CHAPTER-ONE

INTRODUCTION AND LEATHER PREVIEW

<u>1.1 INTRODUCTION:</u>

According to historians, the art of tanning originated before the down of recorded history. Pre-historic people used to live by hunting cloths of some soil were perhaps necessary, for protecting the body from cold and rain. It is very likely that for clothing the pre-historic hunter utilized the skins of the animals he killed. He might have noticed that raw hides and skins putrefied in kept wet and turned hard and rough when dried out. The dry, hard skin was certainly inconvenient to warp up his body. It would thus be only natural for him to try to soften the fur while drying it and in this attempt to render the skin soft and convenient to wear that the foundation of the art of tanning was perhaps laid by the prehistoric people. Primitive men might also have notice that the skins thus smeared with fats dried priced one among them any ways in which the primitive people tried to preserve animal skins. Dressing of skins by the application of fatty and albumin's matter like tallow, oil egg yolk, milk, cured etc. is practiced even today by many. Furs are dressed more or less according to the above process even today.

The preservative properties of wood smoke seen also to have been noticed in pre-historic times and these properties were made use of in making leather. Skins besmeared with grease were perhaps smoked over word fire which also helped the fact to perpetrate the leather.

Tanning of hides and skins by treating them in infusion of banks, fruits and leaves of plants developed perhaps at a later date.

The use of alum in tanning came to be known within his tonic period and that of the salts of chromium of quite recent data, i.e. the latter part of the 19th century. The discovery of chrome tanning is attribute to Knapp in 1885. The first commercial production of chrome-tanned leather was done by an American chemist, Augusts Schultz in 1884. The chrome-tanned leather could be produced quicker than other types of leather and was very resistant to water.

Chrome tanned leather is ideal for footwear and most 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 of chrome and vegetable or synthetic tanning agents. The uppers of our shoes are mistily perspiration absorbed by the leather confers additional ability to stench; leather has a much greater capacity for water absorption the synthetic substitutes.

Leather can be produced to give the optimum combination of elasticity and plastic set required in the shoe for shape retention and Comfort. Synthetics are generally too clash's. It is very difficulty for synthetics are uppers to copy the wonderful arrangement and system that nature has given to leather as for as absorption and dispersion of moisture are concerned fibres.

In spite of many good properties of genuine leather, synthetics are making, inroads in to traditional leather markets due to lover costs of synthetic substitutes and higher cost of genuine leather and competition from leather substitutes in rowing.

It is therefore very important that tanners should endeavor to produce leather with foot comfort, optimum plasticity end elasticity and which feels and looks different from the synthetic substitute. The tanning, industry must be prepared to fight the leather substitute for its survival.

1.2 HINDS AND SKINS:

The outer covering of big domestic animals like cow, buffalo, horse. steer etc. are called hides where as those of small domestic animals like goat, sheep and deer etc. are known as skins. This classification of course, is not true in the case of outer covering of wild animals tiger skin as for example is as or sometimes bigger than cow hide but it is called a skin.

Hides are large in size; thicken in substance and heavier ill weight than skin. An intermediate class is called a kip. A kip is the hide of immature cattle called a kip. It is smaller, lighter, and thinner than a hide, but larger, heavier and thicker than calfskin. Cattle hides above 251 bas in the wet salted condition are classed as hides and those below 15 lbs m calf skins. Cattle hides weighting been 15 lbs in the wet salted condition are classed as kips.

CHAPTER-TWO

2.1 LEATHERS:

Hides and skins are of proteinous substance and therefore putrefy unless preserved. By the application of various chemicals (tanning) and mechanical treatments, such putrescence outer covering are preserved from decay and converted into non-putrescence, which is suitable for convenient use, known as leather.

Leather has been an important and widely used material since ancient times. It has been in use for various purposes including personal protection against adverse forces of nature long before the development of weaving unknotting. Leather is a typical or unique sheet that effectively combined with wind resistance and water vapour permeability.

For leather manufacture several operations are essential these operations can be classed into following three groups these are

- (a) Pre-tanning or beam house operations.
- (b) Tanning operations
- (c) Post-tanning operations

2.2 WHAT IS SHOE UPPER LEATHER?

The upper leather used for footwear upper manufacture is called shoe upper leather occupies the most important place in the leather industry. They have the largest share in the leather production i.e. > 50whereby upper leather made from cattle hides account for the major part followed by calf and goat skins and in descending order sheel skins pig skins horse hides and to small extent buffalo hides kangaroo skins and reptile or fish skins.

2.3 REQUIREMENTS OF PROPERTIE'S OF SHOE UPPER LEATHER:

The main requirements of ideal upper leather are;

- a) Aesthetic appeal that is the leather should have elegant attractive.
- b) Physical properties, such as tensile as tensile strength grain extensibility etc.
- c) Comfort properties and durability
- d) Chemical properties chrome content, fat content etc.
- e) Commercial considerations good cutting value costs etc.

Physical Properties:

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

i) Tensile strength:

It is an indication of the resistance of upper leather to break. Tensile strength figures shoe a great variability over the whole hide.

ii) Stitch tear strength:

It determines the resistance to tear of the upper leather due to Stitches; when the shoe is in regular use.

iii) Slit tear strength:

It indicates the resistance of upper leather to tear in lasting through perforations, sharp angles or along scams. It is a function of leather thickness.

iv) % of Elongation at break:

A certain amount of elongation without break is necessary for pulling over leather on the last.

v) Distension at grain crack:

It is an indication of the creaking of grain in lasting usually at the toe.

vi) Percent set:

Upper leather has to set when lasted and the per cent set depends upon the condition of the leather.

vii) Reaction of Finish to two dimensional stretch:

The changes in the finish of upper leather when the leather is subjected to two dimensional stretch is measured using Tensometer.

viii) Bond Strength:

The bond strength of leather is important in stuck on shoe construction when the upper leather is bonded to soles.

ix) Resistance of upper to heat and pressure:

The upper leather must be able to resist the effects of heat and pressure applied in the direct moulded and the injection moulded sole process of footwear construction.

2.4 FUNCTIONAL PROPERTIES OF UPPER LEATHER:

i) Break and pipiness of Leather:

When the upper leather is folded grain inwards, creases, and wrinkles appear on the finished surface of the leather. A coarse break is usually an indication of an inferior leather or an inferior part of the skin that is inferior to strength and durability. Pipey or loose vamp leather may cause wrinkling at the heel and toe in lasting.

ii) Comfort properties:

Properties, which affect foot hygiene and properties which determine the extent to which the upper material adopts to the shape of the foot during fitting and conform to the shape of the foot during wear.

iii) Flex Endurance:

The supper leather has to undergo a large number of flexes in were without creaking of the Finish or breaking of the grain. A finish which does not damage up to 10,000 flexes in Ba11y Flexometer will be considered satisfactory in wear.

iv) Fastness of finish to Dry and Wet Rubbing:

The finish of upper leather should resist dry and wet rubbing for maintaining its good appearance.

v) Adhesion finish:

One of the most common complaints in the leather shoe uppers is due to the peeling or flaking of the finish. The adhesion of finish test is designed to reproduce the type of failure where the bond between the substrate and the finish breaks down and the finish feels or flakes off.

vi) Light Fastness:

The finish should not change colour when exposed to natural light to a Xenotest apparatus for eight hours than of No. 3-5 of the Grayscale.

2.5 CLASSIFICATION OF SHOE UPPER LEATHER:

The shoe upper leather can be classified into the Following ways:

- 1. Full grain shoe upper leather.
- 2. Corrected grain shoe upper leather.
- 3. Classical box shoe upper leather
- 4. Softic box shoe upper leather
- 5. Sued box shoe upper leather
- **6.** Shoe Nappa Leather
- 7. Nubuck shoe upper Leather
- 8. Amy boot upper leather

2.6 THE IMPORTANT QUALITY REQUIREMENTS OF A SHOE UPPER LEATHER:

S1. No.	Tests	Requirements
1	Flexing endurance in the cold	50000 dry, 10000 wet min.
1.	(-20°c)	30000 flexing
2.	Adhesion of finish	3.0 N Dry 2.0 N WET
3.	Rub fastness	Min. 50 Rub cycles (dry).
4.	Fastness to hot plating	Min. 80°c
5.	Distension of grain	Bulge height min 7.0
C		Min. 18N (with lining)
6.	Split tear force	Min. 25M (with lining)
7.	Elongation at break	Not less than 40%
8.	Light Fastness	Not less than rating 3 (Bluescale)
9.	Fastness to migration	Max rating 3 (Blue Scale)
10.	Tensile Strength	Min. 100 N
11.	P ^H Value	Not less than 3.5
12.	Mineral substances removal by washing	Not more than 1.5%
13.	Water vapour permeability	10.0 mg/h-cm^2
14.	Water vapour absorption	10.0 mg/cm ² (after 8 hrs)
15.	Water Proofing	Penetration of water Min 60 min absorption of water Max 35%
16.	Water spotting test	Drying without staining

CHAPTER-THREE

<u>3.1 TANNING:</u>

Tanning is a process of converting putreficable outer covering of animal to non-putreficable leather with different physical chemical and biological properties so that they can be used in our daily life and industries.

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

- Mineral substances like salts of aluminum, chromium zirconium.
- (2) Vegetable substances containing tannin, oils and fats
- (3) Aldehydes (Glutaraldehyde, Formaldehyde, etc)
- (4) Synthetic tanning agents (Resin syntan etc)

3.2 PURE VEGETABLE TANNED LEATHER:

Pure vegetable tanned leather have some characteristic propelties. The leather is full less elastic than chrome tanned leather. Affected by acidic atmosphere. Dilute alkali treatment strips out tannin, darks the color and the leather becomes slightly soft. Much more easy to wet back and does not shrink or become hard like C.T. Leather on rewetting and drying. It absorbs more fat than chrome tanned leather very quickly. These leathers do not stands the boil test. Loose ness is less than chrome-tanned leathers. Cannot be dyed with direct dyes. Fibers do not come out from the cut portion.

<u>3.3 SEMI CHROMING:</u>

Here the vegetable tanned leather are given chrome treatment since chrome- leathers are empty cationic chrome complexes react with loose tannins with the formation of insoluble compounds. The first object is to remove the loose of insoluble compounds. The first object is to remove the loose tannins from V.T. leathers by scouring process. Tanners generally do this with borax, but better result can be obtained by the following method. The vegetable tanned leathers are first superficially striped with 2.3% Mollescal -C and 1-2% sodium sulphite in a drum at 30 to 35°C". The goods must then be rinsed thoroughly or better still, under go an after treatment with 2% or scouring agent LA power", or similar materials.

Finally the goods are chrome tanned with cationic chrome liquor with a lower quantity of chrome than is required for achieving leathers, which stand the boiling test. Exceptionally soft leathers can be obtained by adding the chromium salt slowly and in small portions which operation maybe prolonged to 12-16 hours.

To avoid hydrolysis of the chrome complexes in the wet semi chrome leathers. Some tanners suggest to pickle the leather before chrome treatment with 0.3 to 0.5% formic acid and 3 to 4% salt.

In vegetable tanning presence of large amount of hardness in Water is responsible for precipitation the vegetable tannins as tannages causing loss of tannins and there by lower yields of leather iron contents in the water leads to formation of colored salts with tannins and darkening of vegetable tanned leather.

3.4 THEORY AND COMMON PRINCIPALES OF VEGETABLE TANNING:

The origin of art of vegetable tanning is hidden in the mists of antiquity. In prehistoric times it was discovered that the properties of raw hides and skins undergo a radical change when they are brought into contact with the aqueous extract of certain roots and herbs.

The active principle which is capable of combining with protein to convert it into an nonputreficable materials is know as "tanning". Most forms of plant life contain tannins are widely distributed throughout the vegetable kingdom. Tanning materials used by the tanners are obtained from various plants in the form of" bark wood, fruits, leaves, twigs, roots and pods. The tannins which appear to be bye products of the metabolism of the plant are water soluble complex organic compound.

According to S.S. Dutta the quick tanning methods with vegetable tannin are based on a common principle as explained below:

Flow of fluid heat electricity and the migration of matters from one place to another are governed are governed by the general principle.

Rate =
$$\frac{\text{Force}}{\text{Resistance}}$$

Rate is increased either by increasing the force or by redacting the resistance or by doing the both. In the case of tannin penetration also the same general principle is followed. In different methods of quick tanning either the force of penetration was increased or the resistance was reduced by different arrangements.

Forces which are used for quick penetration.

- 1. Mechanical force,
- **2.** Force due to osmotic pressure,
- **3.** Force due to heat energy,
- **4**. Force due to electrical energy.

3.5 MECHANISM OF VEGETABLE TANNING:

Vegetable tannin, 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 collage, reticulien 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 iso electric 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-adays 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 desti'LlCt10I1 of NH2 groups of lysine residues and thus collagen is de ammoniated.

$$P-NH_2 + NHO_3 \longrightarrow P-OH + N_2 + H_2O$$

The de animated collagen fixes less amount of vegetable tanning than intact collagen. This reduction of fixed tannin due to de-amination of collagen are involved in vegetable tannin"

 $b \cdot$

More over at low P^{1} ; value of liquor goes down. Schroeder 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.

$$Tan - OH \leftarrow - - - - O \qquad H + H \leftarrow - - - - N - - - Pr otien$$
$$H \qquad H$$
$$H$$

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

$$Tan - OH - - - - N - - Protien + H_2O \rightarrow Tan - - N - - Protien$$

There are some indication 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 - C4HN bonds of collagen because these carbimino links of collagen also become electrically char-ed due to Uneven distribution of electrons and resonance between oxygen and nitrogen.

$$-C = O$$

$$-C - O -$$

$$-N - H$$

$$-N - H$$

Crosslinking reactions between skin substance and tanning agents: Vegetable tanning materials and synthetic replacement tanning a,gents.



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

<u>3.6 CHEMISTRY OF VEGETABLE TANNIN MATERIALS:</u>

Vegetable tannin- materials are obtained from different parts of a plant and are also different in composition,, structure, properties. These are always associated with plant pigments acids salts carbohydrates and many other known and unknown compounds called non-tannins Unfortunately there is at present no suitable process to isolate tannin in the purest from the tanning materials. Therefore, the properties of a tanning materials which are described by chemists and tanners are the overall properties of the mixture of tannins and associated products. Many attempts were made to classify tannins in different groups according to their different properties but the most important one was to classify them into two groups.

- 1. Pyrogallol type and
- 2. Catechol type

But it was observed after wards that a group of tannins could produce both pyrogallol and catechol and there fore this classification was rejected.

According to the modern classification, tannins are divided in to two groups:

1) Hydrolysable type and

2) Condensed type

The hydrolysable types always undergo hydrolysis in aqueous solutions and are gradually splitted into their different constituents where several molecules of catechol ultannins gradually unite together in aqueous solutions and are ulternately separated from the Solution as sludge called reds or phlobaphins.

Quebracho:

It is vegetable tanning materials got from the Quebracho tree (Quebrachia lorentizii). The name Quebracho comes from tile Portuguess and means "break ax". The wood being so hard that it will turn the edge of a good ax. All our quebracho comes form South America. According to Durland, the Quebracho comes from the Notrthern Argentina and southern Paraguay.

The wood of Quebracho tree is very hard and contains 20% tanning 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 specially 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 phlohaphenes 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 sulpllitint; chemicals are a mixture of sodium sulphite and sodium bi sulphite (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.

Name of	Туре	% Tan	% Non	pН	Rate of	Leather	Durability
extract		1 all	Tan		reliettation	rioueceu	
Ordinary	Catech	63-6 5	7-8	4.4-4. 8	Average	Hard L/R light Brown	Very good
Cold soluble Quebracho		65-6 7	15-17	5.4-5. 8	Very High	Soft L/R light colour	Good

The following table shows the properties of quebracho extracts:

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

<u>Chestnut extract:</u>

The wood of the chestnut tree (Capstan Viscera), Growing mainly in France and Italy, but also in Yugoslavia, Switzerland and Spain, yields a pyrogallol tannin which when concentrated into extract form is widely used in heavy leather manufacture. Currently extract is produced in France and Italy and also in Yugoslavia.

In Comparison with Quebracho and Mimosa, it will be sent that chestnut has a much lower PH and this natural acidity imparts to chestnut extract its characteristics of giving a high tannin fixation and firmness to leather tanned with it, lower water soluble and a higher resistance to water penetration.

It has a low viscosity; especially when warm, which makes it a valuable component of hot pit liquors.

Differing from the chatechol tannins, Chestnut is very sable to the effects of light, as it does not appreciably oxidise in air, and for this reason in addition to the acidic properties already mentioned is a suitable constituent of heavy leather tannage lends.

As with most pyrogallol tannins Chestnut imparts Substance and character t0 leather tanned with blends containing this material and in addition gives such leather the cheesy cut so beloved by leather uses. This characteristic is largely due to the fact that leather produced with pyrogallol tannins is less sensitive changes of relative humidity due to the humectant properties of their non-tannins and so tends to resist the drying out of the fibre which leads to a harsh cut or occasion. Numerous special extracts are derived from natural chestnut extract. By sweetening chestnut extract that is reducing its acidity by chemical means and increasing its salt content it is possible to produce an extract which penetrates hide much more rapidly than the natural extract, and also gives a paler, brighter and more yellow colour to the leather being tanned. By varying the degree of sweetening, special extract are obtained which include low viscosity extracts, particularly adapted to the rapid tannage of sole leather or other extracts for the production of lighter vegetable tanned leather.

Chestnut is available in solid or spraydried form. Chestnut extracts can be used alone or in blends with catchall tannins such as Quebracho and Mimosa, or with other pyrogallol tannins such as Myrabolan and Valonea.

 $*P^{H}$ 50 Bk (7 Be) solution

*Acids and salts: titration of 150 Bk(17Be) solution to $p^{H}6.5$

*Reds and Yellows: colour readings. using the Lovibond Tintometer.

Gambier:

Extracted from leaves and twigs of a shrub indigenous to Malaysia and Indonesia, Gambler is available as solid, liquid extract, or in cube form being manufactured under diverse conditions. The cube form can contain sugars, salts, waxes, oils and mineral substances as traditionally a thickening agent, such as rice, was added to the leach liquor as it was concentrated.

The product is non-astringent (termed mellow), having a low acidity, and containing buffer salts. Used alone gambler produces a soft,

supple pale buff coloured leather with a fine grain. Being a catechol, it readily darkens on exposure to light and buffing produces a thick velvety nap.

Myrabolans

Tannins extracted from a dried fruit from the myrabolans tree indigenous to India. The tan liquor has a very high acid content with a plumping, lyotropic effect on the fibre structure. Bloom is deposited, and medium salts content which includes buffer salts protects leather against acid rooting. Myrab is blended with catechols to improve the colour (reduces the redness), provide an acid reserve and a softer feel; but the amount used must be controlled in a warm tannage because of 1yotropic effect. Leather produced show a bright yellow-brown colour.

FIGURE OVERVIEW OF LEATHER MAKING CHARACTERISTICS

Classification	Veg	Tan:	Insoulbl	\mathbf{P}^{H}	Acids	Salts	Reds*	Yellows
	Tanning Agent	Non tans	(sludge)					
Catechol	Quebracho	5.8:1	8.9	4.4	40	90	4.5	11.0
	(Natural)							
	Quebracho	4.3:1	0	4.4	50	350	3.2	7.5
"	Cold							
	Soluble							
,,	Mimosa	3.0:1	0.4	1	40	90	1.3	2.4
	(Natural)							
,,	Mimosa	2.8:1	0.1	4.G	35	230	0.3	0.7
	Sultited							
22	Mimosa	2.9:1	1.2	3.1	280	220	0.4	0.7
	Acidified							
,,	Mangrov	3.0:1	2.0	4.1	130	350.	11.G	13.0_
	Cambier	2.5:1	0.3	4.6	60	220		
	cube							
Pyrogallol	Myrabola	1.9:1	0.7	3.2	550	180	1.0	4.2
Ellagitannin								
>>	Valonia	2.4:1	2.8	3.5	380	270	1.6	4.8
>>	Chestnut	2.9:1	0.1	3.0	280	50	3.0	12.1
	(Natural)							
	Chestnut	2.5:1	0	4.3	115	260	2.8	12.9
"	Sweet							
Pyrogallol	Sumach	1.5:1	~0.6	4.2	345	320	1.2	6.1
Gallotannins								
>>	Tara	4.5:1	0.4	3.9	270	170	0.6	1.8

<u>Valonia</u>

Extracted from the acorn oak tree found in Turlkiye and Greece. The extract has a high acid. Content and medium content of salts including some buffer salts (Lower than myrabs). Valonia deposits a large amount of bloom (appreciable tannin losses) and products a firm, doll gray brown coloured leather.

<u>Sumach</u>

Extract from the leaf of the Sicilian Shrub or used as chopped leaves. The high content of acid and salts (Chiefly buffer salts) Produces a soft, spongy, pulmp leather with a yellow beige colour. It is highly buffered and thus used to protect against ageing in bookbinding leathers.

<u>Tara</u>

Extracted from the tara pod found in North Africa and Peru. The acids and salts content is low compared to sumach. The extract is light coloured and sensitive to staining by iron (small amount of sequestering agent recommended in use). The leathers produced are soft. Very palealmost white, with good light fastness and a fine grain.

1. <u>ELECTROLYTIC EQUILBRUM</u>

By this is meant the necessity of attaining equilibrium between the pelt and the acids and salts or the electrolytes in the tanning liquor. The sooner this can better, as during the period of dis-equilibium changes can occur in the pelt's fibre Structure resulting in distortion of the grain surface causing piper grain. The condition of equilibrium is attained much more quickly if the alkaline pelt from the lime yard is brought to the neutral, or iso-electric point i.e. to the P^H region where pelt has minimal swelling due to balance between the hydrogen lon an the hydroxyl ion concentration, before meeting the tall liquor. This point is an extremely strong argument for a very strictly controlled delimiting stage, confirmed in practice time and time again.

In traditional pit tannage electrolytic equilibrium, as far as the salts are concerned, can be reached in a simple manner by allowing the delimed pelt to come to equilibrium in a run-away liquor, where the salt concentration will be pelt will encounter in its passage up the yard. With more rapid systems of pit/drum or all drtun tanagers, with low or on floats, the same goal is reached by the use of bufiered Suntans or bliffer salts in a pertaning process before tannage proper.

The control and adjustment of the part the electrolytes does not usually present serious difficulty to the tanner.

Equilibrium is attained by delimited pelt very quickly, as the size of the ions of the simpler electrolytes the acids and salts is extremely sall when compared with the lnore bulky colloidal particles of tan. Thus, electrolytic equilibrium is reached in a fraction of the time that tan itself takes to penetrate the hide. The necessity of getting equilibrium quickly lies in the fact that at on time should the grain be over acidified in the presence of tan. If this should take place to the corium generally. Also, it case of liquor of low P^H there will be rapid fixation to tan oil the outer surfaces leading to case hardening, which will hinder if not prevent the later diffusion of tan into the interior of the pelt, leaving the garain coerce and lacking in finish.

At the risk of over emphasis, it Must be stressed how as regressed how as regards acids and salts, as rapidly as possible.

2. DIFFUSION:

Tan must diffuse through the grain and flesh Surfaces of the pelt in toe the fibrous network structure of the corium, until the free water between the fibres is expelled and its place taken by the outside tan solution. The speed of diffusion is obviously controlled to a very large extent by the condition to of the pelt, or rather of the fibres themselves in the pit that is whether they are in a plumped or deflated condition. The sub contaneous tissue of the pelt is much more compact than the corium structure and usually also contains fat cells, conditions which tend to slow-down penetration of tan from the flesh side more than is the case with the, grain. Therefore, good clean fleshing is an essential requirement for rapid tan penetration later. Pelt is not a homogenous structure and consequently diffusion is faster in the capillaries between the fibres than in the fibres themselves. The plumper the pelt the smaller are the capillaries and the slower the diffusion.

Factors influencing diffusion:

A. Mechanical movement:

Mechanical movement of the process of tanning call materially aid diffusion. Firstly, by reason of the agitation of the tanning agent, the water leaving the pelt is more quickly replaced by the stronger liquor is kept outside. Also the concentration of the external liquor is kept uniform, avoiding the formation of pockets of weak and strong liquor which can and do occur under static conditions. Secondly, diffusion is aided by the pumping effect of the continual flexing of the fibres pushing water out and tan Solution in .

Mechanical movement can be achieved in various ways, such as the use of rockers in pits in the initial stage of a pit. Drum tannage or the use of drums for tanning.

Experience has shown that, compared with the uptake of tan in pits where the goods are not move, the take up in drums of tan under similar conditions of time, gravity and temperature is about eight times as fast. The effect of the more gentle movement in a rocker system is naturally much less, but here too the rate of diffusion is accelerated by a factor of about three compared with static pit conditions. Another more practical advantage of recaps order static conditions is that movement give to the goods prevents "touch marks" occurring which can lead to discolored gain on the finished leather.

B. Tan concentration:

Diffusion rate is roughly proportional the ratio between tannin concentration in the outside liquor and that of the internal liquor between the fibres. This point will be discussed more fully later, when factors affecting absorption are being dealt with, but is clear that in the early stages of the tanning process where the internal liquor tan concentration is very low, the stronger the outside liquors are in tan, the faster. Diffusion will occur. Should the early stages of the tannage being operated require the use of pits, it is desirable token the liquor-to goods ratio as low as possible. The importance of the liquor to goods ratio in pit tannge can be best illustrated by conferring two separate counter current pit systems identical is size, liquor strength and pack numbers. If the packs entering one for the rounds are reduced to half the number of pieces the bottom or first liquor will not be so will depleted of tannin by the smaller amount of pelt and after a few days the liquor, as compared with the other round, will be found to have a higher Brume strength (and a higher percentage of tan); later the same effect will be felt in succeeding pits in the series.

<u>C. Temperature:</u>

The rate of diffusion is closely bound up with temperature. If the temperature is allowed to fall to freezing point tannage virtually ceases, whilst a slight increase above normal an increase which must negovernedby the safe upper limits of partly tan limits of partly tanned or raw pelt to heat-will accelerate diffusion of tan liquor into pelt. At higher temperatures there is a reduction in the cohesion of collagen which allows penetrates to become easier and also a certain amount of "bound" water is liberated, which leaves some of the reactive sites on the collagen free for reaction with tan.

<u>3. FIXATION OF TANNIN:</u>

As the tannin solution diffuses into the pelt, tanning proper begins. When this happens tan leaves the liquid phase and becomes attached to the fibre, some bound water being freed in the process. It must again be stated earlier operation), diffusion and fixation effects are all proceeding simultaneously making control very essential.

Factors influencing fixation

A. P^H:

Tanning takes place over a wide range of pH, but fixation varies considerably at different pH levels. In the range of pH normally used in a vegetable tannage, reduction of the pH value has a marked effect in increasing tan fixation. In fact, if the pH is lowered sufficiently fixation is so rapid that capillary orienting in the outer ha yours of the pelt get so filled by deposited tan that further penetration virtually ceases. This state is called "case hardening". It should be noted that at the iso-electric point of collagen (about pH 5, tan fixation is at its lowest. For this reason, many rapid tannage systems recommend commencing tanning proper at about this pH where tanning fixation is at its minimum and penetration at its maximum, due to the deflated condition of the pelt. After full penetration is achieved pH of the whole system is lowered, usually with m organic acid, which has the effect of "fixing" the tan in the interior of the leather. The $p^H O f$ tail liquor is another important factor to control tile tanning process. For most of the tanning materials the fixation of tannin by the pelt is minimum within the pH range 4:0 to 5.0.

If the pH of the liquor at the commencement of tanning is greater or lower than this range there is therefore every possibility of case hardening. It is therefore recommended that the pH value of the starting tail liquor should be very near to 5.5 and gradually it should be lowered with the increase of tannin concentration Of the tall liquor of p'⁻¹ value lower than 3.0 are cranky and of poor strength. This defect, known as acid-rot, is more pronounced ill leather containing mineral acid. The Indian standard recommends the following tests to avoid acid rot of vegetable tanned leather.

B. Salt concentration:

Salts play a role of some importance in determining the degree of fixation taking place in a tannage, and can be quite a potent factor fixing the degree of tannage of the leather being made. They do this by affecting the plumping of collagen which is depressed under acid conditions by the presence of salts. The higher the salt concentration, the less sensitive is collagen to variations of pH in the acid range normally found in the pit liquors is of paramount importance. In general it can be said that to obtain relatively fast penetration in the early liquors which is vital in tannages of this kind, the p^H should be held at as high al level as is consistent with the salts present to give the required as is consistent with the salts present to give the required as is consistent with the salts present too give the required of penetration and the necessary characteristics to the finished leather. If the pretreatment of the pelt has been correctly carried out, oil acidity should be necessary to neutralize pelt alkalinity and all that will be needed is to ensure that the quantity of acid necessary to satisfy the acid combining capacity of the collagen during range is added to the liquors, bearing in mind the salt concentration of the tall liquor itself.

C. Acid content:

A definite amount of acid is required for the tanning operation to perched satisfactory. Firstly, in order to hold the p of the then liquor at the correct level and secondly to satisfy of acid combining characteristics of collagen. This acidity may be derived from the natural acids present in the tanning materials being used, from acid added to the system of possibly from the end products from the fermentation sugars present as a fraction of the non-tannin substances though this latter source can be almost completely discounted. The amounts of acid present can be estimated by titration and the greater quantity of acid found at a given p^{H} the slower the tan penetration into the pelt. High acid content, as distinct from low pH values, contributes to an increase in tan fixation, though within the practical limits of tanning the effects is not very great. But unduly high acid content, especially under conditions of elevated temperature such as in hot pit liquors or liquors heated up by the mechanical effect of drumming, lessen the cohesion of the hide protein and can thus cause series damage to the leather.

D. Tannin concentration:

It may appear at first glance that this factor is self evident; it is obviously necessary to put into the tannage the amount of tan needed to tan the pelt allowing for any unavoidable wastage's and to produce the kind of leather required. As already stated, during tannage the tan liquor diffuses into the pelt structure, whilst water is displaced, with the result that eventually the concentration of tan in the interstices of the fibre is almost, but not quite, the same as that outside. The amount of tan combining with hide substance is governed largely by the actual concentration of tan in the liquid in contact with the fibre. Roughly, if the tan concentration in the outside phase is doubled, fixation is increases by about 7%. An important point now emerges: it has been found by experience that combination between tan and found by experience that combination between tail and collagen is very rapid, and therefore it is necessary to ensure that the concentration of tan is maintained or increased in the internal liquor, or the whole process slows down almost to a stop. Therefore it is not just sufficient to tan the pelt by its diffusion-enough tan must be present and available to maintain the concentration pressure.

Diffusion and combination or fixation thus depend to a large extent on each other. Whilst tanning is proceeding it must be remembered that it is a system which commences very much out of equilibrium, and proceeds at an ever decreasing rate until a virtual equilibrium is established-that is, there is no further appreciable transfer of tan from solution to fixation on the fibre. This of course applies to tonnage in one liquor only, and at one fixed temperature. It is almost creation that this state of near equilibrium is reversible to a great extent.

Therefore, it is fairly obvious that other things being equal, diffusion will be most rapid when the concentration difference between the outside liquor and the liquor in the interfibrillary channels of the pelt in the liquor is greatest. This can only be achieved by chaining the external liquor frequently, because as can be shown graphically, diffusion is a die away process, the initial concentration is soon reduced when the liquor is not replaced, on one hand by the abstraction of tan from solution and by dilution on the other hand by the water being expelled from the pelt. It is Worth repeating in this context what was said when discussion "diffusion" earlier. For the practical reasons stated the liquor to goods ration that is the amount of liquor present, in relation to the weight of the number of pieces of pelt in pack in pit, paddle or drum in which tanning is being carried out should be kept as low as practicable.

E. Particle size and viscosity:

All tan liquors are colloidal solutions of a highly complex nature of mixtures of a polyphonic nature and salt. These complexes are more or less polymerized, and

Therefore the particle size of the tanning aggregates varies considerably. Obviously the smaller the particle the easier it is for it to penetrate the pelt. By chemical means tile particle size of the tannin can apparently the modified considerably. By treatment with Sodium Bisulfate during extraction, and in later stages; it is possible to modify to certain degree the particle size of the vegetable tannin, tough some workers in south Africa consider the mechanism of the reaction worthy of deeper investigation. This operation is normally employed in the production of cold Soluble quebracho extract, as the untreated extract, as the untreated extract is not cold water soluble. Other vegetable tanning extracts are particularly for processes in which good last penetration in desired.

It has already been noted that temperature increases tend to decrease the viscosity of tan liquors and aid penetration. This is due to the increase kinetic movement of the tannin molecule as the temperature rises with a consequent lowering of viscosity. There are natural differences in their molecular conditions, caused many be differences in the molecular weights. Quebracho and mimosa tannins have higher molecular weights that Myrabolaio or Chestnut, and as a result Quebracho and Mimosa solutions are more viscous at the same concentration and temperature as the other tow materials. These differences tend to narrow when the liquors are warned up, and consequently short float drum tannage which tend to rise in temperate due to viscosity of liquors than do cold process. If static liquors can be kept at summer temperatures all the year round, it is a decided advantage.

F. NON TANNINS:

The vegetable tan liquors not only contain tannins but many other soluble maters like carbohydrates, acids, salts and phonemic matters. Theses soluble matters are called non tannins because they cannot tan and therefore cannot prevent putrefaction of proteins. Though these non tannins have whitening power but their presence in the tan liquor is important and essential to control the tanning rate and to impart many qualities of the finished leather. A leather, tanned with a vegetable tan liquor containing insufficient amount of non-tannins, is empty and of poor feel and there fore unsuitable for use.

The distribution of tanning throughout tile thickness of the leather and also the rate of tanning are largely controlled by the non tannin content of the tan liquor. When a piece of delimited pelt IS pill into a vegetable tail liquor of very low content of non-tannin the tannin molecules immediately fix up to the pelt surface and prevent further penetration of the tannins and thus the pelt comes to a stage known as case hardening. This case hardening can be avoided if there is required amount of non-tannins like salts in the tan liquor. Like tannins certain non-tannins form compounds with collagen, which are, of course, very unstable in comparison to tannin-collagen compound.

"The non tannins, having a much smaller molecular weight than the tannins, diffuse more rapidly into the skin. When the slowly moving tannin reaches a point where it would combine with collagen, it can not do so because the point is already occupied by non-tannins. Tannin that would otherwise have; combined with collagen hear the sill face of the skin is thus enable to proceed into the interior and the measured rate of penetration is thereby increased. This action is more marked the greater the concentration replaces non tannin as fast as the collagen-non-tannin compounds hydrolyzes" (Wilson). The non tannin content of the used liquor is much more than that of fresh liquor and therefore the rate of diffusion of the tannin molecules from a strengthened used liquor into the pelt is much liquors into the pelt is much more than the diffusion rate of tannin molecules of a fresh liquor. Thus we see that the nontannin content of vegetable tan liquors is an important factor the rate of vegetable tanning.

The tannin and non-tannin contents very widely in different tan stuffs. The purity, which is defined as the percentage of tannin to total water soluble, of quebarcho, as for example, is 90% where as gambier shows a purity within the range 43.0% to 57.0%. If the non tannin content of a tanning material is more than its tannin Content the tanstuffs is considered of tanning. This type of tanning materials always produce very poor type of leather. The tan/ non ration of a tanstuffs for satisfactory tannage should therefore be always greaten than one and this is the case in all common tanning materials as quoted below.

Name of tanning Materials	Tan	No	Non-tan Ratio	
Quebracho	8	То	10	
Mangrove	2.5	То		
Mimosa	2	То	3	
Chestnut	2	То	3.5	
Myroblan	1.5	То	2.5	
Avaram	1.6	То		
Babul.	1.7	То	1.9	
Sumac	1.5	То	1.8	
Gambier	1.2	То	1.5	
Hemlock	1	То	2	
Divi-Divi	2	То		
Oak Wood	1	То	2	

The tan/non-tan ratio also varies from one sample to another of the same stuff, mainly based on the tree from which it was obtained, season of the girth of the some or branch from which the bark was obtained and many other factors.

CHAPTER-FOUR

<u>4.1. WHAT IS LEATHER FINISHING:</u>

The final stage of leather production is reached with the finishing process. These treatments have the purpose of making the leather usable and suitable for the manufacture of end products.

Leather finishing is a surface coating process applied to dry leather, in order to increases its sales value, to enhance its fashion appeal and to protect its surface during wear.

Treatment of the surface of top section of the leather with materials which will enhance the appearance of the leather and improve its properties for the purpose to which it is a be used are Known as lather finishing and the materials which are used in finishing are called leather finishers.

4.2. PURPOSE OF LEATHER FINISHING:

Finishing may improve the qualities of the leather is so far as;

- a) Levelness of colour on the leather.
- **b)** Uniformity of shade form skin to skin and pack to pack
- c) Changing the colour to that, which is required
- d) Imparting colour or pattern to undyed leathere
- e) Giving a surface of the leather varying form matt to gloss
- **f)** Adding a transparent film through which the natural appearance of the leather may be viewed.

- g) Adding a transparent coloured film to the leather
- **h)** Covering the leather with an opaque film in order to obliterate all defects.
- i) Alter the surface of the material i.e. splits
- j) Improve the scuff resistance of the leathers.
- k) Improve the scuff resistance of the leather i.e. the finish should not discolour or swell and hence protect the leather and retain its good appearance.
- 1) By filling the surface of loose leather improve the break of the rain
- m) Give a leather of optimum cutting value
- n) Seal the leather surface so that it remains clean
- **o**) Render the leather light fast
- **p)** Render the leather heat fast
- **q**) Render the leather fast alkalis
- r) Render the leather fast to acids
- s) Render the leather resistant to a light pull up on lasting.

4.3. TRUCTURE OF FINISHES (SCHEMATIC):

The finish consists basically of three coats:

Base coat --- Pigment coat - Top coat.

All coats are not absolutely necessary their application depends oil 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 - Aniline dyeing - Top coat and Semi aniline leather - light color base coat - Transparent pigment coat Top cost.

4.4. FISHING MATERIALS

There are no standard or universal methods for leather finishing, the finishing materials must be selection according to the condition of the available leather the type of finish to be produced and the properties desired of the finished leather. Although the quantities and the type of materials used in the leather finishes vary considerable following components are the basic materials for leather finishing.

- i) Pigment
- ii) Binder
- iii) Plasticizer
- iv) Diluents
- v) Water
- vi) Essential Oil
- vii) Dyestuff
- viii) Dispersing, agent
- ix) Plate release agent (waxes)
- x) Anti foams
- xi) Malting agent
- xii) Solvent
- xiii) Glazing agent
- xiv) Preservative
- xv) Pearlizer

- xvi) Cross linker
- xvii) Fluorescent agent
- xviii) Slip agent
- xix) Modifiers
- **xx)** Crackle producing agent
- xxi) Thickener
- **xxii)** Oily finishing agent
- **xxiii)** Fixing agent for protein finish
- **xxiv)** Transfer films and foils
- xxv) Lacquers

CHAPTER- FIVE

<u>5.1 Manufacturing procedure:</u>

Production of Full vegetable shoe upper leather using low chrome pre-tannage:

2PC's goat skin

- 1) **Raw wt** 1100gm [Sample –1]
- 2) Raw wt 1000gm [Sample -2]

Total – 2100gm

Pre soaking –	0.33%	soda ash
	0.33%	LD-600
	0.33%	Bactericide
Soaking	0.6%	soda ash
	0.6%	LD-600
	0.6%	Bactericide
Liming	300%	water
	1.0%	Liming auxiliary
	4.0%	Lime
	3.5%	Sodium Sulphide
	0.2%	LD-600
Re-liming 400%	Water	
	4%	Lime
	0.5%	LD-600
		Run 30 min
Chemical Wash		
	200%	Water
	0.5%	Meta-bi-sulfite
		Run 30 min

Deliming		50%	water
		1.5%	Ammonium Sulphate
		0.5%	Meta Bi sulphite
			Run 60 min
		Check with	Phenolphthalalene (Colorless)
Bating	1.5%	Batin	g agent
		1%	Wetting agent
			Run 120 min
Pickling:			
		80%	water
		R	un 15 min
		8.0%	salt
		R	un 15 min
	+	0.5%	Formic Acid
		R	un 30 min
		1%	Imparpal CO
		R	un 15 min
	+	1.2%	Sulphuric Acid 15 + 15 + 30
			Leave Over Night
	+	0.5%	Нуро
		R	un 30 min

Drain half of the pickle bath.

Pre-tanning:

In the same pickle bath.

1.5%	Chrome Powder	[Sample-1]		
4%	Chrome Powder	[Sample-2]		
0.5%	Chrome Stable fat	Chrome Stable fat (OCS)		
	Run 60 min			
50%	water check Penetration			

	+	2%	Нуро
			Run-30 min
	+	2.5%	RWP
			Run-45 min
	+	2%	9P
		0.5%	NaHCO ₃
		0.15%	Busan 302
			Run 30 min
Samming: E	By M/C		
Shaving: By	v M∕C		
Shaved wt -	310gm	[Sample-1]	
	300gm	[Sample-2]	
Acid Wash:		150%	Water
		0.3%	Oxalic Acid
		0.3%	LD-600
			Run 20 min
	+	1.0%	Neosyn wo/DLE
			Run 20 min
	Drain,	Rinse Well.	
Neutralizatio	on:		
		1.50%	Water at 40°C
		2%	Neosyn BS-3
		1.0%	Sod. Formate
			Run30 min
	+	1.5%	Нуро
		1.0%	Remsol C-2
			Run 30 min
	Check	с Р ^н 4.5/4.6	

Drain, Wash well.

Vegetable Tanning:

	150%	Water at 40°C
	3%	Paramal PA
		Run 30 min
+	3%	Taningan OS
		Run 20 min
+	1%	Trisul ML
		Run 20 min
	0.5%	Trilon B
		Run 20 min
+	3%	Relugan D
		Run 20 min
+	2.5%	Brown ERN
		Run 30 min
+	5%	Quebracho
		Run 45 min
	10%	Mimosa
		Run 45 min
	2%	Tanningan OS
		Run 45 min
+	5%	Molasses
		Run 2hr
	5%	Quebracho
		Run 2hr
	10%	Mimosa
		Run 2hr
	3%	Nesoyn WO
		Run 2hr

Check penetration (100%)

Leave over night.

+	50%	Water
	0.5%	Formic Acid
		Run 30 min
+	0.5%	Oxalic Acid
		Run 30 min
Che	ck P ^H 3.6/3.7	

Drain/wash well.

Fatliquoring:

	200%	Water at 50°C
	2%	Filler Syntan
		Run 30 min
+	3%	Remsol B-40
	2%	Remsol C-2
	2%	Trisul ML
	0.25%	Busan 3DL
	0.5%	RNO
		Run 45 min
+	1%	Formic Acid
		Run 30 min
+	1.5	Neosyn PWO
		Run 30 min

Top Fat:

	200%	Water at 60°C
+	1%	Brown ERN
		Run 20 min

+	1%	Formic Acid
		Run 20 min
+	0.5%	Permol NC
		Run 20 min
+	0.5	R.N.O
		Run 20 min

Drain, Rinse, Horse up O/N.



Season coat:

Pigment	100 parts
LB.SD	50 parts
Filler	50 parts
Wax	30 parts
L.L.TE	50 parts
Lustre	50 parts

	RPU-030						
	C.M.B.A.M						
	RA2314	20 parts					
	Protein Binder						
	Water						
Spray 3×, Dry well, Kiss plate 75°C / 70kg							
Top Coat							
	Clear Emulsion	650 Parts					
	Wax TRA	10 parts					
Sensol SW 5 part							
	335 parts						
Spray $2\times$, Dry well, Roto Press $85^{\circ}C / 50$ kg							

5.2 PHYSICAL TESTING LEATHER:

The crust leather sample: and 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.

5.2.1 TENSILE STRENGTH AND ELONGATION AT BREAK BASED ON SLP-G, IUP/6

The tensile strength and elongation at break was measured by tensometer. The process was followed by official method of analysis (19G5), Ref. 4 (c) 4 (d)2, SL,P-G, IIJP / 16.

Tensile strength is the force (Kg.) per unit area of cross- section (sq.crn) required to cause a rupture of the test specimen.

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

Tensile strength = $\frac{\text{Breaking load (kg)}}{\text{Thickness (cm) x width(cm)}}$

Elongation at break for these specimens are calculated from the distance of the jaws after breaking was occurred.

Percentage of Elongation = Distance increased by breaking Distance of the two jaws in normal

5.2.2 LASTOMETER TESTS BASED ON SLP -8 SLP-9, IUP-9, IUP-12.

These test were Performed by following the official method of analysis 1995. Ref 4(d) and 4 (e) SLP-4, SLP-9, IUP-9, IUP-12.

By lastometer tests, grain cracking strength, bursting strength and their corresponding distension values can be obtained. The bursting strength in an index of the overall strength of the leather.

Grain cracking strength testing is an important physical test for a leather sample. The higher the value the better the quality leather, (without some exception).

For lastometer test the specimens were cut from the samples by circle type cutting dice and the specimens were placed on a lastometer being conditioned by clamp whose flesh sides were adjacent to the ball of the instrument. The increasing that is the LIP thrust of the ball with the pressure by handling indicates the distension at a rate of 0.2 min/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,

Grain Crack strength = Grain cracking load (kg) Thickness of the leather sample (cm)

Again, the bursting strength was determined using following formula.

Brusting strength $(hg/cm) = \frac{Brusting load (kg)}{Thickness (cm)}$.

5.2.3 STITCH TEAR STRENGTH. (DOUBLE HOLE) LP8/IS: 5914-1970;E 13/ALCA:

The load (kg) required to tear the sample of leather between two holes of 2 mm diameter each and whose centers are 6 mm apart, expressed on its unit thickness (cm) is the stitch tear strength.

So, stitch tear strength of the specimen was calculated using following formula,

Stitch tear strength = $\frac{\text{Tearing load (kg)}}{\text{Thickness of the leather sample (cm)}}$

5.2.4 VAMP FLEXING: SATRA PM 25:1992

A square specimen of the materials is folded over two inverted V-shaped clamps. The clamps are able to move relative to one another so that as they become closer the specimen is flexed to produce 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 specimens at room temperature, or dry specimens at sub- zero temperature, or dry specimens at sub-zone temperature. After a predetermined number of cycles the test is stopped and the specimen is visually examined for signs of damage or salt spue.

5.5 TEST FOR WATER ADSORPTION:

A circular cylinder of leather Sample at diameter 70mm has to take and need to take initial weight. Then put it into water rand have to take weight after 15 min, 30 min, 1 hour, two hours and after 24 hours.

Then the percentage of water adsorption determine by following formula.

Water adsorption = $\frac{\text{Weight of water adsorbed}}{\text{Weight of leather sample}}$

5.5.6 WET AND DRY RUB FASTNESS TEST BASED ON DIN 54021, SLF -5:

This method determines the fastness of color of light leathers to wet and dry rubbing through the transfer of color to felt with which it is rubbed. For this test, sample of leather is rubbed with a revolving felt pad, and the number of revolution of the pad required to produce certain effect is measure.

The German standard, DIN- 54021, and SLF-5, specifies a method by the "Krais" tester of "Veslic" in which a white felt at a force of 1 kg load moves back and forth on the finish side of the leather through a distance of 10 cm. The felt will be dry for the dry rub fastness test and felt will be wet for the wet rub fastness test. In SATRA

instrument the circular dry felt at a load of 2.5 kg rotates on the finish sides of the leather in the case of dry rub fastness test and in the case of wet rub fastness the wet felt is kept under the load of only 0.75 kg. For this investigation SLF-5, method was followed: In both the cases tile stained felts arc compared with the grey scale.

5.5.7 COLOUR FASTNESS OF LEATHER TO PERSPIRATION (BASED ON SLF 426 AND IUF / 42G).

A piece of specified undyed textile wetted with artificial perspiration is placed on the side of the specimen to be tested. The specimen is also wetted with artificial perspiration. The composite specimen time in an appropriate apparatus. The specimen and textile are dried. The change in calour of the specimen and the staining of the textile are assessed with standard grey scales.

Leather bearing finish may be tested intact or with the finish broken. In the latter case, this must be started in the report.

CHAPTER-6

Results, Discussion and conclusion.

6.1 RESULTS AND DISCUSSION:

The results obtained by different "Physical testing" on the prepared leathers are tabulated in this chapter followed by shout description of the results.

6.1.1' TABLE FOR THE RESULTS OF TENSILE STRENGTH.

Sample no.	Tensile strength. kg./cm ²	Standard value kg./cm ² . (min.)
01	2 50	250
02	251	250

Comparing with the standard tensile strength of shoe upper leather the results obtained from sample Ol and 02 can be considered as appreciable. The result of sample 01 and 02 can be said satisfactory.

6.1.2 TABLE FOR THE RESULTS OF ELONGATION AT BREAK(%)

Sample no.	Elongation at break :(%)	Standard value Kg. /cm'. (Max.)
01	39%	
02	41%	70%

6.1.3. TABLE FOR THE RESULTS OF STITCH TEARS STRENGTH

Sample no.	Stitch tear strength	Standard value kg/cm ²
01	125	
02	128	100

Comparing with the standard stitch tearing strength of shoe upper leather the result obtained is quite nice.

Lastometer test									
Sample no.	Grain crack strength (kg/ cm)	Grain bursting strength (kg/ cm)	Distension at grain crack(mm)						
01	301	472	7.2						
02	309	490	7.4						

6.1.4. TABLE FOR THE RESULTS OF LASTOMETER TEST.

The sample 2 give high grain crack and bursting strength than sample 1 which is very satisfactory for shoe upper leather. The distension at grain crack of shoe upper leather should be min. 7 mm. Here the distension at grain crack of the sample 01 and 02 are above 7mm. So this is suitable; for shoe upper leather.

6.1.5: TABLE FOR THE RESULTS OF SHRINKAGE TEMPERATURE

Sample no.	shrinkage temperature
01	81°C
02	83°C

The full vegetable shoe upper leather show enough shrinkage temperature for the manufacture of shoe upper leather.

6.1.6: TABLE FOR THE RESULTS OF VAMP FLEXING ENDURANCE:

Sample no.	Grain appearance after 10,000 flexes	Grain appearance after 25,000 flexes	Grain appearance after 50,000flexes
01	No creases	Slight creases	Marked creases
02	No creases	Slight creases	Marked creases

The obtained result of vamp flexing endurance is not so satisfactory.

Sample	Dry rub fastness											
no	32 Rev		64 Rev		128 Rev		256 Rev		512 Rev		1024 Rev	
	For	For	For	For	For	For	For	For	For	For	For	For
	leather	felt	leather	felt	leather	felt	leather	felt	leather	felt	leather	felt
01	5	5	5	5	5	5	5	4/5	4/5	4/5	4/5	4/5
02	5	5	5	5	5	5	4/5	4/5	4/5	4/5	4/5	4/5

6.1.7 Table for the results of dry rub and wet rub fastness tests.

Sample	Wet rub fastness											
no	32 Rev		64 Rev		128 Rev		256 Rev		512 Rev		1024 Rev	
	For	For	For	For	For	For	For	For	For	For	For	For
	leather	felt	leather	felt	leather	felt	leather	felt	leather	felt	leather	felt
01	5	5	5	4/5	4/5	4	4	3/4	3	3	3	3
02	5	5	5	4	4	4	3/4	3/4	3/4	3	3/4	3

The obtained results of dry and wet rub fastness test can be considered as satisfactory.

6.2 PRODUCT SAMPLE:

Sample- 01

Full vegetable shoe upper leather using 1.5% chromium in pre tannage operation.

Sample- 02

Full vegetable shoe upper leather using 4% chromium in pre tannage operation.

6.3 Conclusion:

In this project I have manufactured vegetable tanned shoe upper leather by using low chrome in pre-tannage. Now- a –days customers want a product which has no bad effect on environment. So environment friendly tanning system is popular among the tanners. According to a recent survey 90% of the leather productions of the world are produced by using chrome tanning agents which is largely harmful to skin as well as to the environment. In this aspect vegetable tanning materials are suitable than chrome tanning materials. Though the tensile strength of chrome tanned leather is quite higher than vegetable tanned leathers, vegetable tanning leather give better fullness. So it is easy to cover the defects of vegetable tanned leather during finishing operations.

In case of water absorption low chrome using tanned leather absorbs water very fastly. And all other properties are almost same as chrome tanned leather except shrinkage temperature.

Consequently, it can be said that vegetable tanned leather can meet almost all the requirement of shoe upper leather. I think that more research and experiment can overcome the little amount of vegetable leather over chrome tanned leather. In that case vegetable tanning should be preferred to produce shoe upper leather in order to save the earth and next generation from the toxic effect of chrome tanning.

<u>6.4 BIBLIOGRAPHY:</u>

- "An Introduction to the Principles of Leather Manufacture" 2nd Edition. By- S.S Dutta.
- "An Introduction to the Principles of Physical testing of leather" 1st Edition. By- S.S. Dutta.
- 3. "Possible defects in Leather Production" By- John Gerhard.
- 4. "Leather Technicians Handbook" By- J. H. Sharphouse.
- 5. "The Manufacture of Upper Leathers" By- D. H. Tuck.
- "Science for Students of Leather Technology" Volume Editor Reed.
- "Practical Aspects of the Manufacture of Upper Leathers" 2nd Edition. By- Joytirmoy Dey.
- 8. BASF: Pocket Book for the Leather Technologist.
- 9. ALPA: Product mini Guide.
- Official Methods of Analysis 1996, SLP "Society of Leather Technologist and Chemist", Registered Office.