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Md.Tanjimul Karim

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ABSTRCT

AIM OF THE PROJECT WORK

Now days, people are too much conscious about the environment and they try to make the environment pollution free for the next generation. For this they try to eliminate the degree of pollution of environment. Leather industries are one of the main sources of environment pollution. To eliminate the pollution of these industries, the leather tanning industries are changing their tanning process and deduct the toxic and polluted chemicals. Basic chromium sulphate is one of the most popular tanning materials but it causes pollution. Hexavalent chrome is carcinogenic and harmful to our environment. It causes the following disease: Allergic dermatitis, Irritation to mucous membrane, lung cancer etc.

For this reason, the present day trend in the tanning industry to avoid chrome wholly or partly due to its high pollutant nature. Inspite of wide spread applicability of chrome tanning agents to produce almost all types of leather, there is a worldwide interest in developing and alternative to chrome tanning mainly due to ever-tightening restrictions on chromium discharge in tannery effluents, because the suspected toxicity of the metal accumulated in soil causes a serious environmental problem. Process like chrome recycling and high uptake chrome tannage have greatly reduced the chromium content of tannery effluents but still it is difficult it achieve the maximum discharge limit, which is nearly 1 ppm in many countries.

Therefore, the aim of this project work is to avoid environmental harmful substances and using natural vegetable tanning materials for manufacturing shoe upper leather followed by wet white pre-tanning process.

I shall produce chrome free vegetable tanned glaze finish shoe upper leather from cow hide. I shall try to produce good quality shoe upper leather by this project.

I hope, this work will be played an important role for the production of shoe upper leather by using vegetable tanning agents.

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CHAPTER-ONE

INTRODUCTION

Leather is a timeless material- as important in our lives today as it was to our early ancestors. This wonderful material has contributed greatly to mankind's comfort and wellbeing for centuries, and continues to serve us in all sorts of new and traditional ways. Prehistoric man used the skins of animals to provide clothing, footwear and shelter. Presumably the people of the Ice Age, 500, 000 years ago, were the first trot use animal skins to protect their bodies against cold and rain and their feet against rocks and splinters. The first footwear thus consisted of animal skin pieces shaped roughly like bags for covering the feet. The neck of the bag was fastened round the ankle with thin strips of skin. Since, however, nobody knew how to preserve the skins, they putrefied in a short time, gradually, and people learnt how to convert animal skins into durable and usable types of leather. Many centuries passed before the art of tanning was discovered and items such as footwear, clothing, bags and belts could be made.

The earliest tanning agents were leaves barks and fruits contra dining tannins capable of converting raw hides and skins into leather. After the lapse of some thousands of years, humans acquired experience in making different types of leathers. They discovered that alum salts could tan Leather. Later they believed that the sales of other metals, besides aluminum, could be use doffed for making leather, but these were not very successful. It was only in the middle of nineteenth century that the salts of chromium were found to be suitable for tanning. The discovery of chrome tanning is attributed to Knapp in 1858. The chrome- tanned leather could be produced quicker than other type's clef leather and was very resistant to water.

Chrome-tanned leather is ideal for footwear and most of the uppers of the uppers of shoes worn now are made of fully chrome -tanned leather or combination tanned leather, which means leather tanned by a combination tanned leather, which means leather tanned by a combination of chrome and vegetable or synthetic tanning agents.

Leather is still the most suitable material for making footwear and is superior to synthetic leather or other leather substitutes. The reason is to be found in the remarkable structure of leather, which is made up of millions of tiny string- like fibrils, each finer than a hair. These fibrils may be a few inches in length. But they are so fine that it would take 5,000 of them, placed side by side, to span an inch. These fibrils are grouped together into coarser units, called fibers, and the fibers are groupie together into fiber bundles. When we look at leather under a powerful microscope, we see that the fibred bundles are woven together in an intricate comfortable material for footwear because it enables out feet to get rid of perspiration, the two way elasticity, or plasticity of leather allows it to adjust to individual foot shape. Apart from these characteristic, the thermal conductivity of leather is low, keeping the wearer warm when it is cold and cool in the summer heat. No substitute is able to duplicate this quality. This unique characteristic makes leather superior to synthetic leathers.

Leather is always leather!

1.1 HIDES, SKINS AND KIPS:

HIDES:

In the tanning trade **the outer coverings of large domestic animals** are called **hides**. Hides are large in size, thicker in substance and heavier in weight then skin. In Bangladesh Cattle hides above 25 lbs. in the wet salted conditions are classed as **hides** and those below 15 Ibs. as **calf skins**. Light buffalo hides weighing from 14.5 to 18 lbs. are called **'Katta'** and those weighing from 7-14 lbs. are called buff calves or **'Kattais'**.

Example: Cowhide, Buffalo hide, Horsehide etc.

SKINS:

The outer coverings of small domestic animals and wild animals are called skins. Skins are smaller in size, thinner in substance and lighter in weight than hides.

Example: Goatskin, Sheepskin, Tiger skin, Crocodile skin etc.

KIPS:

A kip is the hides of immature cattle. In the western countries cattle hides weighing between 15 lbs. to 25 lbs. in the wet salted condition are classed as **kips**. It is smaller, lighter and thinner than a hide, but larger, heavier and thicker than a calf skins.

1.2 CHEMICAL CONSTITUENTS OF HIDES/SKINS:

The chemical constituents of hides and skins can be divided into four main groups, such as,

1. Protein	-	1 9 % to 33 %	on the green weight
2. Water	-	60 % to 70 %	on the green weight
3. Minerals	-	0.36 % to 0.5%	on the green weight
4. Fatty matter	-	2 % to 30 %	on the green weight

E.g. Cattle, calf : 2.0 %
Goat : 2.0-10 %
Sheep : 5.0-30 %

The relative proportions of these materials vary from skin to skin depending upon the species, age, breed, feeding and other habits of the animals.

1.3 STRUCTURE OF HIDES AND SKINS:

Most hides and skins consist of three parts, such as

(i) Epidermis,
(ii) Corium or true skin and
(iii) Hypodermic or adipose tissue.

The epidermis is a comparatively thin layer which forms the upper boundary of the skin. This layer measures only 1% the total thickness of the skin and serves to protect the corium which is the most important part of the skins.

The corium is a much thicker layer of connective and other tissues which constitute the true leather forming substance of the hides and skins. The corium is divided into two distinct layers:

1.4 ANATOMICAL STRUCTURE OF HIDE/SKIN:

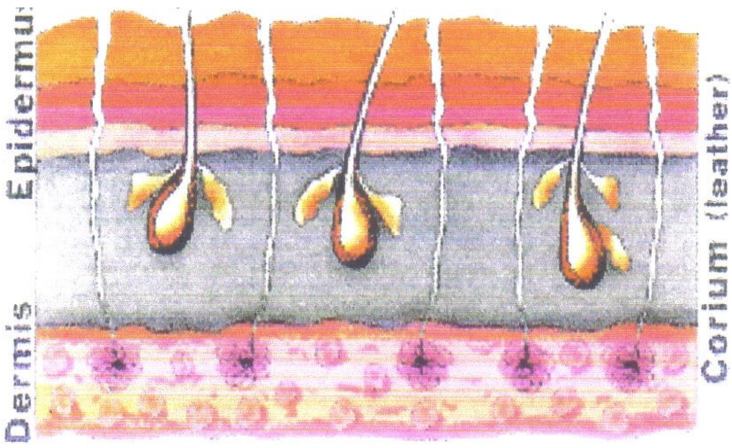


Fig-1: Histological Cross section of Hide/ Skin

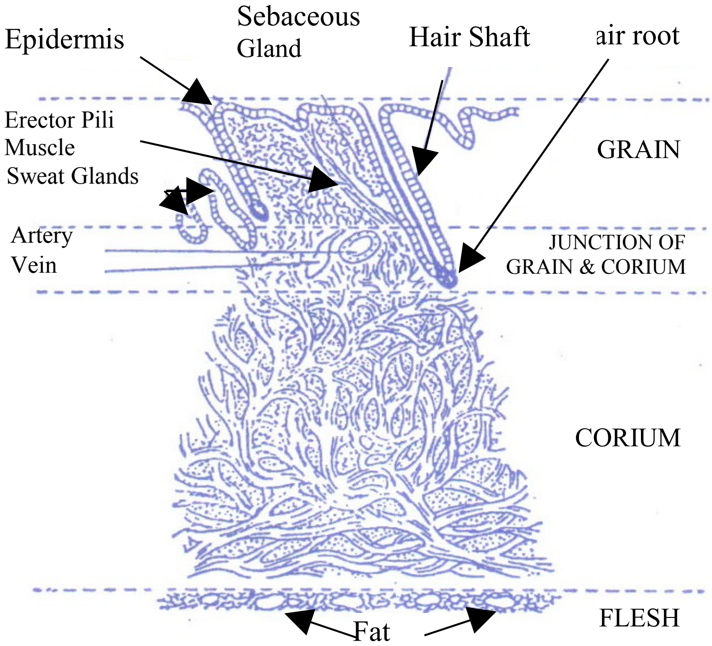


Fig-2: Cross section of Hide/ Skin

(a) Corium minor or grain layer: It is the top of the corium constitute about one fifth of the total thickness of corium and differs structurally from the main part. This layer has a characteristics grain pattern which is actually the pattern of hair follicles depending on the structure of the hides and skins.

(b) Corium major or reticular layer: This is the main part of corium appearing as net like fibers of connective tissues.

The entire corium is an interwoven structure consisting of several fibers grasped together. The fibril again consists of several protofibrils. In practice, the corium or true skin is that portion of the hide or skin. Which is called pelt, and from which the hair has been removed.

The adipose tissue is the tissue left adhering to the flash side of the hide of skin. It consists chiefly of fat cells, containing tallow like fats, with a few scattered fibers. There is also some muscular tissue. All these structure are useless for the manufacture and must be removed in the flashing operating after suitably preparing the pelt in the soaking and liming processes.

So, in the preparation of the hides or skins the epidermis the adipose tissues must be removed leaving curium which is converted into leather.

1.5 STRUCTURAL DIFFERENCE BETWEEN HIDES AND SKINS:

- **PROPERTIES OF COW HIDE:**

  1) Fiber length is medium.
  2) Number of fibers is huge.
  3) The thickness of hair is medium.
  4) The fiber bundles of female are more uniform than male.
  5) Only one hair grows from one hair follicle.
  6) Fiber weaving is parallel.
  7) Fiber structure is compact at butt area and lower in neck and belly side.
  8) The hair is random, scattered on the grain surface.
  9) Fat gland is optimum.
  10) The hair root does not fully enter into the corium layer.
  11) Grain surface is smooth.

- **PROPERTIES OF CALF SKIN:**

  1) The epidermis of calfskin is thinner than cowhide.
  2) Grain surface is smooth.
  3) Fat content is less than cow.
  4) Calf skin has 100% cutting value.
  5) The hair follicles are much smaller than cow.
  6) Collagen bundles have fine structure as compared to cow hides and useful for the finest of leather.

1.6 CONDITIONS OF BANGLADESHI COWHIDES:

Bangladesh has a good source of raw hides and skins. Everyday thousands of hides and skins are produced from whole country by killing animals in the slaughters house and by various ways. Basically, the Bangladeshi cow hides are of poor substance, because we can't take proper care of them.

Bangladesh is an agricultural country. The farmers are having cows to plough the lands, to run the carts and in the dairy firms (less percentage) to get the milk and meat. The farmers utilize the cow carelessly which is enough to spoil the covering parts of the crows. The dammars dare fed swell. Moreover the lesions animal’s parasites, many disease and injuries may occur. As far, we are getting the poor quality cow hides. Besides, various flaying cuts are also seen. Very often faulty curing is done i.e. the butcher does not cure the hides or skins properly. Sometimes, they use mud to make the leather weight and often the customers are confused to detect the correct grading for hiding the defects by mud.

Some times fresh salts are not used and inadequate curing (less salt) is done which causes putrefaction damage and growth of parasites. Further more, temperature are not controlled at the time of storage properly.

So proper curing with suitable salt like fresh NaCI, Naphthalene and bactericides should be used if we like to cure for longer period. In the tanneries of Bangladesh, generally we get high quantity of hides and skins at the time of ‘Kurbani Eid’. Due to faulty and inadequate curing we lose 1 0- 20% of raw stock.

If we take proper care for collections and preservation of raw hides and skins and then converted these raw materials into various types of finished leather with correct manufacturing process, they not only meet our demand but also are an important way of earning a lot of foreign exchange. So, the government and all stages of people should be conscious about this.

1.7 WHAT IS LEATHER?

Leather is defined as the putrecible raw hides and skins of animals which is treated chemically and mechanically to make it non-putrecible stabilized material by virtue of tanning which does not however affected the natural collagen fiber network and that contain Physical, Chemical and Biological properties to make it comfortable and suitable to the users and also can be used in our daily life and industries. It dries out to a soft and flexible material and does not swell when washed out.

Owing to tanning process, a chemical combination takes place between the hide substance (Collagen) and the tanning agents & auxiliaries, which determines the quality and characteristics of the finished leather. Leather can be produced as soft as cloth or as hard as harness by controlling parameters, sequencing, and methodology of manufacturing process as well as selection of raw materials.

The material that is responsible to produce leather from hides and skins is known as tanning agents. For example:

1. Mineral tanning agents like salts of chromium, aluminum, zirconium, titanium and iron.
2. Vegetable tanning agents like mimosa, quebracho, chestnut etc.
3. Oil tanning agents
4. Aldehyde tanning agents
5. Synthetic tanning agents.

The ultimate physical and chemical properties of leather chiefly depend on the nature of these tanning materials.

1.8 WHAT IS TANNING?

The process of converting putrecible hides and skins into leather is known as Tanning. E.g. Chroming tanning, Vegetable tanning, Alum tanning etc.

1.9 WHAT IS TANNINS?

The materials which can tan leather are known as tannins. These can be produced naturally or synthetically.

Example: Basic Chrome power, Basic Aluminum salts, Zirconium salt, Titanium salts, Vegetable tannins- Mimosa, Quebracho. Divi-divi, Ock, Hemlock, Mangrove etc., Various Syntans etc.

1.10SOME COMMON TERMS:

WET-BLUE:

Term for all chrome tanned and still moist leathers are known as wet-blue.

WET-WHITE:

Chrome free pretanned leather which is tanned with alum, titanium or zirconium salts or glutaraldehyde is known as wet-white leather.

CRUST: Light leather which has not been further processed after tanning but has been merely dried out: usually vegetable but sometimes chrome or combination tanned.

CHAPTER-TWO

SHOE UPPER LEATHER

2.1 WHAT IS SHOE UPPER LEATHER?

The leather used for making of upper components of shoe is known as shoe upper leather. Most of the shoe upper leathers are chrome tanned leather. Combination tanning is carried out with a combination of chrome, vegetable, synthetic or other tanning agents to improve the fullness and firmness and some other desire properties of shoe upper. The main combinations are semi-chrome and chrome-retanned leather. Leather is first tanned with vegetable and then retanned with chrome tanning agent is semi chrome retanned leather. Chrome retanned leather is softer and flexible and mostly used as shoe uppers.

2.2 WHAT IS CHROME FREE VEGETABLE TANNED SHOE UPPER LEATHER?

The leather which is first tanned with white tanning agents i.e. alum, zirconium, glutaraldehyde tanning agent in replace of chrome tanning agents and then retanned with vegetable tanning materials i.e. mimosa, quebracho etc., syntans, glutaraldehyde tanning materials etc. for making shoe upper leather is known as chrome free vegetable tanned shoe upper leather.

2.3 TYPES OF SHOE UPPER LEATHER:

GRAIN LEATHER:

Sl. No.	Types	Raw stocks	Thickness mm	Tanned	Properties
1.	Full grain leather	Full grain means that the original grain surface should be exposed without snuffing.			
2.	Side upper leather	Cattle Hides (all classes)	1.2-1.8 mm	Chrome tanned	Good fullness, no loose grain.
3.	Box sides	Cattle Hides (15-25 kg)	1.4-2.2 mm	purely chrome tanned	Full handle with firm structure.
4.	Corrected grain leather	Cattle Hides (all classes)	1.2-2.0 mm	vegetable /synthetic/ additional resin tanning	Given an artificial grain layer by impregnation and thicker, filling finish coat.

Sl. No.	Types	Raw stocks	Thickness mm	Tanned	Properties
5.	Waterproof leather	Cattle Hides (Medium weight classes)	1.8-2.4 mm	chrome tanned /chrome-vegetable tanned.	Full, slightly rubber like handle with tight and smooth grain.
6.	Russet upper leather (Heavy footwear such as hiking and mountaineering boots, army boots industrial shoes)	Cattle Hides & kips (15 kg and more)	1.8-2.8 mm	natural-colored, vegetably tanned side upper leather	Softness, fullness, pliability, sufficient firmness, little washing out loss, good tensile strength, good air permeability etc.
7.	Russian leather (shoe and boot upper, harness and fancy leather)	Light cattle hides & calf skins	1.4-2.6 mm	combined vegetable tanned and chrome tanned	To achieve the characteristic smell, it is impregnated with birch-tar oil.
8.	Polishing leather	Cattle Hides (all classes)	1.2-1.8 mm	chrome tanned, have slightly vegetably /synthetically retanned and have received a polishing finish	Soft, similar to aniline, with a light/dark contrast when the grain is extended.
9.	Sandal leather	Cattle Hides (all classes)	1.6-3.0 mm	Vegetably tanned with reduced fat liquoring.	Mostly used unlined, the fleshed side is processed with short fibres by dry shaving or buffing.
10.	Box calf	calf skins (all classes)	0.8-1.4 mm	chrome tanned, glaze or glaze/plate finish	Full, supple handle with good firmness and good tensile strength.
11.	Calf upper leather	calf skins (all classes)	0.8-1.8 mm	chrome/ Vegetable tanned.	Good firmness and good tensile strength.
12.	glazed kid leather (highest quality and most elegant leathers, used mainly for ladies footwear)	kid skins and light goat skins of good substance (4 sq,ft.)	0.6-0.9 mm	Formerly two-bath today one-bath chrome tanning method, with smooth glaze finish.	Firm grain, no poor substance, no elasticity in all sides and flanks, high gloss, non-coating finish.

Sl. No.	Types	Raw stocks	Thickness mm	Tanned	Properties
13.	Goat skin upper leather	Goat skins of all breeds and sizes.	0.6-1.4 mm	chrome tanned /chrome-vegetable tanned.	Have all degree of softness and all variations of finish.
14.	Chevrettes (imitation of glazed kid leather)	Lamb and sheep skins of good substances from special raw stocks.	0.6-1.0 mm	Strongly vegetable retanned.	Have lower strength properties and a different appearance of grain.
15.	leather of reptiles	Smaller types of crocodiles, lizards, snakes.	0.3-1.2 mm	particularly attractive pigment patterns are received by alum tanning	Dyed and finish with colorless glaze top coats. Are only processed to a small extent for highly fashionable shoes and trimmings.
16.	Horse and foal upper leather	Horse hides (12 kg and more), foal hides (7-12 kg salt weight)	1.0-1.6 mm	more intensive opening up of the skin by stronger liming	Glazed horse upper leather, horse side leather
17.	Pig upper leather	Pig skins (2-4 kgs)	0.8-1.4 mm	vegetable /synthetic/ additional resin tanning and Grain buffing.	Good water repellent and good water proof ness properties.
18.	Kangaroo upper leather	Clear grain Kangaroo skins	0.8-1.2 mm	chrome/ Vegetable tanned. / Synthetic tanning.	Maximum strength properties and used for hard wearing footwear.
19.	Patent leather	Cattle hide, calf skins or goat skins	1.0-2.0 mm	Cold lacquering processes with P.U. lacquers, less frequently by lamination.	Leathers with a mirror bright gloss and with a relatively thick finish coat. Good adhesion, Good cracking resistance.
20.	Shrunken grain leather	Cattle hide, calf skins or goat skins	1.0-2.2 mm	chrome/ Vegetable tanned. / Astringent Synthetic tanning agents/ glutaraldehyde.	Have a grain shrinking effects.
21.	leather of fish skins	some types of seal, shark, dolphin, several types of cod, Pollack and eel etc.		Avoid excessive decomposition of albumen substance, short soaking and liming at below 20ºC.	The strength properties are insufficient in types of fish skins.
22.	Split upper leather	Flesh side lower splits of firm texture made from cow hides.	0.8-2.2 mm	Vegetable / Synthetic retannage.	Smooth short-fibre nap, good filling. Good adhesion.

SUEDE AND NUBACK LEATHER:

Sl. No.	Types	Raw stocks	Thickness mm	Tanned	Properties
1.	Suede upper leather	cow, horse hides, pig, calf, goat and sheep skins etc.	0.6-0.8 mm	Chrome tanned, aluminum, zirconium, glutaraldehyde, resin retanned and buffed on flesh side.	Even, rough or velvety fibre quality on the flesh or split side. Short and firm nap, shower proofness, softness, non-stretchiness and good color fastness etc.
2.	Split suede leather	from lower splits	0.8-1.0 mm	same as suede upper leather	same as suede upper leather
3.	Nubuck leather	cow, horse hides, pig, calf, goat and sheep skins etc.	0.7-0.9 mm	Chrome tanned, aluminum, zirconium, glutaraldehyde, resin retanned and buffed on grain side.	A very fine velvety plush character is achieved on the grain side. Exceptional softness and non-stretchiness and good color fastness etc.

2.4 FUNCTIONS OF SHOE UPPER LEATHER:

- To protect the foot against injury while working, standing or working etc.
- To protect the foot against the cold and/ frostbite.
- To protect the foot from dirt and moisture, acid, alkali, chemicals etc.
- To support the foot (sprain, civilized foot).
- To give cushioning the step (walking on pavement, jogging etc.)
- To give outfit, stylish appearance and fashion context.
- To provide special functions for sports.
- To give satisfaction and comfort, durability and reliability to the user.
- To meet the critical and specific requirements for special purpose.
- To protect the foot from pollutants and contaminants.

2.5 PROPERTIES OF SHOE UPPER LEATHER:

- The physical appearance of finished leather should look attractive with clear grain.
- The leather must possess a soft and mellow 'handle' with fine and tight 'break' on the grain which will not crack in the lasting room of the shoe manufacture.
- The must be stable against repeated tensile and compressive strains and bending.
- The must be stable against repeated flexing.
- The leather must possess high strength properties i.e. tensile strength, stitch tear strength, split tear strength, tongue tear strength, elongation at break etc.
- The leather must possess the hygienic property of being permeable to water vapor and air.
- The finish on the leather should have high adhesion and must be durable against wet and dry rubbing.
- The leather should have high fastness properties i.e. color fastness, rub fastness, fastness to acid, alkali and perspiration, light fastness etc.
- The leather should have high scuff resistance.
- The leather should have high bursting strength and grain crack resistance.
- The leather must be light weight and give foot comfort to the users.
- The leather must be resistance to cracking, shrinking, peeling or curling.

2.6 THE MAIN REQUIREMENTS OF IDEAL UPPER LEATHER:

- **AESTHETIC APPEAL:**

The leather should have elegant attractive appearance. Elegant appearance requires that the grain surface must be distinguishable from that of a leather substitute and colors, gloss and grain appearance should be attractive and appeal to the buyers of footwear. The leather should retain the colour, should not stain wearer's clothes and should have ability to take polish. Not only looks but also the feel of the leather by touch in the shoe are important.

- **PHYSICAL PROPERTIES:**

The most important requirements for shoe upper are long term flex performance (wet, dry and cold) good adhesion (wet and dry) rub fastness and high temperature performance during plating, hot air drying and lasting. Strength and stretch of upper materials used in shoe making are good guides for their suitability. Low strength and stretch of upper leather and consider unsuitable for use as shoe uppers.

The important physical properties of upper leather which determine its suitability use in shoe making are:

(i) Tensile strength
(ii) Stitch tear strength
(iii) Split tear strength
(iv) Elongation at break
(v) Distension at grain crack
(vi) Per cent set
(vii) Reaction of the finish to two dimensional stretch
(viii) Bond strength and
(ix) Resistance of upper to heat and pressure.

- **COMFORT PROPERTIES AND DURABILITY:**
  Flexing endurance, Water vapour permeability, Perspiration resistance, Scuff resistance etc.

- **CHEMICAL PROPERTIES:**
  chrome content, fat content, ash content etc.

- **COMMERCIAL CONSIDERATIONS:**

The upper leather must possess "good cutting value" with least wastage and require the minimum of re-finishing prior to the packaging of the footwear. It should also be inexpensive.

2.7 THE BASIC REQUIREMENTS OF UPPER LEATHER:

- It must give safety and comfort to the users.
- It should contribute to the efficient shoe performance**.**
- It must contribute to the hygiene and comfort of the foot.
- It must meet the arithmetic requirements of fashion and style.
- It must be economical and easily workable and repairable in the shoe making process.
- It should possess adequate wear resistance.
- It must not pinch or squeeze the foot.
- It must not irritate the skin of the foot.
- The colorant used in the upper material must not rub off onto the soak or foot.
- The optical appearance and shape of the upper should be unchanged by wear.

2.8 THE MOST IMPORTANT QUALITY REQUIREMENTS OF VEGETABLE TANNED SHOEUPPER LEATHER:

Sl.No.	Properties	Requirements
1.	Tensile Strength (kg/cm^2)	Min. 250 kg/cm^2
2.	% Elongation at Break	Max. 70 %
3.	Stitch tear strength (double hole) (kg/cm thickness)	Min. 100 kg/cm
4.	Split tear strength (kg/cm thickness)	Min. 40 kg/cm
5.	Water Absorption After 2 hours After 24 hours	 Max. 30 Max. 46
6.	Air Permeability (cc./Min./cm.Hg.pressure)	Min. 80
7.	Water vapour permeability (mg/cm^2)	Min. 200 mg/cm^2
8.	Ash content % (substracting Tanning oxide)	Max. 1.0 %
9.	Cr_2O_3 Content % (Min.)	–
10.	Fat content %	16-23 %
11.	Loss by Washing %	Max. 6.0%
12.	Degree of Tannage	Min. 50

2.9 THE MOST IMPORTANT QUALITY REQUIREMENTS OF SHOEUPPER LEATHER:

Sl.No.	Tests	Requirements
1.	Flexing endurance in the cold (-20°C)	5000 dry, 1000 wet Min.30000 flexing
2.	Adhesion of finish	3.0 N dry,2.0 N wet
3.	Rub fastness	Min. 50 rub cycles
4.	Fastness to hot plating	Min. 80°C
5.	Distention of grain	Bulge height min. 7.0
6.	Split tear force	Min. 18 N (with lining) Min. 25 N (without lining)
7.	Tensile strength	Min. 150 N
8.	% elongation at break	Not less than 40%
9.	Light fastness	Not less than rating 3 (blue scale)
10.	Fastness to migration	Max.rating 3 (blue scale)
11.	P^H value (aqueous extract)	Not less than 3.5
12.	Mineral substances removable by washing	Not exceeding 1.5 %
13.	Water vapour permeability	1.0 $mg/h/cm^2$
14.	Water vapour absorption	10.0 mg/cm^2 (after 8 hours)
15.	Waterproofing	penetration of water min. 60 min absorption of water max. 35%
16.	Water spotting test	Drying without staining
17.	Substances extractable with dichloromethane	depending on adhesive: one-component: up to 9% two-component: up to 14% PU special adhesive: above 14%

CHAPTER-THREE

OPERATIONS INVOLVED IN LEATHER PRODUCTION

In the tanneries raw hides and skins go through different chemicals and mechanical operations and finally come out as finished leathers. The tannery operations can be broadly divided into three sections:

(a) Pre-tanning / Beam House operations
(b) Tanning operations and
(c) Post-tanning or finishing operations.

3.1 BEAM HOUSE OPERATIONS:

Before tanning the main important operations for leather manufacturing are done in beam house. Beam house operations consist of Soaking, Liming, Deliming, Bating, Pickling, Depickling and Degreasing (if necessary) etc. The operations and their objects are given bellow:

3.1.1 Trimming and weighing:

First of all the selected tannable hides and skins are trimmed to remove the tail, shoulder, flanks, neck and trimmable portions correctly. Then these are weighted carefully. All the chemicals % based on these weights.

3.1.2 Soaking:

Soaking is the first tannery operation. During curing, hides and skins lost large amount of its physiological content of water and unless the former regains this water during soaking operations, good quality leather cannot be produced.

Objects of Soaking:

1. To remove the dirt, blood and dung from the hides and skins.
2. To remove the curing salts in case of salted hides and skins.
3. To dehydrate the skins proteins.
4. To open up the contracted fibrous structure of the skins.
5. To clean off surface filth.
6. Softening the hides and skins.

3.1.3 Liming:

Liming is a very important operation for leather manufacture. The qualities of the finished leather are largely controlled in liming process. Liming is the operation in which the soaked hides and skins are treated with milk of lime with or without the addition of sharpening agents like sulphides, cyanides, amines, markeptan etc.

Objects of Liming:

1. To remove the hairs, hooves, nails and other keratinous materials.
2. To remove some of the interfibrillary soluble proteins like mucins etc.
3. To swell up and to split up the fibres to the desired extent.
4. To remove the natural grease and fats.
5. To bring the collagen to a proper condition for satisfactory tannages.

3.1.4 Fleshing:

Fleshing is dome on the flesh side of the pelts. It is done by hand fleshing or by fleshing machine.

Objects of fleshing:

1. To remove fats and surplus flesh from lime pelts.
2. To give a cleaner surface.
3. For good penetrations of chemicals.

3.1.5 Deliming:

After liming the unhaired and fleshed hides and skins known as pelt are taken for the next operations called deliming. The alkali present in the pelt is of two types-
(a) Free alkali & (b) Combined alkali. The free alkalis can easily be removed by repeated washing with water or by pressing the pelt under the high pressure, but for removal of combined alkali chemical treatment is always necessary.

Objects of Deliming:

1. To remove most of the lime and alkaline materials from the pelts.
2. To reduced the swelling of the pelts.
3. Solubilization of Ca-soap.
4. To remove flesh, scud etc.
5. To adjust the P^H suitable for different tannage.

3.1.6 Bating:

Limed and partially delimed pelts sometimes require additional treatment known as bating, Bating is done to remove rest lime and swelling and plumping.

Objects of Bating:

1. To produce smooth, fine and clean grain by enzyme action.
2. To remove some of the non-structured collagen and other proteins like albumins, globulins etc.
3. The scud or dirt, short hairs, greases and lime soap, dark coloured pigments and traces of epidermis are all loosened and are easily removable by scudding.
4. To allow the splitting up of collagen fibres.
5. To make the final leather soft, pliable and stretchy.

3.1.7 Pickling:

In leather processing pickling is very important and essential operations prior to mineral tannage. The treatment of delimed or bated pelts with a solution of acid and salts is known as pickling which takes the pelts acidic condition to absorb chrome and being down the P^H for chrome fixation.

Objects of Pickling:

1. To bring the delimed and bated pelts to a required degree of acidity before chrome tannage, even vegetable tannage.
2. To reduced the P^H.
3. To modify the fibre structure.
4. To reduce the astringency of chrome tanning agents.
5. To preserve the leathers and to achieve the special effect.

Control of Pickling:

1. Temperature, critical at low P^H 28ºC.
2. Salt concentration to be 6ºBe after 20' run.
3. End P^H about 2.8-3.0 for chrome, 4.0-4.5 for vegetable tannage.

3.2 TANNING OPERATIONS:

In leather manufacture the most outstanding process is tanning. The process of converting the putrescible hides and skins into non-putrescible leather is called Tanning. The materials which are used for tanning are called Tannins. There is various process of tanning such as-Chrome tanning, Semi-chrome tanning, Vegetable tanning, oil tanning, Zr tanning, alum tanning, White tanning etc.

Objects of Tanning:

1. To convert the putrescible hides and skins into non-putrescible leather.
2. To raise the shrinkage temperature and to increase the resistance to hot water of the leather.
3. To reduce the ability to swell when wet back.
4. To increase the strength properties of leather.
5. To stabilize the leather against enzymatic degrading.

Control of Vegetable tanning:

1. Avoid all contracts with Iron surfaces / shavings etc.
2. Use sequestering salts e.g. EDTA to remove stains.
3. Check pre-tannage and use weaker tannins for the early colouring stages for penetration.
4. Start at P^H and end at P^H 3.3.

Problems of Vegetable tanning:

1. Leather has a grayish shade and Iron stains, which cannot be covered in the final leather.
2. Poor tan penetration and overtannage of the grain, causing weak grain and poor quality tannage.

3.3 POST TANNING OPERATIONS:

3.3.1 Samming:

To remove the unbound water so that the leather (wet-blue or wet-white) can be split or shaved with even and consistent moisture content.

3.3.2 Splitting:

To split the thick leather through its thickness. It is done by splitting machine.

3.3.3 Shaving:

The final adjustment for thickness (related to orders). An even cutting through a leather with consistent moisture. It is done by shaving machine.

3.3.4 Neutralization:

The process of deacidification or the excess of free or easily liberated strong acid in leather, prior to, retanning, dyeing and fat liquoring, is popularly called neutralization.

Objects of neutralization:

1. To remove the neutral salts and uncombined chromium salts from the leather.
2. Neutralization of free acid in the leather formed by the hydrolysis of the chrome complex.
3. To control the affinity of the leather for anionic materials, particularly dyestuff and anionic oil emulsions by regulating its electrostatic charge.

Common Neutralizing agent:

(1) Borax
(2) Sodium bi carbonate
(3) Ammonium bi carbonate
(4) Sodium acetate
(5) Precipitated chalk (calcium carbonate)
(6) Sodium or ammonium thio sulphate
(7) Sodium sulphite
(8) Sodium or calcium formate
(9) Neutral naphthalene syntan
(10) Sodium tetra phosphate
(11) Sodium silicate
(12) Tetra sodium pyrophosphate
(13) Magnesium oxide, magnesium carbonate
(14) Sodium hexametaphosphate.

3.3.5 Re-Tanning:

Mineral tanned leathers-particularly chrome or aluminum tanned leathers-are always retanned with retanning chemicals with a view to modifying the properties of the finished leather to suit modern demand.

Objects of Re-Tanning:

1. To fill the loose and softer parts of the leathers to produce leathers of more uniform physical properties.
2. To allow for the production of unlined footwear.
3. The retanning may improve the chemical stability of the leather, particularly its resistance of alkalis and perspiration.

3.3.6 Dyeing:

To colour the leather as required by the customer. This should be an even colour and should cover any grain defects. The colour should be light fast and wash fast if the finish is not covering.

3.3.7 Fat liquoring:

It is very important operation for leather manufacturing and it depends on the type of leather to be manufactured. The process of fat liquoring entails the treatment of leather with a warm dilute emulsion of oil in water. The function of fat liquoring are; lubrication, adjust of physical properties.

Objects of Fat liquoring:

1. To improve the softness of the leather.
2. To improve the sliding properties of the leather.
3. To improve the toughness, water-repellent properties of the leather.

3.3.8 Samming and Setting out:
Remove as much as possible of the mechanically held water before drying.

3.3.9 Drying:
Remove the water without damaging the leather value.

3.3.10 Staking:
Soften by separating the fibres which have become attached to each other during drying.

3.3.11 Toggling:
Complete the drying to 14 % and obtain the optimum area by stretching the skin with toggles (clips).

3.3.12 Roto press:
For ironing or embossing the surface of leather with pressure and heat producing thermoplastic flow.

3.4 FLOW CHART OF LEATHER MANUFACTURING:

Raw selection
↓
Shorting
↓
Trimming
↓
Weighing (Raw weight)
↓
Pre-soaking
↓
Soaking
↓
Unhairing (if necessary)
↓
Liming
↓
Fleshing
↓
Weighing (pelt weight)
↓
De-liming
↓
Bating
↓
Scudding (if necessary)
↓
Pickling
↓
De-pickling (if necessary)
↓
De-greasing (if necessary)
↓
Pre-Tanning
↓
Basification
↓
WET-BLUE LEATHER
↓
Pilling
↓
Ageing
↓
Wet-blue selection & grading
↓
Samming
↓
Splitting (if necessary)
↓
Shaving

↓
Weighing (shaved weight)
↓
Wet-back
↓
Re-chroming
↓
Neutralization
↓
Re-tanning& Dyeing
↓
Fat-liquoring
↓
Fixing / Top fat
↓
Horse up
↓
Setting by machine
↓
Vacuum by machine
↓
Hang to dry
↓
Staking
↓
Toggling
↓
Trimming
↓
Hydraulic press / kiss-plate
↓
CRUST LEATHER
↓
Auto / Hand spraying for finishing
↓
Roto-press
↓
Glazing / Embossing / Hair cell
↓
FINISHED LEATHER
↓
Selection
↓
Measurement
↓
Packaging
↓
Ready for Export

CHAPTER-FOUR

DIFFERENT TANNING METHOD

In the tanneries raw hides and skins go through different chemicals and mechanical operations and finally come out as finished leathers. The tannery operations can be broadly divided into three sections:

(d) Pre-tanning operations
(e) Tanning operations and
(f) Post-tanning or finishing operations.

4.1 PRETANNING, TANNING, POST TANNENG:

PRE-TANNING:

In the pre-tanning operations the unwanted proteins and other unwanted materials present in hides and skins are partly or fully removed and the pelt is made active as well as suitable towards the next tanning and finishing operations. Pre-tanning operations consist of Soaking, Liming, Deliming, Bating, Pickling, Depickling and Degreasing (if necessary) etc.

TANNING:

Tanning is the process of converting putreciable outer covering of animals to non- putrecible leather with different physical, chemical and biological properties of that they can be used in our daily life and industries.

Tanning agents that have been found until now to be successful in producing satisfactory commercial leather are as follows:

(i) Mineral substances like salts of Aluminum, Chromium, Zirconium.
(ii) Vegetable substances containing tannin,
(iii) Oils and fats,
(iv) Aldehydes (Glutaraldehyde, Formaldehyde, etc.)
(v) Synthetic tanning agents (Resin, syntan, etc.)

Use of these substances for producing commercial leather has evolved the following established processes of tanning:

(i) Alum Tanning process.
(ii) Chrome Tanning process.
(iii) Zirconium Tanning process.
(iv) Vegetable Tanning process.
    a. Pit Tannage
    b. Accelerated Tannage
    c. Rapid Tannage (BASF RAPITAN process)
(v) Formaldehyde and Glutaraldehyde Tanning process.
(vi) Tanning with synthetic tanning agents, salts of Zirconium, Iron, and recently introduced Titanium salts.
(vii) Combination of two or more of the above-mentioned tannages.

POST TANNING:

The post tanning operations consist of neutralization, retaining, dyeing, fat-liquoring, setting out, Hang to dry, staking, toggling, Kiss-plating and finishing.

PRE-TANNING PROCESS:

4.2 WHAT IS WET WHITE?

Chrome free pre-tannage is to summarize under the term "wet white". Wet white like wet blue is an intermediate in leather manufacture. Because the chemicals used to produce it are colorless, the resulting stock has no color. Wet white leathers can be produced by using aluminum, zirconium, titanium and aldehyde tanning agents.

The ideal wet white, properly protected from dehydrating, is stable to storage or shipping, has a shrink temperature sufficiently high to perms splitting and shaving, and has an essentially reversible pre-tannage so that there is no effect no the subsequent tannages.

4.3 BENEFITS OF WET WHITE:

(1) The most important benefits is that trimmings and shaving are free of chrome and become potentially valuable by products rather than waste.

(2) The wet white process uses the same equipment, processing sequence and timings as those for white for wet blue, so that any plant now producing wet blue could easily switch to wet white.

(3) A comparison of the weight of sammied blue stock to the weight of leather obtained from it shows an approximate one-third of the chrome taken up in tanning becomes waste. With the wet white process, 1 00% of the chrome taken up by the stock stays with it since trimming and shaving take place before chrome tanning.

(4) Hides can be sorted in the sammied state so that the crust to be made from a particular sort can be determined at that time and the entire tanning/retanning can be identified to optimize the quality of the crust.

(5) Wet white leather us very receptive to penetration by extracts so a variety of vegetable leathers can be made with shortened process times, improved quality and reduced waste.

(6) Wet white trimmings can be used for producing edible gelatin and shavings have been studied for animal feed and as fertilizer.

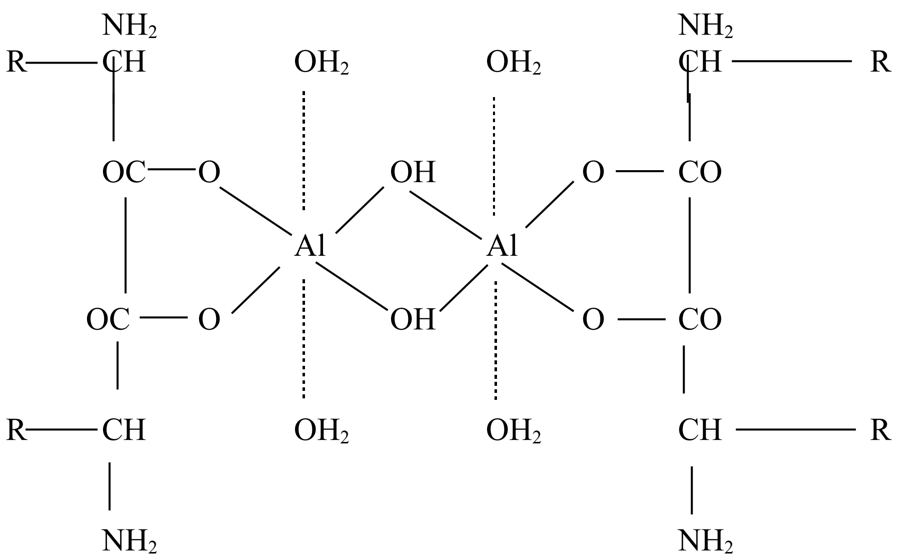
4.4 ALUM TANNING:

The use of aluminum salts for the tanning of skins and furs was employed by the Romans some two thousand years ago and it was probably used by the Egyptians at a much earlier date. Now they are seldom applied as they do not result in real tannage and can easily be washed out with water.

4.4.1 THEORY OF ALUM TANNAGE:

To understand the mechanism of reaction between collagen and aluminum compounds, one must realize that the stability of aluminum tanned leathers is much less than that of chrome leather. Thus aluminum tanned leather can neither be washed with water nor can it be made stand the boil test. Unlike chromium the basic aluminum molecules can be fixed to collagen even at zero basicity and at very low P^H. aluminum can not form acid complexes with sulphate, formate and even with oxalate. The complexes are very unstable.

From the observation, Gall concludes that aluminum, during tanning, very feebly reacts with the carboxyl groups of collagen and does not form any linkage with amino or other groups.



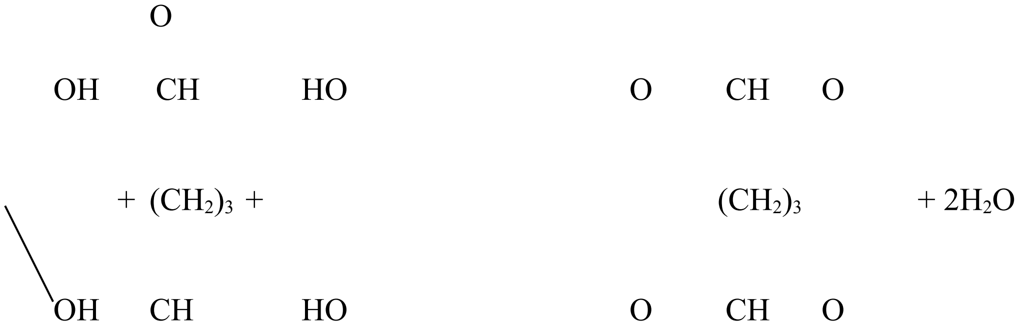
4.5 GLUTARALDEHYDE TANNAGE:

In recent years glutaraldehyde (Glutaralbehyde, CHO-CH2 – CH2- CH2-CHO) has become increasingly popular as a tanning material either giving a coarse grain. It has also a leveling effect for aniline dyes. It can be used in various combination tannages for almost any type of leather manufacture where better resistance to alkali, washing, and perspiration fastness are required. In vegetable tanning it can be used as pretanning or as retanning material. It gives fullness, softness and fine grain. As a result of the increasing demand for softer types of leather, it is advantageously used in the tannage and retinue of well-filled softy upper, garment, nappa and upholstery leather. Because of its permanent softening effect just as one gets in chamois tonnage, glutaraldehyde can be regarded as an ideal retanning maerial for softy shoe upper leather which is required to be impregnated in the finishing process. By itself, glutaraldehyde imparts to the leather a yellowish tone. Due to its objectionable yellowish tone it has not been used in the manufacture of white leather. Products based on formaldehyde, on the other hand, produce white leather with improved resistance to alkali, washing, and perspiration. However formaldehyde produces a relatively flat leather and hence it can only be utilized for clothing or gloving type of leather. Glutaraldehyde tanned leather has a shrinkage temperature of 80° c-85° c. It is largely utilized to make all types of softy leather, namely gloving, clothing, nappa upper upper and suede, upholstery or even softy vegetable tanned uper and luggage leathers. Its remarkable pertaining and retaining properties for chrome or chrome/aluminum tanned leathers lies in the fact that the tanning effect increases with rising pH and that they do not react with one another. Due to its compatibility with chrome and aluminum salts, glutaraldehyde is now being increasingly used as a retanning agent as well as in combination with chrome and aluminum tannages to make Dutch fashion leathers like grain suede nappa clothing, softy shoe upper, nappa upholstery where fullness, grain tightness, soft touch, light weight, satiability and perspiration fastness are considered to be essential properties.

In modern chrome tannage practice glutaraldehyde pretannage is very common especially for very soft leather manufacture (clothing, nappa, gloving, chamois leather). For clothing leather pretanning may commence in the pickle bath. After an initial pickle with formic acid / salt which may also contain 2.5-3% sodium aceate,. an addition of 1.0-2.5% aluminum sulphate is made at pH about 3.2/3.3 Subsequently 1.5-3.0% glutaraldehyde (cone. 50%) is added along with penetration and polymerization of the aldehyde, A low fiat is desirable to assist penetration. The unfixed aldehyde is washed off by through washing in plane water. Glutaraldehyde alone produces a leather of shrinkage temperature 80-85°c but when tanned in combination with chrome cr chrome aluminum salts, the shrinkage temperature is much above the boiling point of water. Like formaldehyde, the rate of tanning action is rapid and increases markedly with rising pH, glutaraldehyde should therefore be fed into drum in two or three installments and the pH must be gradually raised to the desired degree. The most convenient and practical pH for starting prerannage or retannage of chrome leather is between 3.0-3.5. For softy upper and nappa leather the pH is gradually raised to 5.0-5.5 according to the degree of softness desired.

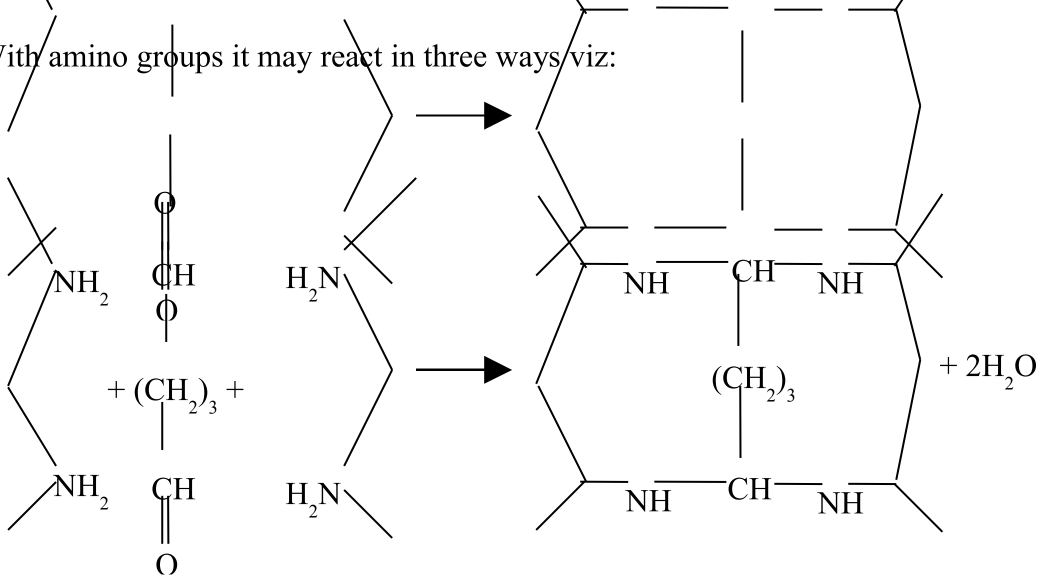
4.5.1 MECHANISM OF GLUTARALDEHYDE TANNAGE:

Glutaraldehyde forms probably semiacetal bonds with hydroxyls of hydroxyl- praline, hydroxyl sine and serine, with phenols it yields insoluble compounds, so it cannot be used with vegetable tannins.



From stoic metric calculations it follows that if the pelt would bind baldheaded by lysine 6- amino groups only, it would bind only 0.7% of aldehyde by weight. The actual amount, however, is greater, which points to the participation of other collagen groups, probably hydroxyls. That is in accordance with the suggestions already made. The use of glutaraldehyde in tannage involves two impotents questions, in what term does it react and why is it considered to decrease the leather strength when used in leather making,

With amino groups it may react in three ways viz:



Or,

$- NH_2 + O = CH\ (CH_2)_3\ CH{=}O + H_2N- \rightarrow - N = CH\ (CH_3)_2\ CH = N - \quad + 2H_2O$

Or,

$- NH_2 + O{=}\ CH\ (CH_2)_3\ CH{=}O + H_2N - \rightarrow - NH - CH\ (CH_2)_3\ CH - HN -$

OH OH

From stoic metric calculations it follows that if the pelt would bind baldheaded by lysine e- amino groups only, it would bind only 0.7% of aldehyde by weight. The actual amount, however, is greater, which points to the participation of other collagen groups, probably hydroxyls. That is in accordance with the suggestions already made.

The use of glutaraldehvde in tanage involves two impotents questions, in what term does it react and why is it considered to decrease the leather strength when used in leather making, The first question has been answered by Gillett and gull, Using pure glutaradehyde solutions they proved by UV spectroscopy (which was later confirmed by Heinemann and Brawler by the NMR technique) that glutaraldehyde in 25-50% aqueous solutions is usually o ligomerized (3-5 molecules), when stored under conventional conditions giving cyclone oligomeres and unsaturated a, b- Aldehydes. Oligomerization may be prevented by adding alcohols, OR STORAGE AT LOW TEMPERATURES (-20° c) What form is tanning-active remains still to be found. Gillett-Gull believe that this is the monomer form, whereas according to commercial experience oligomerization is of little or on influence at all. Recent experiments with chemically modifies, glutaraldehyde gave no indication in this respect, nor is it indicated what is the nature of this modification, although the tanning experiments are prewriting.

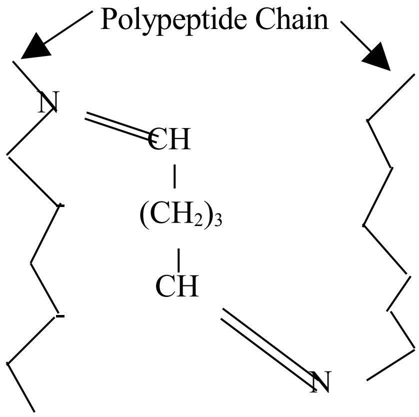
Glutaraldehyde used for tanning gives the leather a perspiration resistance, washing resistance, better fullness and density. The decrease of strength at break has not been elucidated, though it has been confirmed repeatedly. One can expect deep changes in the molecule; perhaps breaking of some peptide bonds by the transfer of the bonds to the baldheaded group- that is, however, the present author's however, the present author's supposition only.

Investigating the problem of leather rear strength and elongation at break decrease due to the glutaraldehyde tonnage Keller and Heinemann concluded that the strength decreases with thichkness increase. This fact may be generalized, as it concerns not only glutaraldehyde tannage.

The same is observed in chrome tanned leather as well as in acetone dried one (Fig.) thus the quoted authors conclude that this is more a matter of changes in thickness, and it is most pronounced in glutaraldehyde-tanned leathers perhaps as a result of the greatest thickness increase occurring in this type of tonnage.
Feairheller recently questioned the poinion that the strength of leather dereases due to glutaraldssehyde tannage as it dhas not been satisfactorly statistically proved.
The exhaustion rate of glutaraldehyde from the bath is greater than that of formaldehyde and of giyoxal, particularly at pH about 8 (Fig,) and the dlower the pH the slower the exhaustion.

Leberfinger at al, have investigated the chemistry and kinetics of glutaraldehyde banding Balancing the amount of aldehyde which may be attached to the functional groups of various kinds of side chains they came to the conclusion that (j>- amino groups may bkind 0.93-l.g/100 g collagen,hydroxyls -3.9-7.8/1 OOg collagen, depending on whether aldehyde is single or two point bound. Pelt may however, atach up to 21% of glutaraldehyde. This has made the authors convenced that glutaraldehyde must be polymerized, which has actually been proved in the recent years. Monomeric glutaraldehyde occurs in water solutions in very smal amounts, When examining the binding of glutaraldehyde to chrome tanned leather the authors found that it will be attached in smaller amounts than to pelt, and the reaction rate is higher. At pH = 2chrome tanned leather binds only 0.75% from a 3% solution, and the equilibrium is established in about 5 hours. At higher PH values the amount of aldehyde bound to chrome leather is still smaller. Glutaraldehyde is most often used for pretanning of skins to be chrome tanned. It binds better to pelt than to chrome tanned leather.

Cross-linking reactions between skin substance and tanning agents (Schematic):
Aldehyde tanning agents; example: glutarldehyde



Cross-linking is effected by principal valences through atomic bonds (Covalences) by reaction of the aldehyde and the NH2 groups of the collagen.

POST-TANNING PROCESS:

4.6 VEGETABLE TANNING:

Vegetable tannage has been practiced for thousands of years and is still widely used today to produce firm, full, solid leather. Vegetable tanned leather is usually used for shoe soles and linings, furniture, upholstery, handbags and luggage, book bindings, belts and straps.

TANNINS: The astringent organic compounds obtained from plant kingdom and capable to convert raw hides and skins into leather are called tannins. Tannins of different plants are different in composition, structure, properties and leather obtained from them also possess different properties.

The most commonly used vegetable tans are: Mimosa, Quebracho, Mangrove, Pine, Oak, Myrobalan, Valonia, Chestnut and sumac leaves.

NON-TANINS: Pigments, acids, salts, carbohydrates, and many other known and unknown compounds are always associated with leather and tannins are known as non-tannins.

4.6.1 CLASSIFICATION OF TANNINS:

A) Tannins were first classified on the basis of plant parts from where the tannins were obtained. The commonly known ones are classified this way in the following table:

Natural tanning materials:

Bark:
Mimosa or wattle, Oak, Hemlock, Pine, Babul, Mangrove, Quebracho, Avaram, Cork, willow, Spruce etc.

Leaves;-Twigs:
Sumac, Gambier, Mangrove, Mango, Eucalyptus, Pistacia, Dhawa, Lentiscus etc.

Woods:
Mimosa or wattle, Oak, Hemlock, Chestnut, Mangrove, Quebracho, Spruce etc.

Fruits:
Myrobalan, Valonia, Divi-Divi, Algarobilla, Tara, Teri, Bablah, Cascalote, Mangosteen etc.

Roots:
Canaigre, Sea-Lavendor, Palmetto etc.

Excrescences:
Gall nuts, Chinese Galls, Turkish Gall, Pistacia Galls, TamariskGalls etc.

Out of the large number of tanning materials available in the different countries of the world, only about twenty are of much importance commercially.

B) Tannins were chemically classified into two groups:

1. Catechol Type
2. Pyrogallol Type

Catechol Type: The tannins of most of the woods and barks (with some exceptions) produced catechol and so they called Catechol Type.

Pyrogallol Type: Most of the fruits and leaves (with some exceptions) produced pyrogallol and so they called pyrogallol Type.

Example: Myrobalan, Valonia, Divi-Divi, Galls, Sumac, Mangrove etc.

C) **According to the modern classification tannins are classified into two groups:**

1) Hydrolysable Type
E.g- Myrobalan, Valonia, Divi-Divi, Chesnut Galls, Sumac etc

2) Condensed Type
E.g-Mimosa or wattle, Quebracho, Babul, Hemlock, Oak etc.

Amount of tanning agents required for various types of leather:
(Percentages on the pelt weight)

1. **Vegetable/ Syntan tanned leather:**

Sole leather	33-40 % pure tan
Insole leather	25-30 % pure tan
Combination tanned bottom leather	30-33 % pure tan
Harness and technical leather	28-30 % pure tan
Bag and upholstery leather	20-25 % pure tan
Upper leather	20-25 % pure tan
Sheep and goat skins	15-20 % pure tan
(Light and lining leather)	
Skivers	12-18 % pure tan

4.6.2 TANNING PROPERTIES OF THE MOST IMPORTANT TANNING AGENTS:

1.Hydrolysable tanning agents (pyrogallol = acid former)				
Tannins	**Colour**	**Fullness**	**Tannage**	**Other**
Oak	yellow brown, dark cut	full	very firm	acid forming
Chestnut	pale yellow, olive tinge	full	firm	Bloom forming
Myrobalan	pale-coloured	medium	little strength	strongly sludging
Sumac	almost white tanning	medium	soft, supple	good lightfastness
valonea	grey-brown, pale-coloured	medium-full	tough, firm	low content of insoluble matters.
2. Condensable tanning materials (Catechol = phlobaphene former)				
Mimosa, untreated	pale, slightly reddish tinge	full	quick, firm, supple	becomes darker on exposure to light
Mimosa, sulphited	bleching, dull beige	medium-full	medium firm, fine grain	bleching, readily soluble
Quebracho-ordinary	very intensive reddish tinge	full	slightly softer than mimosa	strongly sludging
Quebracho-sulphited	intensive reddish tinge	medium-full	slightly softer than mimosa	cold-soluble

4.6.3 DIFFERENCE BETWEEN PYROGALLOL AND CATECHOL TANNING MATERIALS:

Sl.No.	Characteristics	Pyrogallol	Catechol
1.	Tan liquor	Containing highest amount of natural acid.	Containing smallest amount of acids.
2.	Iron alum	Blue colouration.	Greenish black.
3.	Bromine water	No precipitate.	Precipitate
4.	Boiled with formaldehyde and hydrochloric acid.	Incompletely or not precipitated.	Completely precipitated.
5.	Colour of liquors	Yellowish tan to tan.	Reddish.
6.	Colour of leather produced.	Creamy yellow to tan.	Reddish tinged to red-brown.
7.	Action of light on leather	Slightly darkening	Darkens considerably.
8.	Average weight	Much lower than Catechol tans.	Much higher than Pyrogallol tans.

Generally Mimosa and Quebracho are largely used in our point of view. Especially this project work is on the basis of Quebracho. So its properties are given bellow:

4.6.4 Quebracho:

It is vegetable tanning materials got from the Quebracho tree (Quebrachia lorentzi). The word Quebracho is derived from the Spanish words Quebra Hacha, which means "The axe breaker". The wood being so hard that it will turn the edge of a good axe. All our quebracho comes form South America. According to Durland, the Quebracho comes from the Northern Argentina and southern Paraguay.

The wood of Quebracho tree is very hard and contains 20% tannin of catechol variety. Because of its low soluble non tanning content quebracho liquor possesses good weighting properties and in creases the firmness of the leather. Its large particle size makes it especially suitable for use in final drum tanning of sole and other heavy leathers.

Quebracho extracts are of two types.

i) Natural ordinary extract (unsulphited)

ii) Sulphited extract.

Ordinary extract is soluble in hot water. When this solution is cooled, red sediment settles at the bottom. This formation of reds or phlobaphenes in cold solution hinders the penetration of the tannin in to the pelt since tanning is generally carried out at normal temperature which can prevented by the process as sulfating. The sulphiting chemicals are a mixture of sodium sulphite and sodium -bi sulphit (about equal parts). The total amount of sulfating chemicals required: is about 15 to 20% on the weight of extract.

Solutions of sulphited quebracho extract penetrate the pelt quickly. Highly sulphited quebracho extracts do not posses the high weighting properties of ordinary quebracho because the tannin molecules undergo a chemical change during sulphiting. To impart plumpness and fullness of the polt the quebracho extract should be not highly solubilized

The following table shows the properties of **Quebracho extracts**:

Name of the extract	Type	°Be	% Tans	% Nontans	Insoluble	P^H	Rate of penetration	Leather produced	Durability
Ordinary	Liquid	22	35 (30-40)	3	3.0	5.0	average	hard leather, light brown	very good
	Solid	-	65 (57-74)	5	8.0	5.0			
Hot soluble-	solid	-	72 (68-76)	8	0.0	5.5	very high	Soft leather, light color	Good
Cold soluble-	Solid	-	70 (65-73)	11	0.0	6.0			
	Powder	-	82 (78-84)	8	0.1	5.5			

Name of the	Total acids	Natural salts	Ratio Salt/Acid	Ratio Tan/Non-tan	Degree of tannage	Firmly bound tannin after prolonged washing
Ordinary	0.20	0.20	1.15	8-10		
Sulfited (Cold soluble)	0.32	1.76	5.50	Varies according to degree of sulfating.	52.2	20.9

Quebracho wood: Raddish leather colour, growing darker, Sludging, rapid tanning action, imparts weight.
Tan-20.0% (14-26%), Nontan-1.5-2.0%, sugarymatters-0.1-0.3%, Insolubles-61.0%

Mimosa Bark: Gives pale leather with reddish tinge, Good solubility, nonsludging, leather darkens on exposure to light.
Tan-36.0% (22-48%), Nontan-7.5%, sugary matters-2.0% (1-4)%, Insolubles-42.0%

So, Now-a days Quebracho is used one of the best tanning materials in the western region.

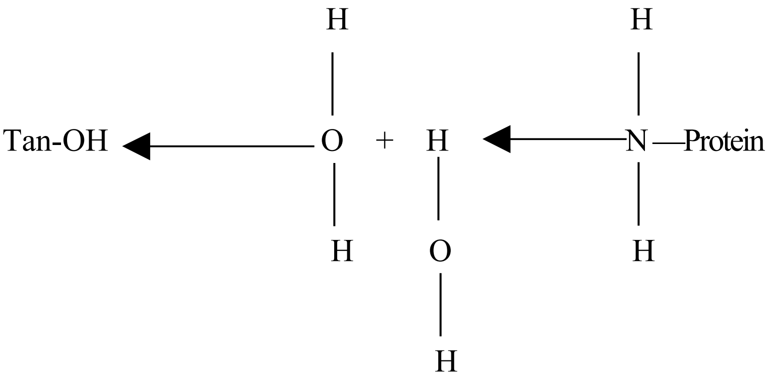
4.6.5 MECHANISM OF VEGETABLE TANNING:

Vegetable tanning processes are based on complicated and involved reactions and hence it is not possible to explain a single comprehensive theory embracing all the features of the probable reactions. After pertaining process the pelt is left only collagen, reticulin and elastien. The most important theory, which explains the mechanism of vegetable tanning for a long time, was Knapp's surface covering theory. According to this theory vegetable tannin coat the collagen fibers and are physically deposited on the latter. This physical theory of Knapp also could not explain why the percentage of fixed tannin reduced due to the destruction or blockage of some of the reactive group of collagen and also why the isoelectric point of collagen shifted due to vegetable tanning. More over if tannin is physically deposited on collagen fibers the ratio of tannin concentrations in the protein phase to liquor phase at the equilibrium state should be constant. But actually this is not the case. These experimental findings can partly be explained only if one believes in chemical combination theory of vegetable tanning. But the draw back of chemical combination theory is that it cannot explain why the combination of gelatins and tannin compound is not of constant composition. Now-a-days it is therefore believed that both physical deposition and chemical combination take place side by side when collagen is treated with tannin solution.

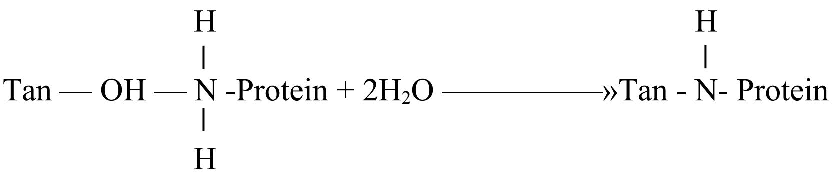
When collagen is treated with nitric acid free nitrogen gas is evolved due to the destruction of NH_2 groups of lysine residues and thus collagen is de ammoniated.

$$P\text{-}NH_2 + HNO_3 \longrightarrow P - OH + N2 + H2\,O$$

The deaminated collagen fixes less amount of vegetable tannin than intact collagen. This reduction of fixed tannin due to de-amination of collagen proves that the α-amino groups of collagen are involved in vegetable tanning. Moreover at low P^H value of liquor goes down. Schoeder therefore concludes that in vegetable tanning the positively charged collagen neutralizes the negative charges of negatively charged colloidal tannin molecules.Polar groups both in tannins and proteins when free have a tendency to co-ordinate water molecules.

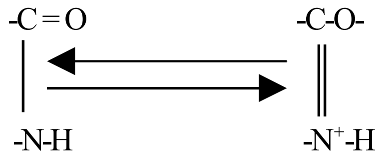


When they interact with each other, the concerned water molecules are shed and the resultant product becomes less hydrated.

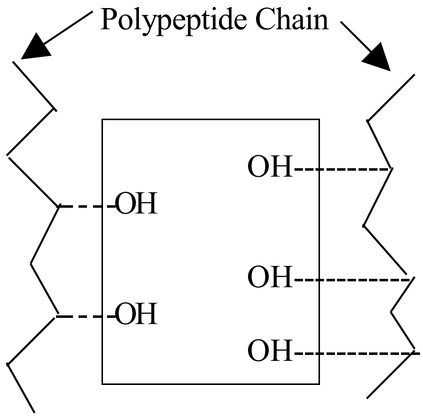


There are some indications that the London and Vender Waals forces also play some role in vegetable tanning. At the end it is better to conclude that there is no such single theory which can explain the mechanism of vegetable tanning clearly and satisfactory.
Very recent another theory has become very popular. According to this theory the electron donating groups like hydroxyl carboxyl etc. attached to aromatic tannin molecules increase electron density in the "Ortho" and "Para" positions of benzene rings. Naturally the tannin molecules behave like dipoles and get attached to – CONH- bonds of

collagen because these carbimino links of collagen also become electrically charged due to uneven distribution of electrons and resonance between oxygen and nitrogen.



Cross-linking reactions between skin substance and tanning agents (Schematic):
Vegetable tanning materials and synthetic replacement tanning agents,



Cross-linking is effected by secondary valences through hydrogen bridges with the phenolic OH of the tanning agent molecule.

4.6.6 PROCESS OF VEGETABLE TANNING:

1. Complete Soaking & Liming.
2. Complete removal of the subcutaneous tissue by through fleshing.
3. Complete Deliming of all sections of the Skins. Dry Deliming & the addition of sodium hydrogen sulphite as well as aromatic sulpho acids is good for thick pelts.
4. The formation of false backs is avoided by slashing the butts along the backbone line.
5. Pretannage with small particle synthetic pretanning agent of loastringency. Also preliminary treatment with glutaradehyde. Polly phosphates or pickles containing Chrome salts or Chromiferrous syntans.
6. Through washing after pretannage & good draining of the residual liquor.
7. Addition of the powder tanning agents for final tanning in 2-3 portions & addition of dispersing tanning agents in appropriate quantities.

Temperature rise not exceeding 30*C.

8. Addition of slip additive or untreated oil to reduce friction.

4.6.7 DIFFERANCE BETWEEN CHROME TANNED AND VEGETABLE TANNED LEATHER:

Chrome Tanned Leathers.	**Vegetable Tanned Leathers.**
1. The leather is empty. **2.** The leather is slightly elastic **3.** Less affected by acidic atmosphere. **4.** Dilute alkali treatment fixes chrome more strongly and the leather tries to become hard. **5.** Difficult to wet back **6.** Shrinks and becomes hard on rewetting and drying **7.** Absorbs fat slowly **8.** Stands the boil test **9.** Tries to become loose if Proper precautions are not taken **10.** Cannot be dyed with basic dyes **11.** Very good embossing is difficult **12.** Fibers to come out from the cut portion.	**1.** The leather is full. **2.** Less elastic than chrome tanned leathers. **3.** Affected by acidic atmosphere. **4.** Dilute alkali treatment strips out tannin, darkens the color and the leather becomes slightly soft. **5.** Not difficult to wet back **6.** Does not shrink or become hard like C.T. leathers on-wetting and drying **7.** Absorbs more fat than chrome tanned leathers very quickly **8.** Does not stand the toll test **9.** Looseness is less than chrome tanned leathers **10.** Cannot be dyed with direct dyes **11.** Embossing impressions are excellent and permanent **12.** Fibers do not come out from the cut portion

4.6.8 EFECTS CAUSED BY VEGETABLE TANNAGE:

1) **Tanning stains:**
Effect: Irregular pale stains.
Causes: Are caused by packed suspension of the hides in the rounds of suspenders.Tanning is less intense where the hides are touching each other.
Remedy: Can be avoided by lifting and rocking the hides from time to time.

2) **Tanning agent stains:**
Effect: Small to large dark brown stains on the grain surface and on the flesh side.
Causes: Are caused by irregular deposits of unbound tanning agent,
Remedy: Reduce the use of tanning agents having a high content of insoluble or poorly soluble substances and avoid flocculation in tanning liquors, creasing of the leather and excessive air in the vessels. No uneven drying at excessive air in the vessels. No uneven drying at excessive temperatures, Stained leathers should be washed or soaked and fixed.

3) **Iron stains Effect:**

Effect: Grey, deep dark blue or blue-black stains of irregular distribution and size, May also cause crackiness of grain in these sections.
Causes: Tanning material soiled by iron particles, iron chips from splitting or shaving, rust particles of pipes, drum fittings or conveyors.
Remedy: Remove by a treatment with bleaching tanning agents, oxalic or hydrochloric acid solutions or complexion agents.

4) **Copper stains:**
Effect: Greenish, irregular stains.
Causes: Soiling or the tanning material or by pipe links and drum fittings.
Remedy: As in the case of iron stains. Slime stains

5) **Slime stains :**
Effect: Whitish, irregular stains.
Causes: Slimy substances caused by bacterial attack in tanning liquors and soaking liquors, particularly in old rounds of suspenders,
Remedy: Discard the affected liquors and add disinfectants.

6) **Mould stains:**
Effect: Whitish, colored or black coat occurring in some sections or all over the surface, producing irregular stains on the leather.
Causes: May occur at all stages of leather production, Increased formation of mould is possible if the leathers are stored under humid and warm conditions,
Remedy: Impossible or very difficult to remove, Can be prevented by using disinfectants during processing, on the factory premises and in the vessels.

7) **Stains through formation of blooms (mud):**
Effect: Light yellow to brownish deposits of pelagic and chebulinic acid which produce map like stains, Was formerly a quality mark of sole leathers, not desired for leathers to be dyed.
Causes: Separation products of bloom-forming tanning agents such as myrobalans, valonea, chestnut and oak,
Remedy: Wiping or washing the leathers, treatment by means of bleaching tanning agents,

8) **Grey-tinge leather color:**
Causes: Use of process water containing iron or finely dispersed iron salts in the tanning liquors,
Remedy: Use condensed water or treated water and completing agents, change the tanning liquors,

9) **Inadequate penetration of tannin:**
Effect: Hard tinny condition of the leather and inadequate elasticity, loose grain and wrinkled grain,
Causes: Incorrect Pertaining with extremely astringent tanning agents, insufficient tanning times, increasing the concentrations too quickly during tanning and retaining,
Remedy: Observation of the Tanner's Golden Rule and regular checks for complete penetration of tannin, the pH value should not be too tow for preliminary tanning, the drumming process should be long enough,

10) Case hardening:
Case hardening Effect: Hare, tinny leathers,
Causes and remedy: as under as under inadequate penetration of tannin.

4.6.9 CONTROL OF VEGETABLE TANNAGE:

Operational:

1. Continuous concentration measurements by determination of the density or the Be degree of the tanning floats in the application vessels.

2. Temperature measurements, in particular during final tonnage,

3. Determination of the pH value by meads of indicators or by meads of electrometric measuring units.

4. Test for complete penetration of color into the pelts by regular cuts at thicker sections in order to verify the penetration depth of the tanning agent.

5. Test for complete tonnage by cutting off a narrow strip of the leather to be checked and putting it into 10-20 percent acetic acid, The untamed or insufficiently at nonce zone swells to a grater or lesser degree, If light falls through that area it appears wax-like and shiny.

Analytical:

1. Determination of the acid and salt content of then liquors or tan solutions, Is determined by titration with 0.05 n sodium hydroxide solution before and after the liquor has run through an ion exchange column which has been filled with a cationic resin.

CHAPTER-FIVE

FINISHING

5.1 WHAT IS LEATHER FINISHING AND FINISHES?

The last and most important operation in a tannery today is finishing where the leather surface is coated with nice looking, colored or colorless, flexible, stretchy, durable film of some film forming materials so that it can attract customers, can protect the leather underneath from all respects and can give comfort to the users. Finishes on leather also serve as a protecting coating.

Most of the leather after tanning, retanning, dyeing and fat liquoring and drying require final finishing. Leather finishing is based on the application of one or more coats of finishing composition or seasons over the surface of leather. The leathers after the application of such season may be allow to dry out, but is often followed by glazing or plating, ironing or polishing. The leather may also be given a pattern by embossing or printing.

Finishing of leather is an extensive and complex technology. Finishing of leather involves application technology based on certain scientific principles, and stimulation of personal creativity aided with sensitive appreciation of art. Thus leather finishing can be linked to a crafts man's work, of real artistic application.

Application part of the technology consists of manual or mechanical operation during which film forming / binding agents are applied on leather surface aiming to improve appearance feel, grain character, and surface protection to aesthetics modes and creative fashion.

5.2 OBJECTS OF LEATHER FINISHING:

- To improve the appearance either by leveling the colour and hiding the surface defects or by providing a base for the production of a polish or gloss.
- Uniformity of shape from leather to leather.
- Changing the colour to that which is required.
- Giving the surface to the leather varying from matt to gloss.
- Adding a transparent film through which the natural appearance of the leather may be viewed.
- To afford protection against moisture, soiling and abrasion.
- To render the colour fast to wet and dry rubbing.
- To render the leather fast to light, heat, acid, alkali and perspiration etc.

- To provide some special effects.
- To provide excellent adhesion properties to continuous flexing and abrasion when in use.
- To provide extra feel smoothness to the leather surface.
- To prevent mould and fungal growth.

5.3 CLASSIFICATION OF LEATHER FINISHING:

In many cases two or more names may exist for the same finish when classified according to finishing techniques finishing materials and finishing effects:

A. Classification according to the finishing technique:

- Glaze finish
- Plate finish
- Glaze/ plate finish
- Corrected grain finish
- Embossed finish
- Spray finish
- Curtain coating finish
- Spray finish
- Roll coating finish
- Film transfer finish.

B. Classification according to the finishing effect:

- Aniline finish.
- Semi-aniline finish
- Opaque finish
- Easy care finish
- Two or multi tone finish
- Brush off finish
- Antique finish
- Fancy finishes
- Invisible finish
- Craquele finish
- Padding finish
- Foam finish
- Solvent free or solvent poor finish

C. Classification according to the finishing materials used:

- Casein finish
- Polymer or binder finish
- Nitro cellulose or colloidion finish
- Cellulose ester finish free from nitro groups
- Polyurethane finish
- Patent finish.

GLAZE FINISH:

Glaze finish is mainly done to get glossy appearance to the leather. It is performed by means of a glazing machine and non-thermoplastic binders. It is used for high quality leathers because it accentuates the natural grain marking particularly well. However, plate finishing is also used to seal the finish.

5.4 THE STRUCTURE OF FINISES:

The finish consists basically of three coats:
Base coat — Pigment coat - Top coat.

All coats are not absolutely necessary- their application depends on the type of leather to be produced. It is possible to choose intermediate stages or to apply the top coast on its own. Basically softer products are chosen for the bottom layers and harder and more resistant products for the final coat.

AS FOR EXAMPLE

Aniline Leather	**Semi-aniline Leather**	**Corrected grain leather**
	Top coat	Top coat
Top coat	Transparent pigment coat	Covering pigment coat
Aniline dyeing	light color base coat	Grain impregnation and base coat

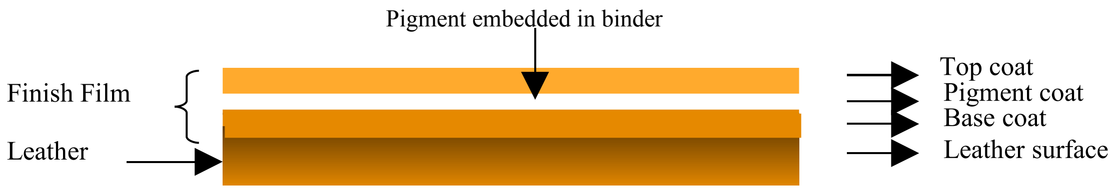


Fig: Different layers of finish film on leather.

Finish Film: Water of the binder solution penetrates the fibers, reaction takes place and precipitates are formed with the formation of gel on leather surface. Copper, Cobalt and Manganese pigments with butadiene binder cause heavy embitterment.

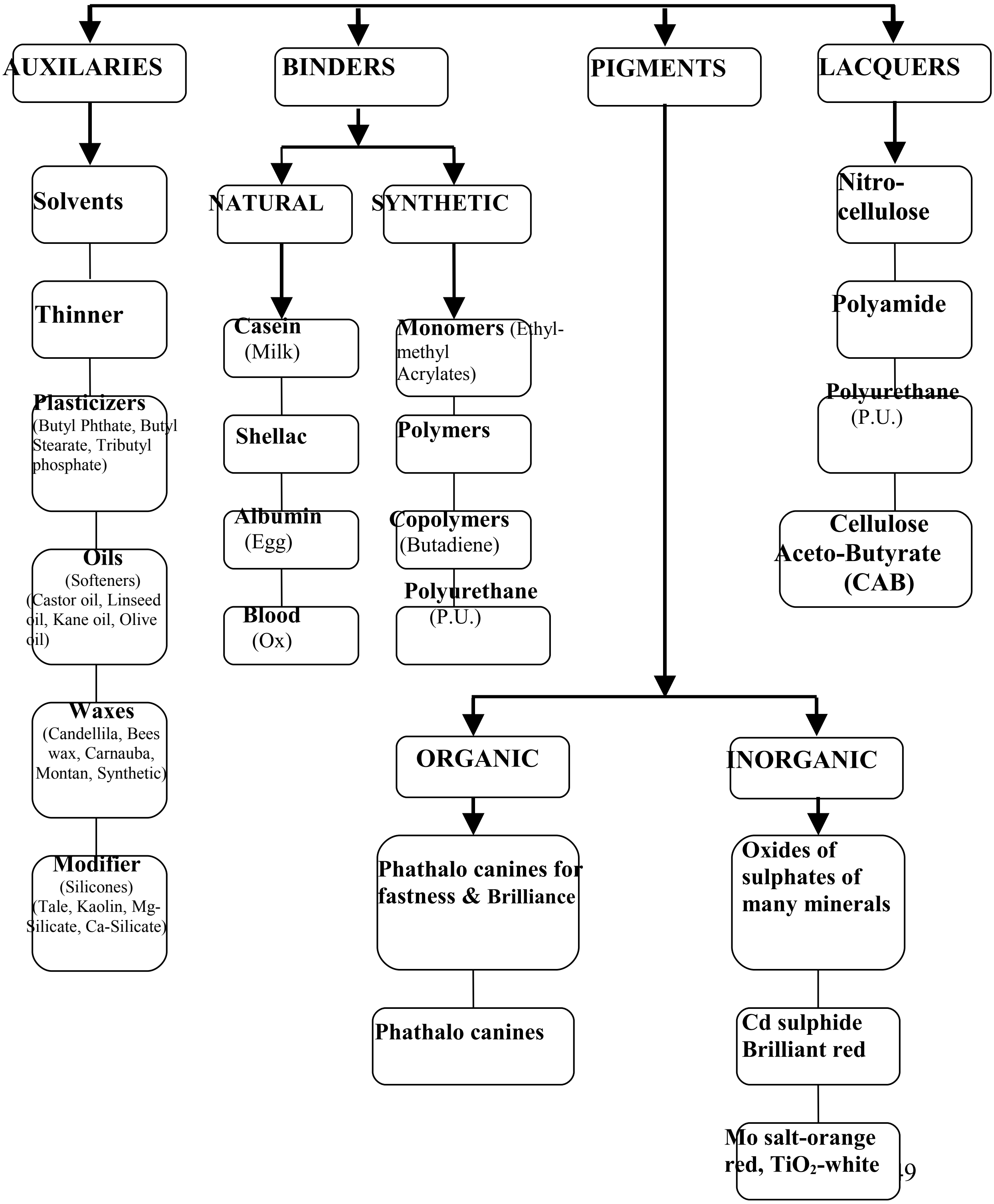
5.5 FINISHING CHEMICALS AND THEIR AUXILARIES:

- Pigment
- Dyes
- Waxes
- Protein binder
- Resin binder
- Polyurethane binder
- Penetrator
- Matting agents / Duller
- Handle modifier
- Gloss giving materials / NC-lacquer
- Fillers
- Solvent
- Plasticizer
- Leveling agent
- Cross-linker
- Thickener

- Protein binder
- Resin binder

5.6 LEATHER FINISHING CHEMICALS AT A GLANCE:

LEATHER FINISHING CHEMICALS AT A GLANCE:



Ref.: National Institute of Leather Technology (Pakistan)-By A.K.M. Moslem Ali.

5.7 TYPES OF LEATHER FINISHES:

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

1). Water type finishes:

These may be based on pigments, protein binders, such as casein shellac, gelatin egg and blood albumin waxes and mucilaginous substances like decoction of linseeds. These finishes are mainly used for glazing or softness. Recently water type finishes based on pigments or days and resin dispersions are increasingly used to achieve special effects on the finished leather. The use of such finishes has produced many improvements over the conventional protein biased finishes such as better adhesion and -legibility of the finish improved filling and sealing properties and greater uniformly of the finish.

2). Solvent type finishes:

Solvent based finishes contain as a binder either polyurethane or colloidion cotton (nitro- cellulose). These finishes are dissolved in organic solvents such as butyl acetate cyclo - hexagon etc These finishes are widely used for finishing upholstery leather, bag leather case leather and certain military lathers where low temperature flexibility is necessary.

3). Emulsion type finishes:

Emulsion type finishes consist of emulsions of nitro cellulose or resins. Such emulsions are being widely used to confer combining properties of water and lacquer finish. Lacquer emulsion top coats for upper garment and glove leather are gaining wide acceptance. In leather finishing the three types of finishes mentioned above can either be used alone one or in combination with one another. The choice-depends on the specific effects desired on the finished leather.

5.8 APPLICATION OF FINISHES:

The final look and qualities of finished leathers largely depend upon how the finish was applied on the leather surfaces. Finishes are applied on leathers by these methods:

a) Pad coating / padding: The chief method for application of base coating floats is done manually with a sponge, a folded cloth cleaning wool or cotton wool covered with a permeable cloth. The pad is first dipped into a lacquer or dye solution and then lightly wiped over the raised parts. This serves to achieve two color effects and high gloss or mat effects,

b) Spraying / spray coating: It is the most common method and is applied by means of compressed air. It is suitable for applying aqueous and solvent containing finishing floats. This is done by means of manual spraying guns in spraying cabling with exhausters or by mans of automatic spraying guns on continues spraying belts

c) Curtain coating: The curtain coating float is poured onto the leather being fed through a lost in the heard or by mans of an overflow system. The unspent float flows back into the supply tank and is continuously re-circulated. To ensure an even flow of the curtain it is important that the float be free from foam bubbles and possess adequate viscosity so that does not break off abruptly due to air whirls or trapped air. It should be ensured that drying takes place in an absolutely dust free environments.

5.9 CHRACTERISTICS OF FINISH FILM:

An ideal film for leather should have the following characteristics:

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 will crack in course of time.

2) **Adhesion:** The film should be firmly fixed to the leather surface and adhere to the pigment particles and others very firmly.

3) **Holding power:** The film should have sufficient capacity to hold in it other substance like pigment, plasticizer etc. and never allow the plasticizer to migrate into the leather.

4) **Gloss:** The film should glaze by itself or should acquire this quality after glazing under glazing machine or hot plating or brushing.

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 colouring materials so tightly that it does not come out when rubbed with a dry or wet cloth.

6) **Waterproofness and water vapour permeability:**
The film should repell water so that the leather under it does not come in contact with water but at the same time, it should allow water vapour to pass through. This is especially important for shoe upper leathers.

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

8) **Resistance to Acid, Alkali and Chemicals:**
During use the leather comes in contact with dirt, mud, acid and alkaline fumes, sweat etc. the film on the leather should have therefore, sufficient capacity to protect the leather from these.

CHAPTER-SIX

PROCESS INFORMATION

6.1 EXPERIMENTAL PROCEDURE FOR CHROME FREE VEGETABLE TANNED SHOE UPPER LEATHER FROM COW HIDE:

Raw Materials:

Wet salted cow hide (good selection)-one piece
Trimming: By hand knife.
Take wet salted weight. (All % based on this salted weight).

Name of Operation	% of Chemicals use	Time	Analytical Checking

Pre-Soaking: (in bowl)

300 %	Water at N.T.		
0.2 %	Soda Ash		
0.2 %	Wetting agent (LD-600)	Run-20’	

Howling 20 minuets,
Keep in the bath for 1 hour. Drain.

Main-Soaking: (in bowl)

300 %	Water at N.T.		
0.4 %	Soda Ash		
0.3 %	Wetting agent (LD-600/NI-extra)		
0.2 %	Preservatives (Busan-40L/Aracite-DA)		
		Run-30’	**P^H=9.0-9.5**

Howling 30 minuets,
Leave Overnight in the bath, Next day washes well and Drain.

Liming: (in bowl/ drums/paddles)

300 %	Water at N.T.
4.0 %	Lime
3.5 %	Sodium Sulfide
1.0 %	Liming Auxiliary (Erhavit MB/ Colapel-DL)
0.3 %	Wetting agent (LD-600/Lisapol)
0.2 %	Preservatives (Busan-40L/Aracite-DA)

Howling 30 minuets, leave for 3 hours. **P^H=12.5-13.0**
Leave in the bath for 2-3 days with regular hauling.
Then scudding by hand very well.

Fleshing:
Fleshing is done by fleshing machine. Then pelt weight is taken,
(All % based on this pelt weight).

Name of Operation	% of Chemicals use		Time	Analytical Checking
Chemical Wash: (in Drum)				
	200 %	Water at N.T.		
	0.25 %	Meta Bi-Sulfite	Run-20’	
Deliming:				
	100 %	Water at N.T.		
	1.5 %	Ammonium Sulphate		
	1.5 %	Ammonium Chloride		
	0.5 %	Meta bi-sulfite	Run-60’	

Check: Cross-section with Phenolphthalein. **Colorless**. **P^H=8.0-8.5**

Bating: (Add to the same bath)
Temperature was adjusted at 37ºC

1.0 %	Bating agent (EG-98)		
0.5 %	Wetting agent (LD-600/Lisapol)	Run-60’	

Check: Bubble test.
Then scudding by hand knife and wash well with lattice door until clear water come out.

Pickling: (in Drum) (Pickling for Alum and Aldehyde Pre-tanning)

	80 %	Water at N.T.		
	8.0 %	Salt	Run-15’	
+	0.5 %	Formic acid (1:10 dilution)	Run-30’	
+	0.2 %	Imprapel CO	Run-15’	
+	1.2 %	Sulfuric acid	0’+30’+30’+90’	
		Leave Over Night		**P^H=2.8-2.9**
+	2.0 %	Alum (fitkiri)	Run-40’	

Drain half of the pickle bath.

Pre-Tanning Aldehyde Tanning Agent:

(Add to the pickle bath)

	2.0 %	Relugan TX-50/GTW	Run-45’
+	2.0 %	Hypo	Run-30’
+	2.0 %	Neosyn RWP	Run-45’
+	1.0 %	Sodium Formate	Run-30’
+	1.0 %	Sodium bi-carbonate	
	0.2 %	Preservatives (Busan-40L)	Run-90’ (0’+30’+30’)
		Drain, Pile for 2-3 days.	**Check: P^H=3.8-3.9**

Next operations:

Samming: Samming is done by machine.

Shaving: Shaving is done by machine (Thickness-1.1-1.2 mm).
Take shaved weight (All % based on this shaved weight).

Acid Wash:

	150 %	Water at N.T.	
	0.3 %	Oxalic acid / Acetic acid.	
	0.3 %	Wetting agent (LD-600)	Run-20’
+	1.0 %	Meta bi-sulfite	Run-20’

Drain, Rinse well.

Neutralization:

	150 %	Water at 40ºC.	
	2.0 %	Neutralizing Syntan (Neosyn BS3/NG/Tamol-A)	
	1.0 %	Sodium Formate	
+	1.5 %	Hypo	
	1.0 %	Remsol C-2 / L.L.-SNS	Run-30’
			Check: P^H=4.5-4.6

Drain, Wash well.

Vegetable Tanning:

	150 %	Water at 40ºC.	
	3.0 %	Paramel PA/Relugan RE	Run-30’
+	3.0 %	Tanigan OS	Run-20’
+	1.0 %	Trisul ML/Silpover liq.1C	
	0.5 %	Trilon B Liquid	Run-20’
+	3.0 %	Relugan D/Sacmatan P-100	Run-20’
+	10.0 %	Mimosa	
	5.0 %	Quebracho	
	2.0 %	Tanigan OS	Run-45’
+	10.0 %	Mimosa	
	5.0 %	Quebracho	
	3.0 %	Neosyn WO/RWP	Run-2 hours

Check: penetration (100 %)

Leave Over-night

	+	50 %	Water at 40ºC.	
		0.5 %	Formic acid	Run-30'
	+	0.5 %	Oxalic acid	Run-30'
		Check: P^H=3.6-3.7		
		Drain, Wash well.		
Fat-Liquoring:				
		200 %	Water at 50ºC.	
		2.0 %	Filler Syntan	Run-20'
			(Butan-1908 / Parvol Filler PP)	
	+	3.0 %	Remsol B-40 / DXL	
		2.0 %	Remsol C-2 / SLP	
		2.0 %	Trisul ML/Silpover liq.1C	
		0.25 %	Preservatives (Busan-30L)	
		0.5 %	Synthol-O	Run-45'
	+	1.0 %	Formic acid	Run-30'
	+	1.5 %	Neosyn PWG /WO/DLE)	Run-30'
Top-Fat:	+	0.5 %	Permol NC / Catalic GS	
		0.5 %	Synthol-O / SK	Run-30'

Drain, Rinse, Horse up Over-Night.

Next morning,

Setting: Setting is done Setting Machine.

Vacuum Drying: Vacuum dry at 50' for 1 min.

Hang to dry: For two days.

Toggling: Dry in toggle dryer with maximum tension.

Staking: Staking is done by Vibration Staking Machine.

Trimming: It is done to reduce unnecessary parts of leather.

Kiss-Plating: It is done by Roto-Press Machine at 70ºC / 75 kg pressure.

Then it was ready for finishing.

6.2 GLAZE FINISH FOR CHROME FREE V.T. SHOE UPPER LEATHER:

POLISH GROUND:

Cationic ground	-	250	parts
Cationic dye liquid	-	50	parts
Cationic Wax	-	20	parts
Penetrator	-	50	parts
Water	-	630	parts

Spray 2-3 cross-coats, Dry well, polished.

SEASON COAT:

Pigment	-	50	parts
Dye liquid	-	25	parts
Protein Binder	-	50	parts
Wax FF	-	25	parts
Glazing Binder	-	200	parts
Binder 1079	-	50	parts
Water	-	600	parts

Spray 2-3 cross-coats, Dry well.

TOP COAT:

Glazing Top	-	250	parts
Paste Top	-	50	parts
Water	-	700	parts

Spray 2-3 cross-coats, Dry well.

FIXING COAT:

Formalin Solution	-	250	parts
Acetic acid	-	30	parts
Water	-	720	parts

Spray 2-3 cross-coats, Dry well.
Glazing by machine, Finally Rotopress at 120ºC / 50 kg pressure.
Now, Finishing is completed.

6.3 TECHNICAL INFORMATION ABOUT CHEMICALS USED FOR THE COMPLETION OF THE PROJECT:

1. LD- 600 : Wetting agent, Charge: Non -ionic.
(BASF, Germany)

2. Busan 40L : Bactericide for leather tanning
(Buckman, USA)

3. Busan 30L : Fungicide for leather tanning
(Buckman, USA)

4. Mollescal BW : Soaking auxiliary. (BASF, Germany)

5. Erhavit MB : Sulphide free liming auxiliary.
P^H value: 9-11 -0 (TFL, Germany)

6. Mollescal MF : Amine and Sulphide free liming auxiliary.
(BASF, Germany)

7. Bate EG- 98 : Bate powder (Hodgson, England)

8. Basozym C-10 : Bating agent based on pancreatic enzymes.
Activity ca. 1000 LVU/g.

9. Neosyn 9P : Basic aluminum tanning and
Retanning agent, total solids: 80%
Basicity: 66% P^H (2% solution): 4.1-4.4
(Hodgson, England)

10. Syntan ZR : Anionic zirconium sulphate,
Total Solids: min, 92%,
P^H: 0.9-1.5. Basicity: 32%

11. Derugan 3080 : Glutaraldehyde tanning agent.
Active substance: 60-64%
P^H (10% solution): 3-5
(Schill & Seilacher, Germany)

12. Neosyn RW : Cresylic multipurpose replacement syntan,
Total solids: 92% , P^H (2% solution): 4.0-5.5

(Hodgson, England).

13. Neosyn BS3 : Naphthalene based neutralizing syntan
Total solids: 94% pH (2% solution):7.0- 8.0,
(Hodgson, England).

14. Neosyn WO : Replacement syntan, based on Cresylic material.
Total solids: 92% pH (2% solution):3.5- 5.0,
(Hodgson, England).

15.Tolcide2230 : Fungicide for leather making, (Albright and willson).

16. Relgan RE : Acrylic copolymer, Charge: anionic.
P^H: 6.5. Active substance: 40%
(BASF, Germany).

17. Paramel P-100 : Amino resin, Total solids: 94%
P^H (10% solution): 8.5-9.7.
(Hodgson, England).

18. Tanigan OS : Replacement tanning materials.
Concentration: 96-98%
P^H (10% solution):3.5
(Bayer, Germany).

19. Neosyn N : Naphthalene auxiliary dye leveling Syntan.
Total solids: 92% P^H (2% solution): 6.5-8.5
(Hodgson, England.)

20. Lipoderm liquor SNS: Synthetic fat-liquor (BASF)

21. Slipover liquor 1C: Supplied oxidized fish oil. Charge: anionic,
Fat content: 90%, P^H (2% solution): 7.0
(BASF, Germany).

22. Trisul ML : Sulphited stabilized fatliquor based on oxidizing
marine oil. Active content: 80 %,
P^H (2% solution): 5.0-6.0
(Hodgson, England.)

23. Lustral UT : Transparent binder that enables very
light and very adherent films.
P^H: 7.5± 1. Charge: anionic (ALPA)

24. Paramal PA : Acrylic Resin Binder (Clariant)

26. Quebracho : Vegetable Extract . (ATO)

27. Mimosa : Vegetable Extract, P^H (10% solution):4.4-4.5

28. Synthol O : Synthetic oil, Active matter: 100%, Clear yellow oil, (Smith & John).

29. Remsol B40 : Sulphited natural/synthetic oils. Anionic, Active matter: 70 %, (Hodgson, England).

30. Remsol C2 : Stabilized synthetic fatliquor. Anionic, Active matter: 50 %, P^H (2% solution):7.0-8.0 (Hodgson, England).

31. Relugan GT50 : Gluraraldehyde, Total solids: 92% P^H (2% solution): 3.5, (BASF, Germany).

32. Relugan GTW : Modified glutaraldehyde, gives leathers with high Light fastness and a fine, flat grain.

6.4 MACHINES AND EQUIPMENTS USED IN LEATHER MANUFACTURING RPOCESS:

1. Plastic Bowl.
2. Trimming knife / Blade.
3. Liming drum / Paddle / Pit.
4. Fleshing Machine.
5. Fleshing knife.
6. Blunt knife for Scudding.
7. Tanning Drum.
8. Wood Horse.
9. Samming Machine.
10. Splitting Machine.
11. Shaving Machine.
12. Retanning Drum.
13. Samming-setting Machine.
14. Vacuum Dryer.
15. Tunnel Dryer.
16. Vibration Staking Machine.
17. Jaw Staking Machine.
18. Toggle dryer.
19. Buffing Machine.
20. De-dusting Machine.
21. Hand Spray Machine.
22. Auto Spray Machine.
23. Roller Coater Machine.
24. Polishing Machine.
25. Roto press Machine.
26. Hydraulic press Machine.
27. Embossing Machine.

28. Hair cell Machine.
29. Glazing Machine.

6.5 PICTURES OF SOME COMMON MACHINES USED IN LEATHER MANUFACTURING PROCESS:

Fig: Fleshing Machine

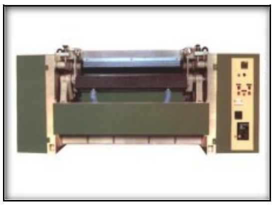


Fig: Fleshing Machine

Fig: Splitting Machine

Fig: Shaving Machine

Fig: Shaving Machine

Fig: Setting Machine

Fig: Staking Machine

Fig: Polishing Machine

Fig: Auto Spray Machine

Fig: Auto Spray Machine

Fig: De-dusting Machine

Fig: Buffing Machine

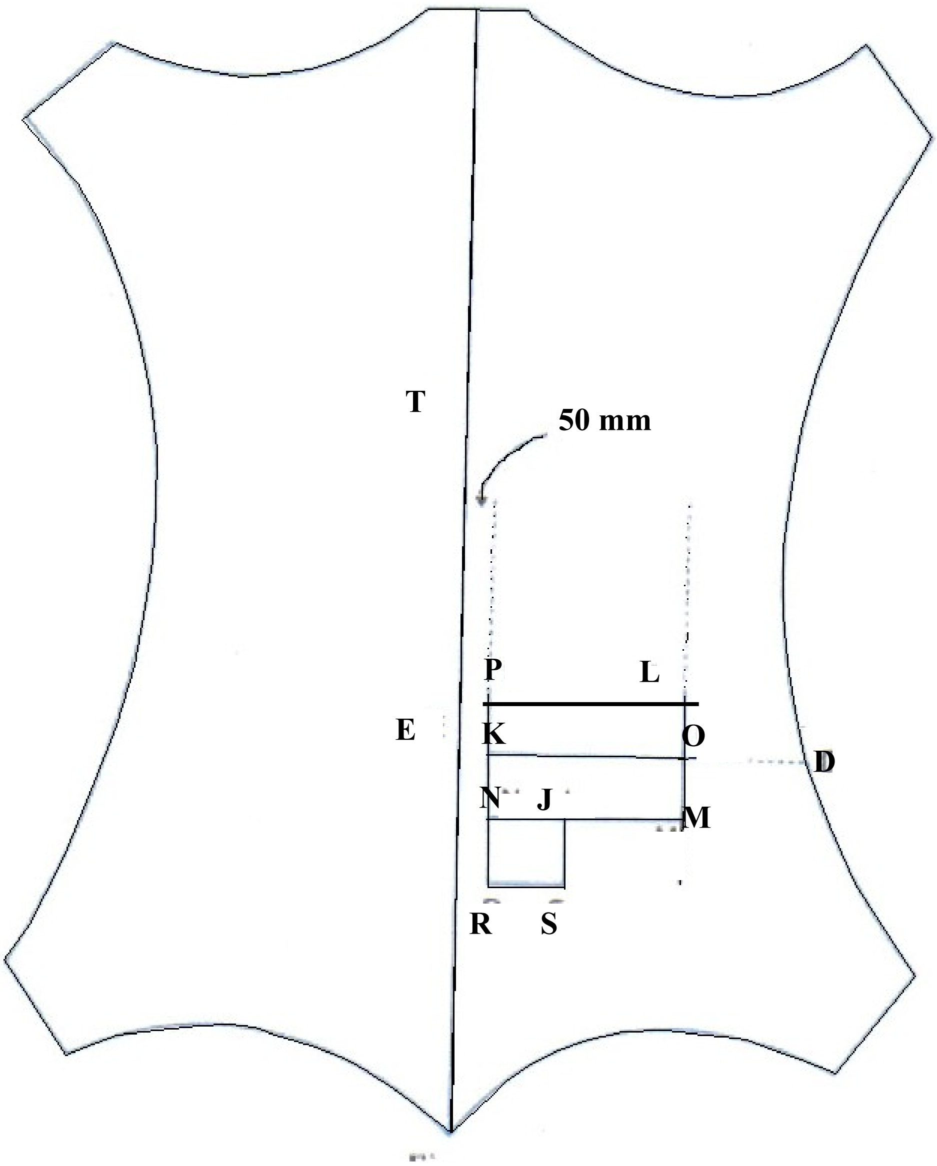
CHAPTER-SEVEN

SAMPLING AND PHISICAL TESTING OF SHOE UPPER LEATHER

SAMPLING POSITION OF FULL HIDES/ SKINS:

PLMN FOR PHYSICAL TESTING

JNRS FOR CHEMICAL ANALYSIS



FOR FULL LEATHER

CHAPTER-SEVEN

PHYSICAL TESTING OF SHOE UPPER LEATHER

The shoe upper leather samples and their finished leather samples were tested for their various physical properties. These properties indicate the quality of the finished leathers produced. Due to limitation of time and the availability of instruments, selected physical tests were accomplished and these tests are briefly discussed below:

7.1 Tensile Strength And Percentage Of Elongation At Break Based on SLP-6, IUP/6:

The tensile strength and elongation at break was measured by Tensometer. Tensile strength is the force (Kg) per unit area of cross-section (Sq. cm) required to cause a rupture of the test specimen.

So, Tensile strength of the specimens was calculated using following formula.

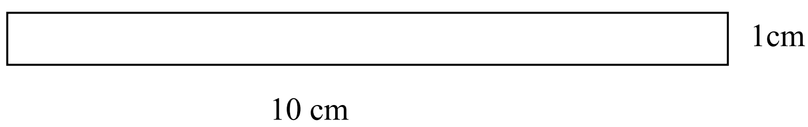
$$\text{Tensile strength} = \frac{\text{Breaking load (Kg)}}{\text{Thickness (cm) X Width (cm)}}$$

Breaking load mainly depends upon the number of collagen fibers acting in the direction of applied load, so it is more or less constant for a piece of leather specimen because the number of fibers in that piece is always constant.

The extent of elongation of the leather specimen at the time of its breaking, while applying the tensile force, expressed as the percentage on the original length of the said specimens the elongation at break. Elongations at break for these specimens are calculated from the distance of the jaws after breaking was occurred.

$$\text{Percentage of Elongation} = \frac{\text{Final length} - \text{Initial length}}{\text{Initial length}} \times 100$$

$$= \frac{\text{Length increased}}{\text{Initial length}} \times 100$$

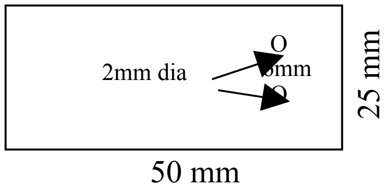


Sample for the determination of tensile strength

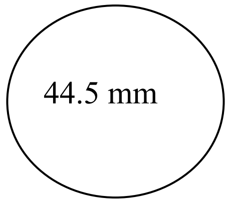
7.2 Stitch Tear Strength (double hole); SLP-8

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

$$\text{Thus, stitch tear strength Kg/cm thickness} = \frac{\text{Tearing load (Kg)}}{\text{Leather thickness (cm.)}}$$



Sample for Stitch tearing test



Sample for Lastometer test

7.3 Lastometer Tests (SLP-8, SLP-9, and IUP-12):

These tests were performed by the following official method of analysis 1965. By lastometer tests grain cracking strength, bursting strength and their corresponding distension values can be obtained. The bursting strength is an index of the overall strength of the leather. For lastometer test the specimens were cut from the samples by a circle type cutting disc and the specimens were placed on a lastometer being conditioned by clamp whose flesh sides were adjusted to the ball with the pressure by handling indicates the distension at a rate of 0.2mm/sec. and simultaneously watch the grain surface for the occurrence of a crack and the ball and distension of grain cracking and bursting were noted.

Then the grain crack strength was determined by the formula,

$$\text{Grain crack strength (Kg/cm)} = \frac{\text{Grain cracking load (Kg)}}{\text{Thickness of the leather sample (cm)}}$$

Craking distention= mm

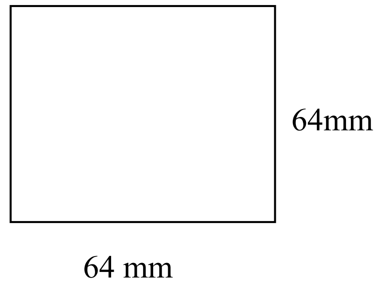
Again, the bursting strength was determined using following formula,

$$\text{Bursting strength (Kg/cm)} = \frac{\text{Load in Kg to burst the sample}}{\text{Thickness of the leather sample (cm)}}$$

Bursting distention= mm

7.4 Vamp Flexing Endurance (SATRA PM 25):

The test was followed by official method of analysis SATRA PM 25:1992. A square specimen(64mm X 64mm) of the leather is folded over two inverted v-shaped clamps the clamps are able to move relative to another so that as they become closer the specimen is fixed to production one downward crease surrounded by four upward creases during the test the clamps oscillate at a constant speed so that the specimen is repeatedly flexed the test can be carried out with either wet or dry specimen at room temperature or dry specimen subzero temperature After a predetermined number of cycles the test is stopped and the specimen is visually examined.



Requirements:

Outer materials (Dry 20ºC) – 10,00,000 cycles
Outer materials (Wet 20ºC) – 10,00,00 cycles
Lining materials (Dry 20ºC) – 3,00,000 cycles
Cold test (-5 to -30ºC) – 1,00,000 cycles

7.5 Tearing strength:

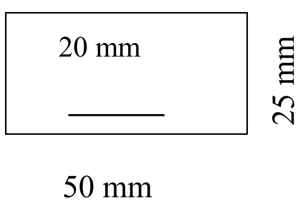
It is the load required to tear a sample of leather of unit thickness.

$$\text{Tearing strength, kg/cm thickness} = \frac{\text{Tearing load in kg}}{\text{Thickness of the leather sample (cm)}}$$

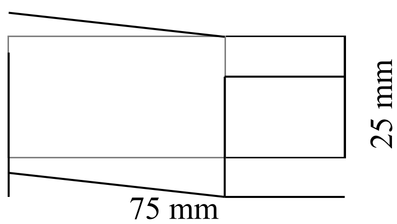
7.6 Split Tear strength:

It is the load in kg required to continue splitting of half splitted leather into two layers. Splitting is done at the centre of the leather thickness and parallel to the leather surface. Specimen size 75 mm x 25 mm. It gives the idea about the fibre strength of the leather and also the weaving nature of the fibres.

$$\text{Split Tear strength, kg/cm thickness} = \frac{\text{Tearing load in kg}}{\text{Thickness of the leather sample (cm)}}$$



Sample for test no. 5



Sample for test no. 6

7.7 Measurement of the Shrinkage Temperature:

8cm. long and I cm wide leather sample is taken, then attached to the hooks of the shrinkage meter and are put into the water of the beaker, then heat the water until the specimen shrinks considerably. Leather sample is cut into two ways-parallel to the back bone and perpendicular to the back bone.

Shrinkage temperature (Ts) was determined using following formula,

$$Ts = \frac{T1+T2}{2}$$

Here, T1 = parallel to the back bone.
T2= perpendicular to the back bone.

7.8 Tests For Dry And Wet Rub Fastness (SLF-5 / IUF- 450 / DIN 53339):

The tests were carried out by official method of analysis SLF-5.This is a very useful test for finished leather. A revolving pad is made to rub the leather for a successive number of revolutions and the effects of such rubbing under both the wet and dry condition are studied using a grey scale. While a 2.5 kg load is used for dry rubbing and 730g load used for wet rubbing.

Dry rub fastness: leather dry, felt dry.
Wet rub fastness: leather dry, felt wet.

Assess the degree of damage or change in the finish coat, staining of the felt pad and change in colour of the test specimen.

7.9 Tests for wash fastness:

By treatment of the color of leather to washing is meant its resistance to washing under domestic condition. In washing leather, not only many changes in color occur in the leather but also colored substances my bleed from it and may stain adjacent materials. In this method specimens of leather in contact with specified undyed textile of wool land of cotton are mechanically agitated underspecified condition of time and temperature in a soap solution then rinsed and dried. The change in color of the specimens and the staining of the textiles and assessed with standard grey scales.

7.10 Water vapour permeability (WVP) Test:

Almost all upper leathers should be permeable of water vapour because the perspiration formed inside the shoes, as for example, should go out through the leather to give wear comfort to the users. The WVP of tanned leather is gradually high but it gradually goes down with the incorporation of fats, oils and waxes into the tanned leather during finishing. The finish coat specially that contains resin, casein, shellac and similar film forming materials in excess amount, reduces the WVP of leather considerably. The oil treatments and finishing of leathers should be such that the WVP of tanned leather is reduced to minimum extent.

The basic technique of all WVP tests develop for leather is the use of leather specimen as a diaphragm with a region oh high relative humidity on the other. The gain in weight per unit area on the low relative humidity side in unit time is expressed as the WVP property of the leather.

$$WVP = \frac{7639\ M}{d^2 t} \text{ in mg/ cm}^2\text{/ hr}$$

Where, M = the increase in mass of the jar (M_2-M_1) in mg.
d = the average diameter of the neck of the jar, in mm.
t = time between the first and second weighing in min.

Standard value for shoe upper leather: 180 – 250 mg/ cm^2/ hr.

7.11 THE MOST IMPORTANT QUALITY REQUIREMENTS OF VEGETABLE TANNED SHOEUPPER LEATHER:

Sl.No.	Properties	Requirements
1.	Tensile Strength (kg/cm^2)	Min. 250 kg/cm^2
2.	% Elongation at Break	Max. 70 %
3.	Stitch tear strength (double hole) (kg/cm thickness)	Min. 100 kg/cm
4.	Split tear strength (kg/cm thickness)	Min. 40 kg/cm
5.	Water Absorption After 2 hours After 24 hours	 Max. 30 Max. 46
6.	Air Permeability (cc./Min./cm.Hg.pressure)	Min. 80
7.	Water vapour permeability (mg/cm^2)	Min. 200 mg/cm^2
8.	Ash content % (substracting Tanning oxide)	Max. 1.0 %
9.	Cr_2O_3 Content % (Min.)	–
10.	Fat content %	16-23 %
11.	Loss by Washing %	Max. 6.0%
12.	Degree of Tannage	Min. 50

CHAPTER-EIGHT

PHYSICAL TESTING RESULTS AND DISCUSSION FOR DIFFERENT TESTS:

The results obtained by different physical testing on the prepared leathers are tabulated in this chapter followed by short description of the results.

a) Table for the results of tensile strength and percentage elongation at break:

Sample	Results for tensile strength and Elongation at break			
	Perpendicular		**Parallel**	
	Tensile strength kg/sq cm	Elongation %	Tensile strength kg/sq cm	Elongation %
Sample-1& 2	400	44	423	36
Standard for shoe upper: Tensile strength = Min. 200-300 kg/cm^2 % Elongation at break = Max.45-55 %				

b) Table for the results of stitch tearing strength :

Sample No	**Thickness (cm)**	**Tearing load (kg)**	**Stitch tearing strength (kg/cm)**
Sample No-1	.13	22	170
Sample No-2	.13	20	155
ISI Standard for shoe upper: Stitch tear strength = Min. 60-120 kg/cm			

c) **Table for the results of Lastometer test:**

Sample No	**Lastometer test**			
	Grain Crack strength (kg/cm)	Distension at grain crack (mm)	Grain bursting strength (kg/cm)	Grain bursting distension (mm)
Sample No-1	231	4 mm	546	7.5 mm
Sample No-2	385	9 mm	692	11.5 mm
ISI Standard for shoe upper: Cracking load = min. 20 kgf, Distention = max.6-7 mm.				

d) **Table for the results of Vamp flexing endurance :**

Sample No	Grain appearance after **5,000 flexes**	Grain appearances after **10,000 flexes**	Mandrel scale rating
Sample No-1	Slight creases	Marked creases	Rating- 5
ISI Standard for shoe upper: Crease rating = 3-4 (acceptable)			

e) Table For the results of shrinkage temperature:

Sample No	**Shrinkage temperature**
Sample No-1	82ºC
Sample No-2	85 ºC
Vegetable tanned leather	70-84 ºC
Basic Aluminum tanned leather	70-80 ºC
Gluteraldehyde tanned leather	80-85 ºC

The combination tanned leathers show enough shrinkage temperature for the production of shoe upper leathers.

f) Table for the results of wet and dry rub fastness tests:

Sample No	**Dry rub fastness**											
	32 rev		64 rev		128 rev		256 rev		512 rev		1024 rev	
Sample No-1	5	5	5	5	5	5	5	5	5	5	4/5	4/5
Sample No-2	5	5	5	5	5	5	5	5	5	5	4/5	4/5
Sample No	**Wet rub fastness**											
	32 rev		64 rev		128 rev		256 rev		5 1 2 rev		1024rev	
Sample No-1	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5
Sample No-2	5	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5

g) Table for wash fastness test:

Sample No	**Grey Scale rating**	
	For leather	For cloth
Sample No-1	3/4	2/3

Sample No-2	3/4	2/3

h) Table for water Proof ness test:

Sample No	**No of flexing**
Sample No-1	575
Sample No-2	567

CONCLUSION AND RECOMMENDATION

From the physical testing results and comparing with standard value, it is seen that the leather manufactured for this project work has excellelent strength properties. Considering the physical properties like tensile strength, grain cracking strength, grain bursting strength, distension at grain crack, shrinkage temperature, rub fastness, flexing endurance of the leather studied, it can be concluded that the vegetable tanned leathers are suitable for the manufacture of upper leather.

But vegetable tanning agents produce thick leather. They increase the fullness and firmness of leather. They can fill the void space between the fibres. As a result the water vapour permeability, air permeability properties of the leather produced is not satisfactory. Moreover, the flexing endurance and vamp flexing result is lower. But these are the very important properties of shoe upper leather.

The shrinkage temperature of vegetable tanned leather is good though it is lower than chrome tanned leather. Vegetable tanned leather has less soft than chrome tanned leather and it became darker in contract with water, air and light.

Inspite of these disadvantages vegetable tanned leathers are widely used from ancient time to still now. They can be used for making protective shoes like army shoes, industrial shoes and various fashionable shoes or children shoes, ladies shoes, sport shoes etc. They can be used not only for shoe upper leather, but also used for making belts. Shoe soles and lining, upholstery, handbags and luggage, bookbinding and straps.

Embossing, Boutique effects, glazing and different plating effects can be easily done on vegetable tanned leathers. The feel, grain smoothness, glazing properties of the studied leather are good.

At present, people are more conscious about protecting their environment. They try to avoid using harmful and toxic substances. They try to eliminate or reduce chrome containing solid waste from tannery effluent. As a result the use of vegetable tanning and environment friendly tanning process increases day by day.

Finally, my opinion is that this tanning process can be used for manufacturing good quality shoe upper leather and I think it will be popular in the leather industries at present and in near future.

CHAPTER-NINE

COSTING OF LEATHER

(Per Sq.ft.)

Costing is an important matter for any industry. For the production of any product, companies profit or loss can be known from costing. How much will be the product price, which price of product will be profitable, is fixed from calculating different cost related to the industries. Costing is determined in the following way:

Costing = Direct cost + Indirect cost + Profit.

Direct cost = Material cost + Production cost + Electricity / gas / fuel cost + etc.

Indirect cost = Administration cost + Helping equipment or machine tools + lighting cost etc.

In leather industries, costing is calculated for hundred or thousand sq. ft. of leather. From these, costing for per sq. ft. leather can be calculated. Here, given a rough idea about costing for per sq. ft. of leather.

Costing (for per sq. ft. leather)

Purposes		Cost in Taka
1. Raw materials cost	=	70
2. Chemicals cost / pre costing cost:		
i. Wet blue	=	07
ii. Crust	=	10
iii. Finishing	=	15
3. Labour cost	=	03
4. Machine depreciation cost	=	10
5. Utility cost	=	03
6. Maintenance cost	=	03
7. Administration cost	=	10
8. Vat / Tax	=	04
9. Others	=	05
10. Profit (20 %)	=	28
Total cost	=	170 Taka

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SAMPLE ATTACHMENT

SAMPLE: 01

CHROME FREE VEGETABLE TANNED GLAZE FINISHED SHOE UPPER LEATHER FROM COW HIDE.