

## Origin of Leather Making:-

Leather making is an ancient art that has been practised <sup>for</sup> more than 7000 years. Fresh skin was dried in the sun, softened by ~~the~~ <sup>the</sup> ~~beating~~ <sup>beating</sup> in animal fats and bacin. and preserved by salting and smoking.  
 ↳ called curing. ↳ decrease moisture content by 45%.

Beginning with simple drying and curing, subsequently the process of vegetable tanning was developed by Egyptians and Hebrews about 400 BCE.

During the middle age, Arabs preserved the art of leather making so improved that it became highly polished leather.

By the 15<sup>th</sup> century, leather tanning was more widespread in Europe.

By the mid 19<sup>th</sup> century, power driven machines that perform such operations as splitting, splaining and debawing were introduced.

Towards the end of 19<sup>th</sup> century, <sup>use of chemical</sup> which include the use of cap, sumat and chrome salt was introduced.

## Modern leather making:-

The modern commercial leather making process involves three basic phases:-

- a) Preparation of tanning (Pre-tanning stage)
- b) Tanning
- c) Processing of tanned leather

### a) Pre-tanning stage

↓ Beamhouse operation

① Soaking → water (to hydrate)  
 → Blood, dirt, dung removal

② Liming → ① Liming  
 (pH = 12) ② Liming agent

③ Dulling  
 (pH = 8)

④ Bating

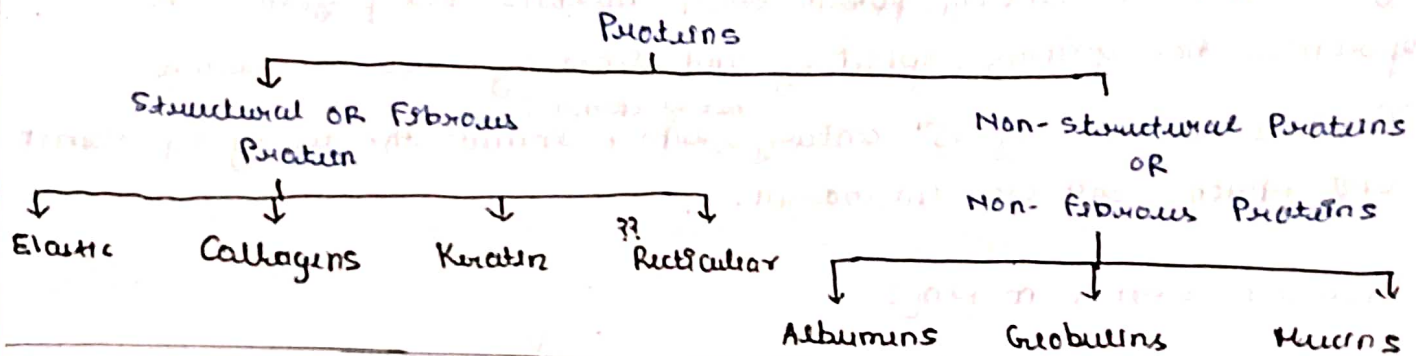
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⑥ Pickling → NaCl  
 → H<sub>2</sub> SO<sub>4</sub> (pH = 3-3.5)

- Tanning → Chrome tanning  
 → Vegetable tanning  
 → Oil tanning

### Composition of Hide/skin:-

Water	64%.
Protein	33%.
Fat	2%.
Mineral Salt	0.5%.
Other substance [pigments etc.]	0.5%.



06-Dec-2022

Structure of hide and skin are classified into two parts:-

- 1) Anatomical Structure
- 2) Chemical Structure

### Anatomical Structure:-

The hides and skin are mainly consist of three layers:-

- (1) Epidermis OR Outer layer
- (2) Dermis OR Corium layer
- (3) Flesh layer

### Epidermis OR Outer layer-

It is comparatively thinner than corium layer. It's thickness is only 1-2% of total thickness of the entire skin. It is divided into two layer of cells.

- (1) The outer OR Horny layer
- (2) The inner or Soft layer



The inner layer takes their food in form of blood from with corium layer when this food transferred to outer layer it will be layte and all the cells were dead in the form of dandruff.

Dermis OR Corium layer-

This layer consist of two layer: (a) Grain layer (b) Corium layer

Grain layer-

Minor corium

Major corium

Grain layer is also known as corium minor. It is the top of the corium layer about  $\frac{1}{5}$ th of total thickness. This layer has the characteristic grain pattern due to presence of hair follicles. The grain pattern depends upon the density and structure of the hair follicles.

8 Dec 2022

Corium layer-

This layer is main layer of hides or skin constituting about 98% of its thickness. The hair papilla contains nerves and blood vessels.

Due to blood circulation of animal's body lot of cells are produced. As the new cells are formed the older ones are pushed upward to the follicles forming the hair. The rate of growth of the hair is determined by the rate at which the cells surrounding the papilla reproduced. The newly formed cells of hair substance are slowly move upward are formed and hardened. In forming the hair they take the shape of follicles. In the bottom of hair follicle the hair root expanded and has bulb like shape. The position of the hair above the surface of the skin is called shaft and lower position the root. The hair is also divided into three layers - (1) Hair cuticle i.e. upper hair

(2) Medulla.

This is surrounded by

which contain

corium and which has pigment color. The pigment give color to hair.

(3) Fat glands - Fat glands are made of cells having nucleus and are arranged like grapes in a bunch. The oil present can act as barrier to water penetration during the soaking operation. The fat glands on the other hand maintain the body temperature by covering the body with the films of oil and thus regulates the surface evaporation of water.

In structure, corium is entirely different from epidermis. There is the typical epidermis structure and is entirely the product of epidermis. The cells of the epidermis dip down into the body of dermis and form a hair pocket in which the hair grows.

### Hypodermis or flesh layer:-

This layer is formed below the dermis layer. It is the loose connective tissue lying between the hide or skin and the actual body of the animal. At the time of flaying, a part of this tissue remain attached to hide or skin. The flesh is removed in flaying operation after liming.

### Protein

Proteins are structural and non-structural unit of living things containing Carbon, Hydrogen and Nitrogen and Sulphur.

Proteins are classified into two parts

(1) Structural protein or fibrous protein

(2) Non-structural



Keratin:-

It is dissolved with lime liquor and sodium sulphide, it will be used and when we apply the mechanical operation on the pelt it will be totally removed from the pelt.

Collagen:-

It is the most important protein in hide and skin and occurs in large part/amount. It is the protein constituents of the white fibre of the corium and form about 30.33% of the weight of the whole fresh skin.

12-Dec 2022.

Composition of dried collagen-

Carbon - 50.2%.

Hydrogen - 6.4%.

Nitrogen  $\rightarrow$  17.8%.

Oxygen & Sulphur - 25.4%.

Collagen is a complex protein containing various amino acids. It is insoluble in organic solvent, water and dilute acids and alkalis at ordinary temperature. It is collagen which combines with tanning substance and is converted into leather.

Elastin:-

This type of protein is removed in operation called bating.

The Elastin is removed by enzymatic treatment.

Reticuline:-

Reticuline is removed by sodium sulphide (antichroming agent)

Non-Structural protein:-

Albumins:- Soluble in water. It is removed during soaking.

Globulins:- When salt is added in raw skin, it is present in skin but when we wash it for removal of salt in soaking, it is automatically removed with skin fibres.

Mucins:- It is soluble in dilute alkali and it is removed in liming process with addition of lime.

Various Operation in leather processing:-

- (1) Curing:-
- The protective treatment soon after the hides or skins are tanned to strengthen the soaking property.
  - It creates an environment for hides and skins in which the protein destroying micro-organism can't function.
  - It can be done with various methods like wet salting, dry salting, drying and freezing etc.

13-Dec-2022

- 2) Trimming and Sorting:-
- Trimming is done to remove unwanted long shank, hair, hooves, ears, tails etc.
  - Sorting & It gives a proper shape of hide and skin after trimming.
  - Sorting is carried out according to size, weight, thickness and grade etc. and formed into batches to maintain the quality of leather.

- (3) Weighing:-
- Weight of hide & skin is taken in order to measure the chemical required for subsequent operations.
  - The weight is known as green weight or salt weight.



(4) Soaking:- Soaking is the first operation carried out in drums, paddle or pits with subsequent water, wetting agents and bactericides to rehydrate and restore the hide and skin to its natural condition and to remove adhering dirt, blood, curing agents and some soluble proteins. The method and duration of soaking varies according to the condition of raw stock.

Objective of soaking -

- To remove dirt, blood and dung from hide and skin.
- To remove curing salts in case of salted hide and skin.
- To rehydrate skin protein.
- To open up the contracted fibrous structure of hides and skin.
- To clean of surface flesh.
- Softening the hide and skin.

(5) Liming:- The treatment of soaked hide and skin with lime, sodium sulphide (saponifying agent), surface active agents etc. in a drum, pit or paddle drums. This is known as liming operation.

The purpose of liming is to remove hairs, epidermis, natural fats and greases (basically skin oil - made up of fats), interfibrillary proteins (cementing substance) to swell and split up the fibre bundles into fibres, to soften the collagen fibre lattice and make the final leather non-patchy, soft and pliable. In this operation pH maintained at 12.5-13. After this stage the hide and skin is called limed pelt.

Objective of liming:-

- The object of liming is to loose the hair, hooves, nails and other keratinous material.
- To remove some of the inter fibrillary soluble proteins like mucins etc.
- To swell up and to split up the fibres to the desired extent.

- (d) To remove the natural grease and fats.
- (e) To bring the collagen to a proper condition for satisfactory tanning operation.
- (6) **Fleshing and Unhairing**:- Fleshing is mechanical removal of unwanted flesh, connective tissues and fat by hand knife or fleshing machine. Unhairing is done by scrubbing with blunt unhairing knife or unhairing machine to remove hairs from the grain side.

Objective of fleshing:-

- (a) To remove fats and surplus flesh from lime pelt.
- (b) To give a cleaner surface for good penetration of chemicals.



Tanning:-

15 Dec 2022

In the leather industry, the most outstanding process is tanning. The objective of tanning is to convert the putrescible pelt to a substance which doesn't putrefy, dries out and doesn't swell when wetted. This substance is known as leather or wet blue/wet white. There is a huge difference in the properties of raw pelt and tanned leather. For instance, raw pelt becomes hard and horny on drying. While tanned leather doesn't putrefy, wet back or dries out. Leather has a very long life that is doesn't perish/damage for many years.

The real tanning can be done only by those material which doesn't cause separation of fibres or alter them chemically. These material are known as tannin stuffs or tanning agent.



The following tanning agents are used to produce leather at commercial level:-

- (I) Mineral substance such as salt of chromium, aluminium, zirconium, titanium and iron.
- (II) Vegetable substance that containing tanning properties.
- (III) Aldehyde and dialdehyde.
- (IV) Synthetic tanning agents.
- (V) Oil and fats.

By using the above substance the following commercial tanning process has evolved.

- Alum tanning process
- Chrom tanning process
- Vegetable tanning process
- Oil tanning process.
- Formaldehyde and Gluteraldehyde tanning. (Aldehyde tanning)
- Hybrid tanning or Competition tanning of two or more above mentioned process.

19 Dec 2022

### Vegetable Tanning:-

The organic compounds obtained from the plants and capable to convert raw hide and skin into leather are known as vegetable tanning materials. These tanning material used by various tanners are obtained from the various parts of plants such as bark, wood, fruit etc. The main vegetable tanning plants are babool, wattle, myrobalan, gambier, quercus, chestnut, Oak, Drui-drui, sumac etc. Infusion of these tannins obtained from a different sources greatly differ in colour, tanning properties and texture of leather produced from these tannings.

This difference due to presence of soluble non-tans in tannins.  
A blend of several above mentioned tannins is used to get the desirable property i.e. solubility, flexibility, fullness and color. Proper blending also influence the rate of penetration of tannins.

Vegetable tanning is classified into two categories-

(1) Pyrogallol

(2) Catechol

Chrom-tanning process:-

The process of tanning hides and skin into leather with basic chrome sulphate salts is known as chrom-tanning.

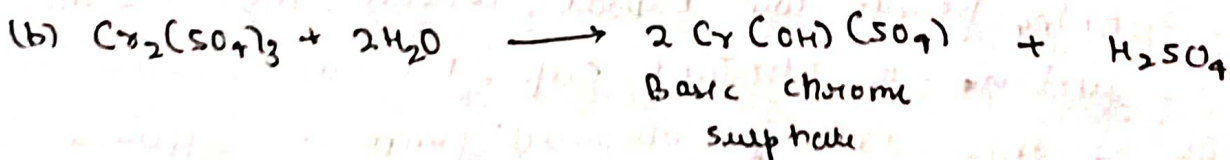
$\text{Cr}_2\text{O}_3$  is a trivalent chromium salt which is generally used for chromium tanning.

Chromium can acts as di-valent and hexo-valent element producing its oxide as  $\text{CrO}$  and  $\text{Cr}_2\text{O}_3$  respectively.

The properties of these oxides are as follow:-

- $\text{Cr}_2\text{O}_3$  is known as chromic oxide. It is amphoteric in nature that is it behaves as both acidic and basic.
- $\text{CrO}$  is chromous oxide. It is basic in nature.
- $\text{CrO}_3$  is chromium dioxide or chromium anhydride is intensely acidic in nature.

Chromium salts ( $\text{CrCl}_3$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ) are the salts of basic chromium hydroxide ( $\text{Cr}(\text{OH})_3$ ). On dissolution in water, these salts yield extremely acid solution as follows:-



Normal chrom salt has no tanning properties. On hydrolysis of above chrome salts a small amount of acid is formed.



The formic acid is neutralised by the basic salt. Therefore the tanning properties increased as the amount of neutralised acid increase in the solution.