, chemically dosed and settled, with full biological treatment before discharge.

The company has been a pioneer in using treated effluents for irrigation purpose. With an ideal climate for growing, flowers and woodlands now surround using selected plants and trees, the factory. Presidency Kid Leathers has remained at the forefront of environmental progress being the site of the major UNIDO investigation into reed bed technology.

# 5.1 MANUFACTURING PROCESS OP GLAZE KID LEATHER

#### **Raw materials:**

2 (two) pieces of locally available wet salted goat skins of mediam size and of medium selection are supplied and used for this investigation

#### Weighing:

(% based on wet salted goatskin)

#### Pre soaking:



#### **Painting:**



#### Liming:



#### Fleshing:

Fleshed by fleshing machine

#### Weighing:

(% based on lime pelt)

#### **Chemical wash:**

 200% water

 0.25% Meta-By-Sulfite

 **Bun 15 min, drain Deliming:** 



#### **Bating:**



Run 60 Min, Check P" 3.6-3.7, And horse up minimum Over night

#### Samming:

By samming machine

**Shaving:** By shaving maching (Thickness 0.8-1.0)

#### Weighing:

(% Based on shave wt.)

#### Acid Wash:



#### **Re-chroming:**



#### Nuetralisation:



#### **Re-tanning:**



#### Top dye and fat:



Drain, Rinse, Horse up, Setting, Vacuum dry, Hang to dry, Staking, Togging, Trimming; now it is crust for finishing.

#### **METHODOLOGY FOR THE FINISHING**

#### **Polish ground:**

Ingrassante E-123	100 parts
Lustrul binder EG	50 parts
Water	850 parts
Black dye	30 parts

Spray IX, Dry well, Stone polish.

#### Season coat:

Water	400 parts
Dye	20 parts
Lustrul wax LL	15 parts
SFT 5007	10 parts
Lustrul UT	80 parts
Prefondal D-55	20 parts
Prefondal K-53	20 parts
RPU-022	15 parts
Nerospecial-2611	15 parts
Black pigment-DS	60 parts

Padding 1, Spray 2-3X, Glazed by glazing m/c, spray 1-2 X, Roto press at 100°C/30 kg pressure.

#### Top coat:

Water	750 parts
Dye	05 parts
Soft-01	40 parts
SFT-6007	10 parts
Lustrul wax LL	15 parts
Lustrul-622	100 Parts
Alpatop M-32	60 parts
RPU-558	50 parts
Nero special-2611	05 Parts

Spray 2-3X, Fixing 1 X, Glazed by glazing m/c, Roto press 120°C/100 kg pressure.

#### 5.2 CHEMICAL NOTE BOOK

#### (i) LD-600:

It is a wetting agent.

**Typical analysis:** Charge Product of BASF, Germany.

: Non-ionic.

: Anionic.

:11

#### (ii) Relugan D:

Condensation product based on melamine resin.

#### Typical analysis:

Charge pH Product of BASF, Germany.

#### (iii) Paramol PA:

It is low molecular weight synthetic organic resin tanning agent based on a water soluble Acerilic polymer.

#### **Typical analysis:**

Charge pH Product of Hodgson, England. :Anionic : 7.2

#### (iv) Relugan RE:

Co-polymer

Typical analysis:: Anionic.Charge: Anionic.PH: 6.5Product of BASF, Germany.

#### (v) Busan 880L:

Economic disinfectant for use in soaking.

#### **Typical analisis:**

Density	: 1.11 gm/ml.
pH	: 8-10
Product of Buckman	

#### (vi) Chromitan B:

Chemical constitution of chromic sulfate.

Typical analysis:	
Basicity	:33%
Chromic oxide	:26%
рН	:2.5
Product of BASF, Germany	

#### (vii) Neosyn HL:

A chrome retanning syntan, which in appearance is a pale green powder

Typical analysis:	
Total solids	:88%
pН	:2.5-3.0
Cr <sub>2</sub> O <sub>3</sub>	: 12.5%
Product of Hodgson, England	

#### (viii) Neosyn TX -50

A masked aldehyde which has a strong affinity for hide protein . It is a pale yellow liquid.

#### **Typical analysis:**

Active matter pH Solubility water. Stability

#### : 97% :8.0-9.0 :Readily miscible with

:Stable through the pH scale .

Product of Hodgson, England

#### (ix) Leather Black VM liquid:

Basic dye.

# Typical analysis::CationicCharge:CationicLight fastness: 1 - 2Product of BASF , Germany: 1 - 2

#### (x) Tanigan OS:

A replacement tanning material. Universally application synthetic integral tannin material for the retannage of chrome and for vegetable tanage.

Typical analysis:	
Concentration	:96-98%
pН	:Approx 3.5
Product of BAYER, Germany	

(xi) Neosyn $BS_3$	
solid content	:80 - 85%
pH	:6-7
charge	:Anionic
Hodgson, England	

#### (x) Eskatan GLH

White liquid Chrome stable fat

pH Charge Boome

#### (XI) Lustrul binder

Appearance	: Whitish liquid	
Constitution	:Special compound based	
	on natural and synthetic	

:6-8

:Anionic

oils and waxs

рН	:8-9
Charge	:Anionic
Dry content	:38%
ALPHA, Italy	

#### (xii) Prefondal D-55

Appearance Constitution PH Charge Dry content ALPHA,Italy

#### (xiii) Lustrul wax LL

Appearance liquid Constitution

pH Charge Dry content ALPHA,Italy :Whitish viscous liquid :Waxy oleo-pritic ground :9 :Anionic :12%

:Yellow semi transparent

:Syntetic wax in water emulsion :8-9 :Anionic :35%

#### (xil) Prefondal K-53

Appearance Constitution pH Charge Dry content ALPHA, Italy

#### (xiii) RPU 022

Appearance Constitution of

#### рΗ

Charge Dry content ALPHA, Italy

#### (xiv) Lustrul 622

Appearance Constitution modifier

#### pН

Charge Dry content ALPHA, Italy

#### (xv) Nero-special 2611

Appearance Constitution lacquer Charge Dry content ALPHA, Italy :Whitish liquid :Oily additived emulsion :5-6 :Cationic-Nonionic :50%

:Colourless limpid liquid :Anionic water solution

Aliphatic iso cyanate polyurethane :8-9 :Anionic :20%

:Clear yellow matt liquid :Binder based on

proteins :9 :Anionic :10%

: Black viscous liquid :Water soluble organic

:Anionic : 16%

#### (xvi) SFT 5007

Appearance Constitution pH Charge ALPHA, Italy :Opale scente fluid liquid :Surface active agents :7-8 :Anionic

#### (xvii) Alpatop M-32

Appearance Constitution pH Charge ALPHA, Italy :Clear yellow liquid :Modified protein binder :8-9 :Anionic

#### (xviii) Ingrassante E-123 Appearance

Constitution fat

Charge ALPHA, Italy

#### (xix) Lustra UT Appearance Constitution

Charge ALPHA, Italy

#### :Light yellow liquid :Self-emulsifying natural

liquid :Non-Anionic

:A pale yellow past :A speciality based on a mixture waxes :Anionic

#### **5.3 OPERATIONAL STEPS OF LEATHER PROCESSING:**

Steps of procedure	Objects		
Pre-tanning operation			
1) Raw hide collection	High collagen contented, desirable sized hides and skins are collected		
2) Selection	Defects free hides and skins should be selected		
3) Trimming	To get regular shape and to prevent loss of chemicals		
4) Weighing	To calculate the chemicals for next operation		
5) Washing	To clean the hides and skins		
6) Soaking	To wet the collagen properly and back to the state of green hides and skins		
7) Liming	To remove the hair, grease, interfibrillary materials, fats and to swell up and split up the fibre.		
8) Fleshing	To remove the flesh		
9) Deliming	To remove the lime		
10) Bating	To make the grain silky touch		
11) Scudding	To remove hair roots and excessive surface grease		
12) Pickling	To bring the pelt to right acidity for tannage		
Tanning operations by chrome / Vegetable/ Zirconoum/ Alum / Aldehyde / Combination / Synthetic tanning etc.			
13) Tanning	To make the pelt non-putrescible substance		
Post tanning operation			
14) Samming	To remove excess water from wet- blue leather		
15) Splitting	To split the leather into two or several layers		
16) Shaving	To get uniform thickness		
17) Weighing	To calculate the next operational chemicals		
18) Neutralisation	To bring the suitable affinity of retanning chemicals		
19) Retanning	To get the required stability of collagen.		
20) Dyeing	To get the desirable colour.		
21) Fat liquoring	To achieve the desired softness.		
22) Setting	To remove creases and excessive moisture.		
23) Drying	To remove water and excess moisture.		
24) Finishing	To achieve a nice looking.		

#### 5.4 NAME OF THE EQUIPMENTS USED:

- 1) Liming Drum/Pit
- 2) Fleshing machine
- 3) Blunt knife for scudding
- 4) Tanning Drum
- 5) Horse
- 6) Samming Machine
- 7) Shaving Machine
- 8) Retanning Drum
- 9) Samming setting machine
- 10) Tunnel dryer
- 11) Vibrating Stacking Machine
- 12) Toggle Dryer
- 13) Spraying Chamber
- 14) Polishing Machine
- 15) Roto Press machine

**Glazing Machine** 

### Chapter Six

Physical testing of leather indicates the quality of the finished leathers produced. Due to limitations of time and the availability of instrument, selected physical tests were accomplished and these tests are briefly discussed here:

# 6.1 Tensile Strength: (SLP-6, IUP/6:BS3144-method 5)

Tensile strength is actually the force (Kg) per unit area of cross section (sq cm) required to cause a rupture to cause a rupture of the test specimen,

Breaking load (Kg)

Thus, Tensile strength =

Cross section area (sq cm)

Breaking load mainly depends upon the number of collagen fibers acting in the direction of applied load.

## 6.2 The Percentage of Elongation at break: SLP-6 (IUP/6: BS 3144-method 5)

The extent of elongation of the leather specimen at the time of its breaking, while applying the tensile force, expressed as the percentage of the original length said specimen is the elongation at break. The elongation at break is taken by the difference between the initial strength and the length.

The % Elongation at break = Final distance between the jaws - Initial distances between the jaws

Initial distance between jaws

X100

#### 6.3 Double hole stitch tear strength:

The double hole stitch tearing strength can be defined as load (kg) required to tear the sample of leather between two holes of 2 mm diameter each and centers are 6 mm apart by pressed an its unit thickness (cm).

Thus, Stitch tear strength kg/cm thickness= $\frac{\text{Tearing load (kg)}}{\text{Leather thickness (cm)}}$ 

The sampling for this test is carried out in both parallel and perpendicular directions to the backbone.

#### 6.4 Rub fastness:

This involves the assessment of the change in shade of the leather surface after testing and the transfer of color to the material used in the rub test. There are effectively three of rub test:

- Circular rubbing e.g. using the SATRA circular rub machine
- To the fro rubbing e.g. the veslic machine
- Crock fastness testing using the crock meter

The first two are generally more suited to testing grain leathers while the crock meter is more suitable for assessing the rub fastness of suede's and nubucks. However, it is not unusual for the circular and fro rub rests to be used for assessing suede's and nubucks also. The degree of staining or change of color is assessed using gray scales (BS 1006:A02 and BS 1006:A03) and results quoted for dry rub or wet rub.

#### 6.5 Flex Resistance of finish (BS 3144: Method 13)

This test should be considered in conjunction with the adhesive of the finish. A thin finish with adequate adhesion should show withstand 50,000 dry or 10000 wet flexes. The type of failure itself is often more important than the number of flexes required to cause it. Peeling or flaking of the finish is far more objection able than cracking, and high levels of contrast between the finish and the substrate will make any failure more objectionable.

This is usually done with a bally type flex machine. It is important to examine samples before will often be dry milled and could already exhibit signs of cracking as a general rule, thinner films give better results than thicker films.

#### 6.6 Adhesion testing of finishes

This test mainly applicable to resin/pigment finishing systems whether they are classed as pigmented or semi-aniline. Results it is important to note where the adhesion figure but the reason may be that the test adhesive has not stack to the surface possibly because of the use of a particular type of top coat. It is also worthy nothing that a finish with very poor flex resistance can have a giod adhesion. However, a finish withn poor adhesion will almost certainly have poor flex resistance also.

#### 6.7 Waterproof ness test (SATRA model STM IOCD)

Principle: A square test specimen is folded and secured in two Vshaped clamp, which have closed ends so as to form a trough. The trough is then immersed in water and the clamps oscillate at a constant speed so that the specimen is repeatedly fixed. The test is stopped at the first sign of water penetration through the test specimen. 6.8 Lastometer test based on (SLP-8, SLP-9, IUP-9, IUP-12)

This test were performed by following the official method of analysis 1965.Ref. 4(e)2, SLP-8, SUP-9, IUP-9, IUP-12. By lastometer test, grain-cracking strength, busting strength and their corresponding dissension values can be obtained. The bursting strength in an index of the overall strength of the leather. For lastometer test the specimens were cut from the samples by a circle type cutting dice and the specimens were placed on a lastometer being conditioned by clamp whose flesh sides were adjacent to the ball of the instrument. The increasing that is the up thrust of the ball with the pressure by handling indicates the dissension at a rate of 0.2mm/sec. And simultaneously watch the grain surface for the occurrence of a crack and the ball and dissension of grain cracking and bursting wear noted.

```
Grain cracking load (kg)
Grain crack strength =.....
Thickness of the leather sample (cm)
Again, the bursting strength was determined using following formula,
Bursting load (kg)
Bursting strength (kg/cm) = .....
Thickness (cm)
```

### 6.9 Test of heat fastness of finish film based on SLF-2:

This method is intended for testing the color fastness of leather to heating such as may occur when shoes are flamed, hot blasted, or ironed, or subject to other shoe making operations involving contact with hot tools, machine parts air or gasses, the test is used primary to ascertain of changes of color occur, but other changes in appearance are also noted.

A specimen of the leather under test, previously conditioned in as atmosphere at  $20^{\circ}+20^{\circ}c$  and 65 + 2 percent r.h, is placed in contact with the felt face of a heated metal member for a period of 5 seconds, with a contact pressure of 3 lb/sq. inch. When cool the resultant change of color is assessed and other changes in appearance of the finish are noted. The test is carried out at three temperatures,  $100^{\circ}c$ ,  $150^{\circ}c$ , and  $250^{\circ}c$  each tests being done on a separate area of the leather.

#### 6.10 RESULTS AND DISCUSSIONS 6.10.1 The results of different physical tests are summarized are as follows.

Test	Sample- 1	
	Parallel	Perpendicular
Tensile strength	$244 \text{ kg/ cm}^2$	$277 \text{ kg/ cm}^2$
Percent (%) elongation at	50%	54%
break		
Stitch tear strength	$110 \text{ kg/cm}^2$	$133 \text{ kg/cm}^2$

### 6.10.2 The determination of fastness to rubbing (wet and dry) of correcting grain leather:

The rub fastness of a piece of finished correcting grain leather was to assess the resistance of the finish to colour transfer leather during wear.

(SLF-5 BS 1006:UK-LC).

#### **Principle:**

A sample of the leather under was rubbed with a revolution of the pad (dry or wet) required to produce certain effect, was measured with grey scale. The procedure was following by the method of SLF-5 with SATRA instrument.

#### Result of dry and wet rub fastness test:

Results of dry and wet rub fastness test of leather under investigation.

#### Table Dry rub fastness.

Sample	For Leather					For felt							
No													
INO	32	64	128	256	512	1024	32	8	16	32	64	128	256
	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev	Rev
1	5	5	5	5	5	4/5	5	5	5	5	5	4/5	4/5

Remark: the result of the sample is between best and excellent.

#### Table Wet rub fastness.

Sample	mple For Leather				For felt							
No	32 Rev	64 Rev	128 Rev	256 Rev	512 Rev	16 Rev	32 Rev	64 Rev	128 Rev	256 Rev	512 Rev	
1	5	5	4/5	5	3	5	5	4/5	4	3/4	3	

Remark: the result of the sample is between best and excellent.

Result of the test of modified colourfastness to washing. This modified test was carried out with the leather sample under investigation.

#### 6.10.3 Adhesion test:

The test is meant where by the strength of the adhesive bond between the finish film and the leather can be measured quantitatively (SLF-11).

#### **Principle:**

One end of a piece of leather under test was stucked finish side to a metal strip, by a selected adhesive chosen to give an adequate bond between the finish and metal without affecting the adhesion of the finish to the leather, when the adhesive is fully set of cured increasing force is applied to the loose end of the leather until the finish feels away from the leather the load required to peels the finish is recorded.

### 6.10.4 Table Experimental data for adhesion of finish film of the sample leather.

Sample No.	Adhesion (N)				
	Parallel	Perpendicular			
1	450	580			

Result: The good bondage between the leather and finish film.

#### 6.10.5 Flexing endurance:

This test carried out with the leather samples under investigation following the method (SLP-14IUP).

#### Table Results of test of flexing endurance:

Sample No.	Flexing endurance test at 80,000 flexes				
	Break pipeness after	Leather film			
	flexing				
1	3	Slight change			

The sample No. 1 gave a pipe ness rating 3.

#### 6.10.6 Water proofness test:

Sample	After 150	After 200	After 250	After 300	
	cycles	cycles	cycles	cycles	
1	No	No	Slightly	Full	
	penetration	penetration	penetration	penetration	

Sample no.	Grain crack strength kg /cm	Grain bursting strength kg/cm
1	266	311

#### 6.10.7 The lastometer test result of leather under investigation:

#### 6.10.8 Results of the test of heat fastness of finish film:

Sample no	Grey scale	Grey scale	Grey scale	Grey scale
	rating at	rating at	rating at	rating at
	150°C	200°C	250°C	300°C
1	5	5	5	4/5

#### 6.11 Chemical Test:

The result of % of chromic oxide content is 3.21% The result of Fat content is 5.5%
## 6.11 Costing (for per sq. feet)

1. Raw Material:		70 taka
2. Chemical costing/proc	essing cost:	
i. Wet blue:		7 taka
ii. Crust:		10 taka
iii. Finishing:		15 taka
3. Labour Cost:		3 taka
4. Machine Depreciation:		10 taka
5. Utility Cost:		3 taka
6. Maintenance Cost:		3 taka
7. Administration Cost:		20 taka
8. VAT + Tax:		4 taka
9. Others:		5 taka
10. Profit (20%):		28 taka
	Total 1	70 taka

## CONCLUSION and RECOMMENDATION

This dissertation has been involved the film forming properties of commercial process for the production of quality glaze kid leather. I tried my best to produce the quality glaze kid leather. Analyzing all the physical and chemical testing results of the prepared leather sample under investigation, it may be concluded that all required characteristics properties of quality glaze kid leather like adhesion of finish, flexibility, dry and wet rub fastness, tensile strength, vamp flexing, stitch tearing strength etc, are likely present in my leather sample.

So my point of view, all the chemical and physical properties of quality glaze kid leather are fulfilled.

SAMPLE ATTATCHED

Quality Glaze kid leather from goat skin

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