

CHAPTER-1

DEFINITION OF HIDES & SKINS

The outer coverings of big domestic animals like cow, buffalo and horse are called hides. Whereas those of small domestic animals like sheep, goats are known as skin.

Primitive man covered himself with the skins of animals he killed. They had three major defects:

- They were dump,
- They would putrefy,
- They lost their flexibility and softness upon drying (they dried the skins to stop putrefaction.)

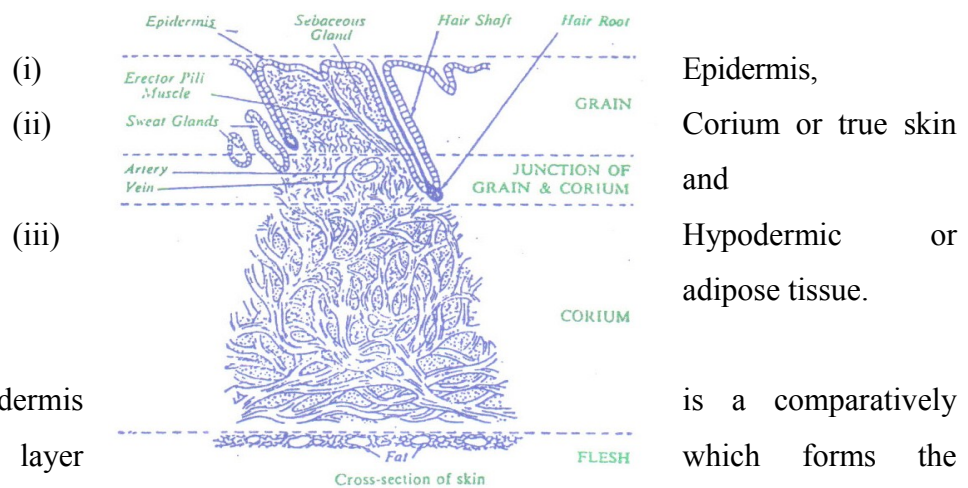
CHEMICAL COMPOSITION OF HIDES & SKINS

The chemical composition of fresh hides and skins falls approximately within the following limits:

- Water 60%-65%
- Protein 25%-30%
- Fats 5%-10%

STRUCTURE OF HIDES AND SKINS:

Most hides and skins consist of three parts, such as



The epidermis is a comparatively thin layer which forms the upper boundary of the skin.

This layer measures only 1% of 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:

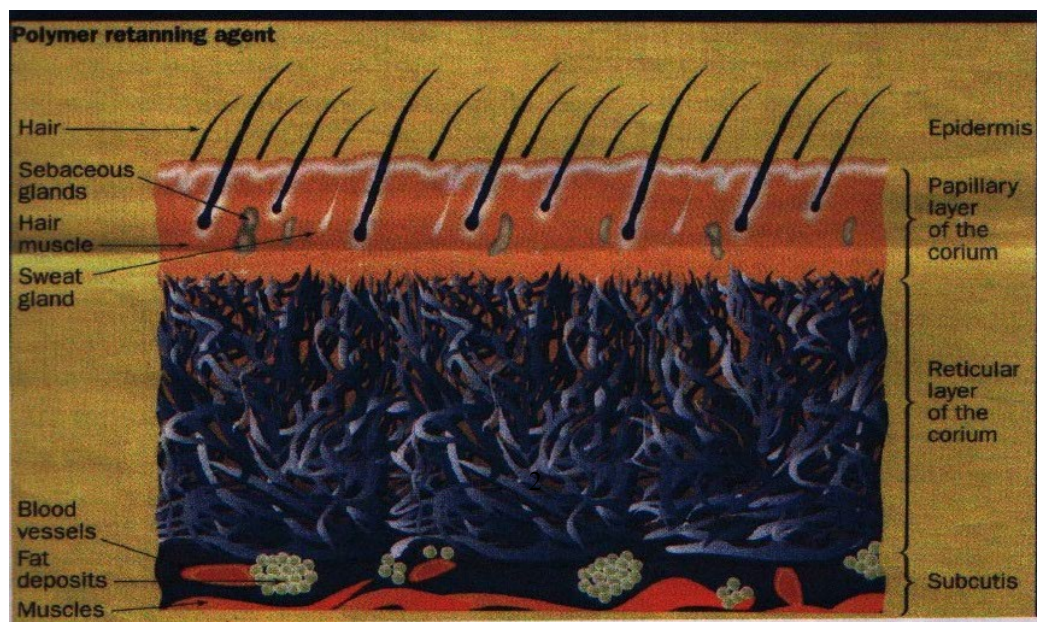


fig. : Histological Structure of Bovine Hide.

(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.

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:

- 12) The epidermis of calfskin is thinner than cowhide.
- 13) Grain surface is smooth.
- 14) Fat content is less than cow.
- 15) Calf skin has 100% cutting value.
- 16) The hair follicles are much smaller than cow.
- 17) Collagen bundles have fine structure as compared to cow hides and useful for the finest of leather.

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 farms (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.

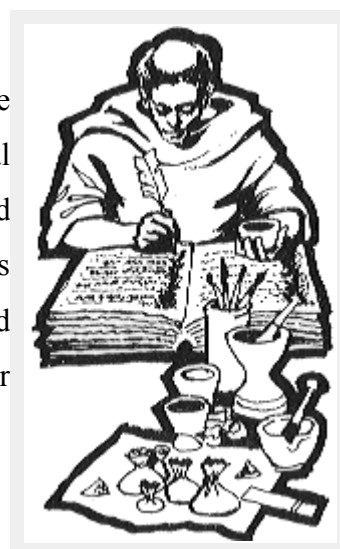
So proper curing with suitable salt like fresh NaCl, Naphthalene and bactericides should be used if we like to cure for longer period. In the tanneries of Bangladesh, generally we get high quantity of hides and skins at the time of 'Kurbani Eid'. Due to faulty and inadequate curing we lose 10-20% of 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.

CHAPTER 2

The story of leather

Primitive man hunted wild animals for food; he removed the hides and skins from the dead animal carcass and used them as crude tents, clothing and footwear. The earliest record of the use of leather dates from the Palaeolithic period, cave paintings discovered in caves near Lerida in Spain depict the use of leather



clothing. Excavation of palaeolithic sites has yielded bone tools used for scraping hides and skins to remove hair.

The skins rapidly putrefied and became useless, so a method of preservation was



needed. The earliest method was to stretch the hides and skins on the ground to dry, rubbing them with fats and animals brains while they dried. This had a limited preserving and softening action. Primitive man discovered also that the smoke of wood fires could preserve hides and skins, as did treating them with an infusion of tannin-containing barks, leaves, twigs and fruits of certain trees and plants. It seems likely that man first discovered how to make leather when he found that

animal skins left lying on a wet forest floor became tanned naturally by chemicals released by decaying leaves and vegetation🌿.

Much later the use of earth salts containing alum 🌿 as a tanning agent to produce soft white leather was discovered. The alum leathers could be dyed with naturally occurring dyestuffs in various plants.

Wall paintings and artefacts in Egyptian tombs indicate that leather was used for sandals, clothes, gloves, buckets, bottles, shrouds for burying the dead and for military equipment. The ancient Greeks and Romans also made extensive use of leather and it has remained an important industrial raw material since those times. The Romans used leather on a wide scale for footwear, clothes, and military equipment including shields, saddles and harnesses. Excavation of Roman sites in Great Britain has yielded large quantities of leather articles such as footwear and clothing.

The manufacture of leather was introduced to Britain by invaders, the Romans, and by religious communities, whose monks were expert at making leather, especially vellum and parchment for writing purposes. The ancient Britons had many uses for leather from footwear, clothing and leather bags, to articles of warfare. The hulls of the early boats, known as coracles, were also covered in leather.

Through the centuries leather manufacture expanded steadily and by mediaeval times most towns and villages had a tannery, situated on the local stream or river, which they used as a source of water for processing and as a source of power for their water wheel driven machines. Many of these tanneries still exist, but in many towns the only remaining evidence is in street names, like Tanner Street, Bark Street and Leather Lane.

Early Leather Production

The earliest crude leathers were made by first immersing the raw hides and skins in a fermenting solution of organic matter in which bacteria grew and attacked the hides or skins, resulting in a loosening of the hair or wool and some dissolving out of skin protein. The hair or wool was then scraped off with primitive blunt stone or wooden scrapers and fat or meat still adhering to the flesh side was removed in a similar manner. Tanning, the conversion of pelt into leather, was done by dusting the rawstock with ground up bark other organic matter and placing them in shallow pits or vats of tannin solution. Further additions of ground bark, were made from time to time until the tannin solution had penetrated right through the skin structure, taking up to two years for very thick hides. The leather was then hung up for several days in open sheds. The dressing of the leather involved paring or shaving it to a level thickness, colouring, treatment with oils and greases, drying and final treatment of the grain surface with waxes, proteins such as blood and egg albumins, and shellac to produce attractive surface finishes.

During the middle ages leather was used for all kinds of purposes such as: footwear, clothes, leather bags, cases and trunks, leather bottles, saddlery and harness, for the upholstery of chairs, and couches, book binding and military uses. It was also used to decorate coaches, sedan chairs and walls. Many leather articles have been recovered from the Mary Rose, a Tudor vessel which sank in 1545.



The majority of the leather was tanned with oak bark but soft clothing, gloving and footwear leathers were tanned with alum, oil, and combinations of these two materials.

With the discovery and introduction of basic chemicals like lime and sulphuric acid, tanners gradually abandoned their traditional methods and leather production slowly became a chemically based series of processes. Sir Humphrey Davy, the inventor of the miner's safety lamp, investigated some of these processes.



The growth of industrialisation in the 18th and 19th centuries created a demand for many new kinds of leathers, eg, belting leathers to drive the machines being introduced into industry, special leathers for use in looms in the textile industry, leathers for use as diaphragms and washers, leathers for use in transport and for furniture upholstery.

At the end of the nineteenth century, the invention of the motor car, modern roads, new ranges of coal tar dyestuffs, the demand for softer, lightweight footwear with a fashionable appearance, and a general rise in the standard of living created a demand for soft, supple, colourful leather. The traditional vegetable tanned leather was too hard and thick for these requirements and thus, the use of the salts of the metal chromium was adopted and chrome tanning became the tannage for modern footwear and fashion leathers. It produces soft, supple, beautiful and fine leathers, reflecting the way we live



The Worshipful Company of Leathersellers

The Worshipful Company of Leathersellers supervised the control of the quality of mediaeval leather produced in the City of London. They received their first Charter of Incorporation in 1444 from King Henry VI, having been granted articles for the regulation of their craft during the first Mayoralty of Richard Whittington in 1398.

Through the centuries the Company has played an important role in the leather industry, particularly in the field of technical education. The Company founded a technical college in Bermondsey in 1909 and in 1978 donated £500,000 for the erection of The National Leathersellers Centre at University College Northampton. The Company continues to maintain close links with the college and the industry as a whole and has recently been involved with the development of new premises for the Leather Conservation Centre, also located on the University College Northampton site.

DEFINITION OF LEATHER

Real leather is a natural product. It breathes, is warm and durable and has individual characteristics which make each hide unique. Leather will always bear the marks of its natural origin and these characteristics can show as scratches, growth marks, areas of differing fibre density and hair pore structure.

These characteristics in no way detract from the wearing qualities of the leather. With use it develops a patina which enhances its beauty

Legal Definition

In the UK a definition of leather is set out in the British Standard Glossary of Leather Terms (BS 2780) and this definition is used as a guide in applying consumer protection legislation such as the Sale of Goods Act and the Trade Descriptions Act. In short, if a product is made from reconstituted leather fibres or if the surface coating is too thick then it cannot be sold as 'leather'.

British Standard Definition (BS 2780)

Hide or skin with its original fibrous structure more or less intact, tanned to be imputrescible. The hair or wool may or may not have been removed. It is also made from a hide or skin that has been split into layers or segmented either before or after tanning.

Note 1: If the leather has a surface coating, the mean thickness of this surface layer, however applied, has to be 0.15mm or less.

Note 2: If the tanned hide or skin is disintegrated mechanically and/or chemically into fibrous particles, small pieces or powder and then, with or without combination of a binding agent, is made into sheets or forms, such sheets are not leather.

Properties

The physical properties which make leather a unique and valuable material for upholstery purposes are:

High tensile strength

Resistance to tear

High resistance to flexing

High resistance to puncture

Good heat insulation

- Leather contains a great deal of air, which is a poor conductor of heat. This is an important comfort consideration.

Permeability to water vapour

- Leather fibres will hold large quantities of water vapour. This property enables leather to absorb perspiration, which is later dissipated. A significant factor in comfort.

Thermostatic properties

- Leather is warm in winter and cool in summer.

Mouldability

- Leather can be moulded and will retain its new shape. It has both elastic and plastic properties in wear.

Resistance to wet and dry abrasion

- These properties, concerned with wear and maintenance, are controlled by the tannage and surface finish. These have now reached high levels of excellence.

Resistance to fire:

- Leather is inherently resistant to heat and flame.

Resistance to fungi

- Leather is resistant to mildew.

Resistance to chemical attack

- The atmosphere of modern cities is polluted from the burning of carbon fuels with sulphur dioxide gas, which can accelerate the deterioration of leather. Modern leathers are tanned and dressed to resist these harmful chemicals.

The Natural Characteristics of Leather

Real leather is a natural product. It breathes, is warm and has individual characteristics which make each hide unique. Leather will always bear the marks of its natural origin and these characteristics can show as healed scars, growth marks, areas of differing fibre density and hair pore structure. These hallmarks in no way detract from the wearing qualities of the leather. They are signs discerning owners cherish when buying leather. With the passing of time and use, it develops a patina which enhances its beauty.

Growth Marks and Veins - These are an indication of the age of the animal and in that respect are similar to the graining on a piece of timber. They range from often quite pronounced marks in the neck area to subtle bands across the hide

perpendicular to the backbone. Heavy growth marks are often placed on the outside backs of seating.

Scars - These form usually as a result of barbed wire damage or by the horns of other cattle. In their healed form the new skin is as strong as the remainder of the hide but unhealed damage should be avoided as tension on these parts may cause the leather to split or burst.

Grain Variation - The fibre texture varies greatly from being loose in the belly and flank areas to being relatively tight across the backbone. The looser areas consequently have more stretch.

The variation in hair pore structure is particularly noticeable in untextured leathers where clusters of open pores can sometimes be seen.

Shade Variation - No two hides are alike and due to the varying grain structure mentioned above the dyes and finishes penetrate to differing degrees in different parts of the hide to give an attractive variation. Whilst every attempt is made to achieve uniformity this is not always possible and sometimes not desirable.

TANNING

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

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.

Types of leather

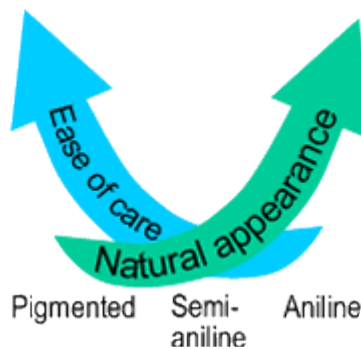
When choosing leather products there are a trade-off between natural appearance and ease of care:

Aniline leather is the most natural looking but is less resistant to soiling

Pigmented leather is the most durable but is less natural in appearance

Semi-aniline leather is somewhere in-between on both counts.

The choice is a matter of personal taste but the following information should help you understand the options



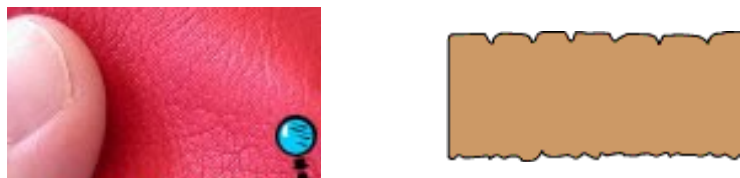
Aniline leather is the most natural looking leather with the unique surface characteristics of the hide remaining visible. Aniline leather is coloured only with dye and not with a surface coating of polymer and pigment. A light surface coating may be applied to enhance its appearance and offer slight protection against spillages and soiling



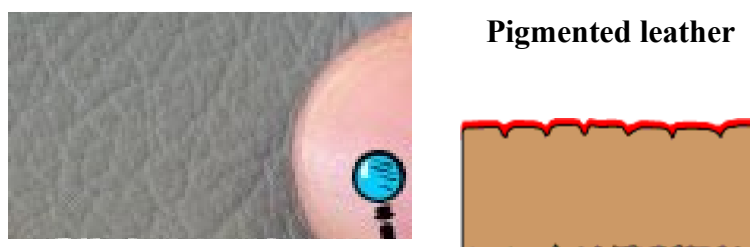
Aniline leather



Semi-aniline leather is more durable than aniline whilst still retaining a natural appearance. The increased durability is provided by the application of a light surface coating which contains a small amount of pigment. This ensures consistent colour and imparts some stain resistance.



Pigmented Leather is the most durable and is used in the majority of furniture upholstery and almost all car upholstery. The durability is provided by a polymer surface coating which contains pigments.



The surface coating allows the manufacturer more control over the properties of the leather, e.g. resistance to scuffing or fading. The thickness of the surface coating can vary but if the mean of pigment. This ensures consistent colour and imparts some stain resistance. more than 0.15mm then the product can't be sold as leather in the United Kingdom due to consumer protection legislation.

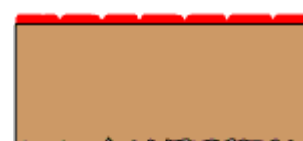
Full grain pigmented leather

The grain surface is left intact before applying the surface coating.

Corrected grain pigmented leather 🔄

The grain surface is abraded to remove imperfections before the surface coating is applied.

A decorative grain pattern is then embossed into the surface.



Finished split leather

The middle or lower section of a hide with a polymer coating applied and embossed to mimic a grain leather. Finished splits should only be used in low stress applications because they are weaker than grain leather.



Antique grain (two-tone or rub-off)

A special surface effect has been created to mimic the unique 'worn' appearance of traditional leathers. This is achieved by applying a contrasting top-coat which is applied unevenly or partially rubbed off to reveal a paler underlying colour.



Pull-up leather (also known as waxy or oily pull-up)

A leather with a natural appearance which lightens in colour when stretched during wear to produce a unique worn-in effect with time.

Nubuck

Aniline dyed leather which has been lightly abraded on the grain surface to create a velvety finish or nap. In some cases the grain pattern is still visible. The nap is very fine because of the tight fibre structure in the grain layer.

Suede

A split which has been abraded to create a distinctive nap. The nap can vary in appearance but is not as fine as the nap on nubuck because of the looser fibre structure.

British Standard (BS2780) Definitions

Aniline leather

Leather that has been dyed by immersion in a dyebath and has not received any coating of pigmented finish.

Semi-aniline leather

Leather in which the base coat of the finish contains pigment but later coats contain only dye or a contrasting pigment, to give a two-tone appearance, designed to imitate aniline leather.

Pigmented leather

Leather to whose grain surface a finish containing fine pigment particles in a binder has been applied.

Corrected grain leather

Leather from which the grain layer has been partially removed by buffing to a depth governed by the condition of the raw material and upon which a new surface has been built by various finishes.

Waxy leather

- (1) Upper leather finished on the flesh side and dyed. It is vegetable tanned with a high content of hard grease, though not necessarily wax.
- (2) Leather bearing a wax finished.

Suede

Leather whose wearing surface has been finished to produce a velvet-like nap.

Nubuck

Cattle-hide leather buffed on the grain side to give a very fine velvety surface : white or coloured.

Split

(1) A single layer from a hide or skin that has been separated over its whole area into two or more layers. (grain split, middle split, flesh split)

(2) Leather made from the flesh split or middle split.

Finished split

A split leather that has been finished by the application of a surface coating to simulate the appearance of a grain leather.

The leather making process:

Curing

Raw hides and skins must be preserved to stop them deteriorating before the leather-making process can begin. Methods of preservation include salting, chilling, freezing and the use of biocides.



Soaking

Cured hides or skins are soaked in water for several hours to several days. This allows them to reabsorb any water they may have lost in the curing process or during transportation. It also helps to clean them of salt and dirt.

Painting

Painting is a method by which wool can be removed from sheepskins using a sulphide based mixture.

Liming

Liming removes the epidermis  and hair. This also results in alkaline swelling of the pelt to cause a controlled breaking of some of the chemical crosslinks of the collagen .

Fleshing

After liming the pelt is passed through a machine to remove fleshy tissue from the flesh side. Hides may be split into layers at this stage or after tanning.



Deliming

The principal action of deliming is to gradually neutralise the alkali in the pelt, avoiding rapid changes in pH which could lead to distortion or disruption of the tissues.

Bating

A long delime can significantly improve the removal of any remaining lime, scud (miscellaneous debris) and residual components broken down during liming. Bating - based on the use of enzymes - completes this process so that the pelt is flat, relaxed, clean and ready for pickling and tanning.

Pickling

Weak acid and salt solutions are used to bring the pelt to the weakly acid state required for most tanning processes. Stronger pickling solutions are used to preserve pelts so that they can be stored or transported in a stable form over periods of several months.

Degreasing

Solvents or water-based systems can be used to remove excess grease before tanning.

Tanning

Tanning converts the protein of the raw hide or skin into a stable material, which will not putrefy and is suitable for a wide variety of purposes. Tanning materials form crosslinks in the collagen structure and stabilise it against the effects of acids, alkalis, heat, water and the action of micro-organisms. The main types of tanning materials are :

Mineral tannages

Most leather is tanned using salts of chromium🔗.

Aldehyde and oil tannages

Tanning with aldehydes and oils produce very soft leathers and this system can be used to produce drycleanable and washable fashion leathers and also chamois leather.



Vegetable tannages

Various plant extracts produce brown coloured leathers which tend to be thick and firm. This type of tannage is used to produce stout sole leather, belting leather and leathers for shoe linings, bags and cases.

Splitting

A splitting machine slices thicker leather into two layers. The layer without a grain surface can be turned into suede or have an artificial grain surface applied.



Shaving

A uniform thickness is achieved by shaving the leather on the non-grain side using a machine with a helical blades mounted on a rotating cylinder.

Neutralisation

Neutralising removes residual chemicals and prepares the leather for further processing and finishing.

Additional tanning material may be applied to give particular properties which are required in the finished leather.



Dyeing

The dyeing of leather into a wide variety of colours plays an important part in meeting fashion requirements. Some leathers are only surface dyed, while others need completely penetrated dyeings, as is the case with suede leathers.

Fatliquoring

Fatliquoring introduces oils to lubricate the fibres and keep the leather flexible and soft. Without these oils the leather will become hard and inflexible as it dries out.

Samming

This process reduces water content to about 55% and can be achieved by a number of machines, the commonest being like a large mangle with felt covered rollers.

Setting out

The leather is stretched out and the grain side is smoothed. This process also reduces the water content to about 40%.

Final drying

Leather is normally dried to 10-20% water content. This can be achieved in a number of ways and each method has a different effect on the finished leather:

Staking and dry drumming

A staking machine makes the leather softer and more flexible by massaging it to separate the fibres. To finish off the leather may be softened by the tumbling action inside a rotating drum.

Buffing and Brushing

The flesh surface is removed by mechanical abrasion to produce a suede effect or to reduce the thickness. In some cases the grain surface is buffed to produce a very fine nap, e.g. nubuck leathers. After buffing the leather is brushed to remove excess dust.



Finishing

The aims of finishing are to level the colour, cover grain defects, control the gloss and provide a protective surface with good resistance to water, chemical attack and abrasion.

Final grading

Leather will be graded before despatch to the customer. This grading may consider the colour intensity and uniformity, the feel of the leather, softness, visual appearance, thickness, design effects and natural defects such as scratches.

Measurement

The area of each piece of leather is measured by machine. Nearly all leather is sold by area so accurate measurement is important.

CHAPTER 3

ORGANOMETALLIC COMPOUNDS

History of Organometallic compounds

Early developments in organometallic chemistry include Louis Claude Cadet synthesis of methyl arsenic compounds related to cacodyl, William Christopher Zeise's platinum-ethylene complex, Edward Frankland discovery of dimethyl zinc, Ludwig Mond discovery of Ni(CO)_4 , and Victor Grignard organomagnesium compounds. The abundant and diverse products from coal and petroleum led to Ziegler-Natta, Fischer-Tropsch, hydroformylation catalysis which employ CO, H_2 , and alkenes as feedstocks and ligands.

Recognition of organometallic chemistry as a distinct subfield culminated in the Nobel Prizes to Ernst Fischer and Geoffrey Wilkinson for work on metallocenes. In 2005, Yves Chauvin, Robert H. Grubbs and Richard R. Schrock shared the Nobel Prize for metal-catalyzed olefin metathesis.

Organometallic compounds

Organometallic compounds are also known as organo-inorganics, metallo-organics and metalorganics. Organometallic compounds are distinguished by the prefix "organo-" e.g. organopalladium compounds. Examples of such organometallic compounds include all Gilman and Grignard reagents which contain lithium and copper, and magnesium respectively. Tetracarbonyl nickel, and ferrocene are examples of organometallic compounds containing transition metals.

In addition to the traditional metals and semimetals, elements such as boron, silicon, arsenic, and selenium are considered to form organometallic compounds. Examples include organomagnesium compounds such as iodo(methyl)magnesium MeMgI , diethylmagnesium (Et_2Mg); organolithium compounds such as butyllithium (BuLi), organozinc compounds such as chloro(ethoxycarbonylmethyl)zinc ($\text{ClZnCH}_2\text{C(=O)OEt}$); organocopper

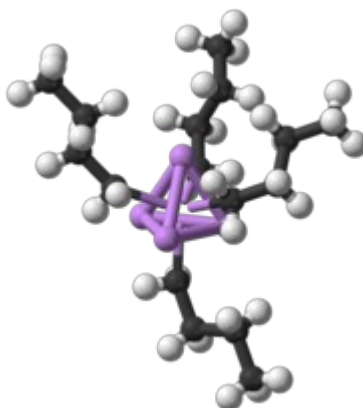
compounds such as lithium dimethylcuprate ($\text{Li}^+[\text{CuMe}_2]$); and organoborane compounds such as triethylborane (Et_3B).

Many organometallic compounds exist in biological systems. For example, hemoglobin and myoglobin contain an iron center bonded to a porphyrin ring; magnesium is the center of a chlorin ring in chlorophyll. The specialized field of such inorganic compounds is known as bioinorganic chemistry.

Organometallic chemistry,

The reactions and use of a class of compounds (R-M) that contain a covalent bond between carbon and metal. They are prepared either by direct reaction of the metal with an organic compound or by replacement of a metal from another organometallic substance. Their use is based on the polar R-M bond, in which the carbon atom carries a partial negative charge, and on the nature of the metal atom. In synthesis they act as nucleophiles that can bond with relatively positive carbon atoms in compounds such as alkyl halides, aldehydes, and ketones. For example, the Grignard reagent, RMgX (where X equals Br, Cl, or I), and organolithium compounds react with ketones to give secondary alcohols. In industry, butyllithium is used for the polymerization of isoprene in the manufacture of synthetic rubber; metalloorganic compounds serve as catalysts. The semimetals, boron, and silicon are important organometallics; organoboranes are used in synthesis, while organosilicones are polymerized to manufacture plastics and elastomers. Many organometallics are toxic primarily because of the toxicity of the metal. For example tetraethyl lead has been banned as gasoline additive and the conversion of mercury to mercury alkyls by fish has had serious consequences in Japan.

organometallic chemistry



n-Butyllithium, an organometallic compound.

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal. Since many compounds without such bonds are chemically similar, an alternative may be compounds containing metal-element bonds of a largely covalent character. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry.

Structure and properties

The status of compounds in which the canonical anion has a delocalized structure in which the negative charge is shared with an atom more electronegative than carbon, as in enolates, may vary with the nature of the anionic moiety, the metal ion, and possibly the medium; in the absence of direct structural evidence for a carbon metal bond, such compounds are not considered to be organometallic.

Depending mostly on the nature of metallic ion and somewhat on the nature of the organic compound, the character of the bond may either be ionic or covalent. Organic compounds bonded to sodium or potassium is primarily ionic. Those bonded to lead, tin, mercury, etc. are considered to have covalent bonds, and those bonded to magnesium or lithium have bonds with intermediate properties.

Organometallic compounds with bonds that have characters in between ionic and covalent are very important in industry, as they are both relatively stable in solutions and relatively ionic to undergo reactions. Two important classes are

organolithium and Grignard reagents. In certain organometallic compounds such as ferrocene or dibenzenechromium, the pi orbitals of the organic moiety ligate the metal.

Concepts

Electron counting is key in understanding organometallic chemistry. The 18-electron rule is helpful in predicting the stabilities of organometallic compounds. Organometallic compounds which have 18 electrons (filled s, p, and penultimate d orbitals) are relatively stable. This suggests the compound is isolable, but it can result in the compound being inert.

To understand chemical bonding and reactivity in organometallic compounds the isolobal principle should be used. NMR and infrared spectroscopy are common techniques used to determine structure and bonding in this field. Scientists are allowed to probe fluxional behaviors of compounds with variable-temperature NMR.

Organometallic compounds undergo several important reactions:

- oxidative addition and reductive elimination
- transmetalation
- carbometalation
- electron transfer
- beta-hydride elimination
- organometallic substitution reaction
- carbon-hydrogen bond activation
- cyclometalation

Applications

Organometallic compounds find practical use in stoichiometric and catalytically active compounds. Tetraethyl lead previously was combined with gasoline as an antiknock agent. Due to lead's toxicity it is no longer used, its replacements being other organometallic compounds such as ferrocene and methylcyclopentadienyl manganese tricarbonyl (MMT). The Monsanto process utilizes a rhodium-carbonyl

complex to manufacture acetic acid from methanol and carbon monoxide industrially. The Ziegler-Natta catalyst is a titanium-based organometallic compound used in the production of polyethylene and other polymers.

Ryoji Noyori's chiral ruthenium-BINAP complex catalytically reduces beta-ketoesters to secondary alcohols in the production of fine chemicals and pharmaceuticals,

Most commonly used organometallic compounds are-

- Organochromium chemistry.
- Organotitanium compound.

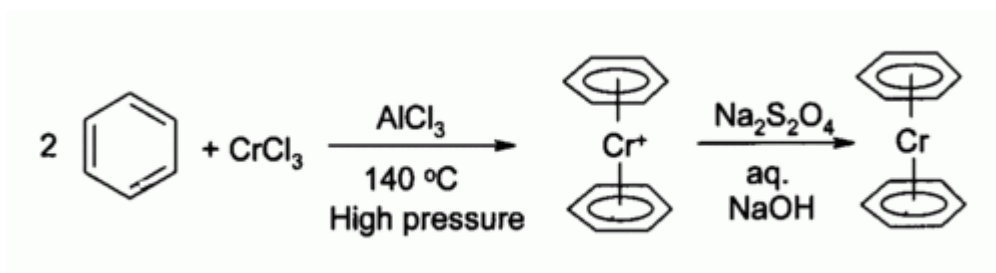
Organochromium compounds

Organochromium compounds can be divided into these broad compound classes:

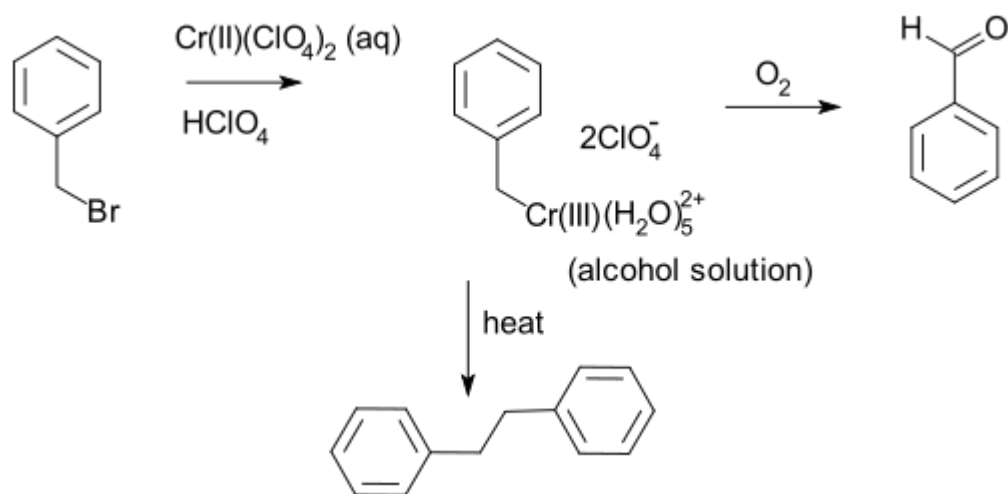
- Sandwich compounds: chromocenes (Cp_2Cr) and Bis(benzene)chromium derivatives (Ar_2Cr)
- Chromium carbenes ($\text{R}_1\text{R}_2\text{C}::\text{CrL}_n$) and carbynes ($\text{R}:::\text{CrL}_n$)
- Chromium(III) complexes R_nCrL_n ^[15]

History

The first organochromium compound was described in 1919 by Franz Hein ^[3]. He reacted phenylmagnesium bromide with chromium(III) chloride to a new product (after hydrolysis) which he incorrectly identified as pentaphenyl chromium bromide (Ph_5CrBr). Years later, in 1957 H.H. Zeiss et al. repeated Heins experiments and correctly arrived at a cationic bisarene chromium sandwich compound (Ar_2Cr^+) ^[4]. Bis(benzene)chromium itself was discovered around the same time in 1956 by Ernst Otto Fischer by reaction of chromium(III) chloride, benzene and aluminum chloride ^[5] ^[6]. The related compound chromocene was discovered a few years earlier in 1953 also by Fischer.



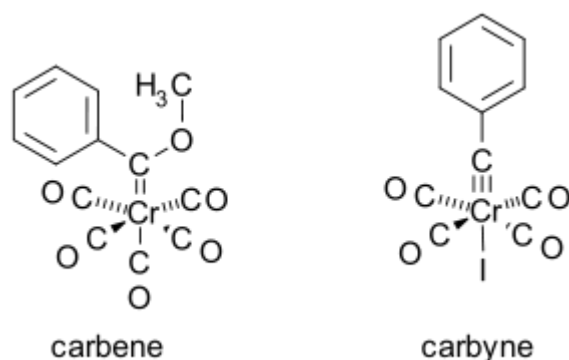
In another development, Anet and Leblanc also in 1957 prepared a benzyl chromium solution from benzyl bromide and chromium perchlorate. This reaction type is oxidative addition of chromium into the carbon-bromine bond, a process which was shown by Kochi ^[9] ^[10] to be a case of double single electron transfer first to the benzyl free radical and then to the benzyl anion.



G. Wilke et al. introduced tris-(η -allyl)chromium in 1963 as an early Ziegler-Natta catalyst (but not successful in the long run) ^[11] Chromocene compounds were first employed in ethylene polymerization in 1972 by Union Carbide and organochromium catalysts are used today in the industrial production of high-density polyethylene.

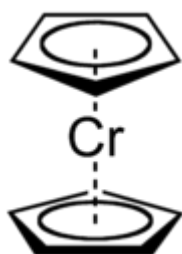
The organochromium compound (phenylmethoxycarbene)pentacarbonylchromium $(\text{Ph})(\text{OCH}_3)\text{C}=\text{Cr}(\text{CO})_5$ was the first carbene ever structurally characterized (X-ray

diffraction) by Fischer in 1967 (now called a Fischer carbene). The first ever carbyne, this one also containing chromium, made its debut in 1973



Two organic reactions involving chromium with use in organic synthesis are the Nozaki-Hiyama-Kishi reaction (1977) (transmetallation with organonickel intermediate) and the Takai olefination (1986)(oxidation of Cr(II) to Cr(III) while replacing halogens).

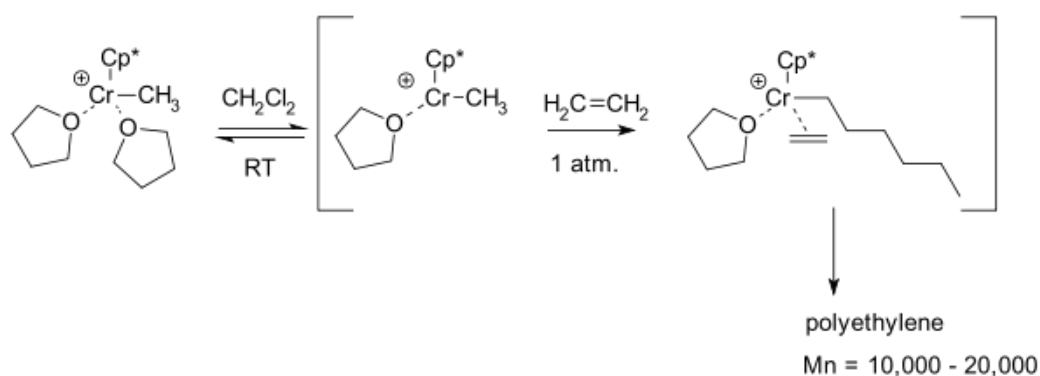
Organochromium chemistry



Organochromium chemistry is a branch of organometallic chemistry that deals with organic compounds containing a chromium to carbon bond and their reactions ^[1] ^[2]. The field is of some relevance to organic synthesis.

Ethylene polymerization

Chromium catalysts are important in ethylene polymerization ^[16]. Two industrial catalysts exist: the **Phillips catalyst** is deposited chromium(III) oxide on silica with activation by hydrogen. A Union Carbide catalyst is based on silica and chromocene. Exactly how these catalysts work is unclear. One model system describes it as coordination polymerization:

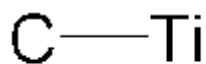


With two THF ligands the catalyst is stable but in dichloromethane one ligand is lost to form a 13 electron chromium intermediate. This enables side-on addition of a ethylene unit and a polymer chain can grow by migratory insertion. See also

Other bonds of carbon with elements in the periodic table:

[illegible]

Chemical bonds to carbon	
Core organic chemistry	many uses in chemistry.
Academic research, but no widespread use	Bond unknown / not assessed.



Organotitanium compounds in organometallic chemistry contain carbon to titanium chemical bonds. **Organotitanium chemistry** is the science of organotitanium compounds describing their physical properties, synthesis and reactions. They are reagents in organic chemistry^{[1][2]}

Brief history

Although the first attempt at an organotitanium compound dates back to 1861, it took until 1953 for the first such compound to arrive. In that year titanium phenyltri(isopropoxide) was prepared by Herman and Nelson from titanium isopropoxide, phenyllithium and titanium(IV) chloride. Titanocene dichloride was invented in 1954 and the first methyltitanium compounds were introduced in 1959. Ziegler-Natta catalysts as a major commercial application soon followed for which the Nobel Prize in Chemistry of 1963 was awarded.

Properties

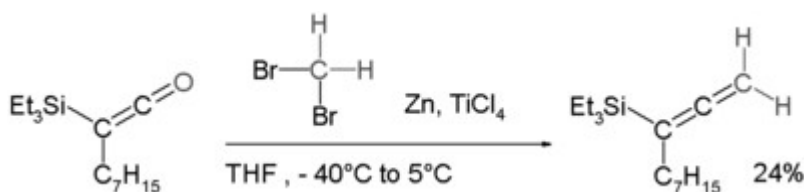
The titanium electron configuration ($[\text{Ar}]3d^24s^2$) resembles that of carbon and like carbon the +4 oxidation state dominates and like carbon compounds, those of titanium have a tetrahedral molecular geometry. Their bond lengths are much longer than that of C-C bond, with a recorded 210 picometer for the Ti-C bond in tetrabenzyltitanium. Simple tetraalkyltitanium compounds are monomers in solutions and in the gas-phase while their tetra-alkoxy counterparts can be tetrameric.

Due to its low electronegativity, Ti-C bonds are very polarized towards carbon and in many titanium compounds the carbon atom behaves as a carbanion. Organotitanium compounds are lewis acids with vacant coordination sites which can be occupied by forming octahedral complexes with bidentate ligands such as bipy.

Chemistry

Organotitanium compounds are important reagents in organic chemistry.

- The Ziegler-Natta catalyst (1954) is obtained from titanium(III) chloride and diethyl aluminumchloride and important in ethylene polymerization.
- **Methyl titanium trichloride** CH_3TiCl_3 (1959) is a nonbasic nucleophilic reagent. It can be prepared by reacting titanium(IV) chloride with dimethylzinc in dichloromethane at -78°C . It is used in nucleophilic addition of methyl groups to carbonyl compounds and in $\text{S}_\text{N}1$ methylation of alkyl halides. **Methyltriisopropoxytitanium** is a related reagent prepared in situ from titanium isopropoxide, titanium(IV) chloride and methyllithium^[3]
- Tebbe's reagent (1978) is related to the Ziegler-Natta catalyst and prepared from titanocene dichloride and trimethylaluminium. It is used as a methylenation agent for carbonyl compounds. It is an alternative for Wittig reagents when the carbonyl group is sterically challenged or when it easily forms the enol.
- Another methylenation reagent combination is the carbenoid **Lombardo's reagent** or Dibromomethane-Zinc-Titanium(IV) Chloride (1982),^[4] for example applied in a conversion of a ketene into an allene:^[5]



- The Petasis reagent or dimethyl titanocene (1990) is prepared from titanocene dichloride and methyllithium in diethyl ether. Compared to Tebbe's reagent it is easier to prepare and easier to handle. It is also a methylenation reagent.

CHAPTER-4

Pigment

A pigment is any particulate matter that is insoluble in and essentially physically and a chemically unaffected by the media into which it is dispersed.

According to part, of course, all insoluble dispersed and inert materials are not pigment. When all the desirable factors like, particle size and shape, nature of surface, refractive indices, crystal structure etc. Of insoluble dispensable inert materials are satisfactory, then only they can be considered as pigments. Some of those desirable factors for a pigment are explained bellow: -

Particle size:

The covering power of a pigment largely depends upon its particle size. Smaller the particle size, higher is the covering power. The particle sizes of commercial pigments vary from fine colloidal particles (0.01 μm) to relatively coarse particles (100 μm).

Shape:

The shape of pigment particles determines, to a great extent, the strength of bondage is strong when the particles are irregular is shape and pointed sharp edge.

Nature of surface:

The nature of surface of a pigment particle should be such that it can easily reflect that light waves which represent the colour of the pigment

Refractive Index:

The covering power of a pigment also depends upon its optical density, which can be represented by its refractive index.

Fastness:

Pigment must be fast to light, heat smoke, dust, and different gases present in the atmosphere common organic solvents.

Compatibility:

If the pigment particles are not chemically inert, they may precipitate out many ingredients from the binder solution into which the pigment is dispersed. A good pigment should be compatible, i.e. it should satisfactorily tolerate all the materials used in paint preparation.

Flocculation:

A good pigment power should completely disperse when it is sprinkled on stirring vehicle containing other necessary materials at slightly elevated temperature.

Bleeding and Migration:

Bleeding and migration of colour are another two important factors to be considered before selecting a pigment.

Abrasion:

The particles of a good pigment must show high degree of resistance to abrasion.

Crystallization:

If a pigment crystallizes out when present in dilute paint emulsion, it must be discarded as a pigment.

Classification of pigment:

Pigments are broadly classified into two groups: -

(1) Inorganic & (ii) Organic pigments.

Organic colour pigments are generally brighter, purer and richer in colour than their corresponding inorganic pigments. However, they are also generally more susceptible to such degrading and destructive

Influences sunlight, chemical attack and bleeding. The body, the covering power, the intensity, the light fastness etc. of inorganic are always superior than organic pigments. Considering all those factors most of the aqueous and non- aqueous paints of today are prepared by mixing inorganic and organic in required proportion.

Classification of inorganic pigments:

Inorganic pigments are two types-

(1) True/Earth colours &

(2) Prepared pigments.

Earth Colors

The naturally occurring insoluble colored materials come under this group. True pigments or Earth colours are found in different parts of world. Some of the true pigments based on iron oxide are listed below:

(a) Yellow coloured iron oxide called limonite ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$).

(b) Red colored natural iron oxide (Fe_2O_3).

(c) Brown colored limonite contain carbon and MnO_2 . This pigments trade name is "Burnt Umber".

(d) The natural black coloured iron oxides are called Magnetic (Fe_3O_4).

(e) Through the body, converting power, light head and chemical fastness of earth colors are better than prepared pigments, their uses in pigment preparation have reduced considerably because those are always associated with other materials as impurities. It is highly expensive to purify those ores, but unless those are purified standard colour can be obtained.

Prepared pigments:

The inorganic pigments which manufactured in chemical factories are called "Prepared Pigments" or "Synthetic Inorganic Pigments". Those pigments are classified into three groups:

- (a) White prime or White hiding or White pigments.
- (b) Extender or Filler pigments and
- (c) Colour inorganic pigments.

(a) White pigments

The materials, which have high refractive indices (above 2.0) and produce perfect white pigments, are allowed in this group. Example:

- (i) Titanium dioxide (C 1 -77891: Pigment white 6)
- (ii) Zinc oxide (C 1-77947: Pigment white 4)
- (iii) Lithopone (C 177115: Pigment white 5)
- (iv) Basic carbonate white lead (C 1-77597: Pigment white 10)
- (v) Antimony trioxide (C 1-77052: Pigment white 110)

(b) Extender

The extenders are also inorganic white or colorless prepared materials but they cannot produce white colour to the paints as their refractive indices near about 1.5.

Example:

- (i) Light alumina hydrate
- (ii) Kaolin
- (iii) Precipitated chalks and Silica
- (iv) Talc
- (v) Asbestos
- (vi) Mica barium sulphate
- (vii) Aluminium oxide etc. come under this group, extenders.

c) Colour inorganic Pigments

Those are also synthetically prepared colored inorganic compounds of high density and hardness. The materials given bellow can produce color to paints. Example:

- (i) Different colored oxide of iron & chromium
- (ii) Ultramarine
- (iii) Red lead
- (iv) Colored compounds of different metals
- (v) Dust of different metals etc.

Classification of organic pigments:

According to U.S Tariff Commission the organic pigments should be classified into two groups (1) Toners & (2) Lakes.

Toners

Toners are metal chelates formed from water-soluble anionic dyes and are available in scarlet to maroon shades. Toners generally have good resistance to bleeding. Example:

- (i) Barium toners
- (ii) Strontium toners
- (iii) Calcium toners
- (iv) Manganese
- (v) Copper toners etc.

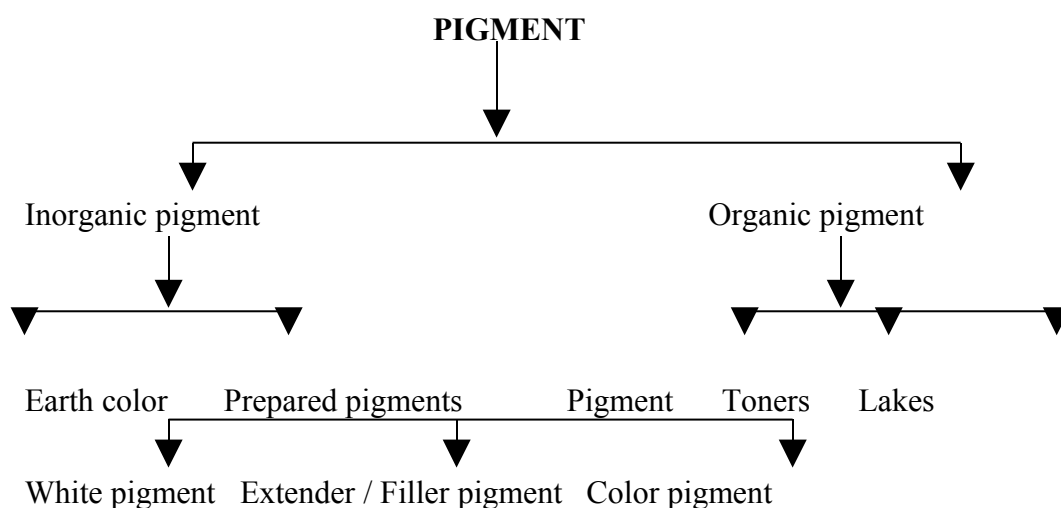
Lakes

A lake on the other hand is an organic colouring matter that has been more or less definitely combined with some inorganic substrate or carrier. The classification of organic pigments in Europe and Great Britain differs slightly from American classification. In Europe organic pigments are classified into three distinct groups as mentioned below:

- (1) Pigments Dyestuffs,
- (2) Toner Pigments &
- (3) Lakes.

It is thus clear that the American classification and Europe classification of organic pigments are basically the same except that L.S toners represent both pigments dyestuffs and toners of Europe. In India the British specification is generally

followed and therefore in the following specification chart system has been expressed.



Difference between organic & inorganic pigment:

Organic pigment	Inorganic pigment
Good brilliancy.	Less brilliancy.
Less covering power.	Good covering power.
Tendency to cause bleeding.	No bleeding.
Less setting.	More setting due to high fastness.
Less body.	Good body.
Less light fastness.	Good light fastness.
Available in the purest form etc.	May contain impurities if made out of earth colours.

Pigment in leather finishing:

Coloring substances are the base materials for leather finishes. A pigment is any particulate matter this is insoluble in, and essentially and chemically unaffected by the media into which it is dispersed.

The light fastness of selected is either than that of soluble dyes. This is especially apparent on pale finishes for which only small amounts of coloring substance of applied. Another effect, the transparent organic pigments too are superior to soluble dyes in this respect. With pigments it is therefore also possible to achieve a uniform coloring even of leather with unsettled surface appearance and cloudy shades so that the cutting value is improved. In contrast to soluble dyes, most of the pigments do not have the tendency to bleeding when they brought in which water or solvents, furthermore, pigments have the advantage they can be fixed during the production of the leather and large batched of leather can be uniformly produced and stored.

The pigments of course do not have only advantage. In addition, they are not fixed to the direct but the anchored to the leather surface by means of suitable binders. Therefore, any use of pigments means that the leather surface to the behavior of the leather and to wearing properties for the processing and the use intended as efficiently as possible.

Coloring substances of various origins are used as pigments for leather finishes. There are essentially two main groups, inorganic and organic pigments. Both group are manufactured synthetically so that pureness specific shades, fastness properties and are ensured.

Inorganic pigments (e.g. titanium white, zinc white, cadmium yellow and red chrome yellow and orange, iron oxide, yellow red brown and black, molybdate orange and red and red) generally have covering power. They are, however, less brilliant and process less tinctorial strength than organic pigments (e.g. yellow, orange, red, blue, and green types). The range of finishes therefore, usually contain members with inorganic and others with brilliant colors and obtain specific shades, organic and pigments are used together on the finish.

The pigments cannot be used for leather finishing in the form in which they are produced. In order to render them really embeddable in binders, they are used in form of pigment preparation in which they are uniformly and finely dispersed. The finishing effect is decisively dependent on this form of dispersion. Thus, leather finishes are always pigment preparation in which the pigments are dispersed by a treatment, which involves a great deal of work and rubbed off. The finishing agents should level out the appearance of the leather on the whole surface as much as possible and should either remain transparent or cover up the surface entirely. The requirements may lie in any graduation between the two extremes.

Properties of the pigments:

Any surface coating pigments may be asked to carry out some or perhaps all of the following tasks:

- (i) To provide color,
- (ii) To obliterate color,
- (iii) To improve the strength of paint film,
- (iv) To improve the adhesion of the paint film,
- (v) To improve the durability and weathering

Properties.

- (vi) To reduce gloss.
- (vii) To modify flow and application properties.

To choose pigments to carry out a given selection of those seven functions, we must know about the following properties of the pigment.

- I) Tinting strength.
- (ii) Light fastness.
- (iii) Bleeding characteristics.
- (iv) Hiding power.
- (v) Refraction index.
- (vi) Particle size.
- (vii) Particle shape.
- (viii) Specific gravity.
- (ix) Chemical reactivity.
- (x) Thermal stability.

Pigment selection:

To sum of the paint formulator is method of pigments selection is as follows:

- (i) Examine a pattern of the color to be produced in paint. Estimate the number of different hues that will have to be blended to be produce the color. A suitable pigment has to be found to provide each hue.
- (ii) Define the properties required from the pigments,
- (iii) Select a suitable pigment or pigment in each hue. In order to obtain pigments with the required properties, consult the following sources where necessary.
 1. General paints and pigment literature. There are traditional pigments for particular uses and binders.
 2. The color index (Society of Dyes and Colorists, Bradford, York's). The properties of pigments are given together with the name of commercial grades and their manufactures.

3. Pigment manufactures literature example of color may be given.

(iv) Match the color with one or more pigment combination.

(v) The test paint produced.

Ultra metallic colors:

Ultra Metallic Colours are available in thirteen shades specifically design to produce lustrous metallic shades on leather.

They are bases mica platelets that are coated with oxide of iron or titanium and are dispersed in an aqueous medium. These platelets good resistance to heat and chemicals.

Pigments, general physical properties:

A pigment can be defined as a finely divided powder, which can be dispersed in media of various types to produce paints or inks. It is insoluble in the medium and confers the following properties on the mixture.

1. Colour for decorative effect or appeal.
2. Obliteration or hiding power: It should obliterate the surface whether it is metal, wood, stone or an earlier coat of paint. As will appear later, pigments differ considerable in their hiding power and in some Instance, several coats of paint may be necessary to effect complete obliteration on the surface.
3. Protective properties: These are important in paint on exposed wood and certain types of metals. A suitably pigmented varnish is more weather-resistance and therefore more protective than unpigmented materials.
4. Corrosion repression: Primers for iron and steelwork contain special pigments chosen for their corrosion-repressing properties. A special class of pigment, usually described as 'extender', generally possesses little or no colour or hiding

power. Such materials are often included in paints to modify physical characteristics such as gloss and flow properties.

Metallic pigments:

Aluminum (CI pigment metal 1)

Aluminum pigment is an interesting material in the particle are in the form of small flakes, which process a high metallic luster and exhibit the properties of leafing in organic media. The particles oriented themselves with their planes parallel to the surface of the paint film.

Types of aluminum pigment:

The pigment is marketed in both paste and powder forms, and each of these is available in leafing or non leafing types.

Aluminum paste:

The leafing and non leafing types are graded according to particle size into the following grades.

Standard: a general purpose grade, very widely used containing approximately 67% pigment.

Polish or brilliant (leafing type only): This is designed to give a more mirror like finish than the standard. The past usually contains about 75% pigment.

Naphtha base standard: A paste containing 67% aluminum in which the solvent is naphtha in place of which the solvent is white spirit.

Ink and fine liming: These comprise the finest particle-size pigments.

Paste: Non leafing type there are certain paints where the continuous metallic luster is not required but where the presence of the flake particles is desirable. These include primers for woodworm and the industrial finishes where special

effects are required, for example, polychromatic and hammer finishes. The non-leafing paste is preferred for these materials.

Powder, Leafing: The properties of this material are similar to those of the paste type, but the finishes produced are somewhat brighter but less smooth. For this reason, and the dust nuisance, the powders are now used to a very limited extent.

Powder, Non-Leafing: The uses of these materials are similar to those of the paste type, but the latter is used whenever possible to avoid the dust hazard.

Identification:

Aluminum pigment has a characteristic appearance and when heated strongly in the air will burn to the oxide. It is soluble in acid and alkali. The acid solution gives the normal reaction for aluminum ions.

Lead:

Metallic lead produced in a very state of division, but on account of the great affinity for oxygen, it is supplied, as dispersion in water or in an organic medium presents no difficulties.

Properties and uses of lead:

According to Wild [9], metallic lead pigment absorbs oxygen very readily from its environment and therefore probably by inhibiting the cathodes reaction. This 'Oxygen barrier' idea would explain the efficiency of metallic lead in media other than drying oils such as isomerized rubber, chlorinated rubber, and epoxy resins.

Metallic lead is a highly toxic pigment and is subject to the lead paints regulations. Application of primers containing metallic lead is by brush or hand roller only, but on account of its high toxicity the pigment is declining.

Identification:

Metallic lead is dissolved by nitric acid and the solution gives the normal reaction for lead ions.

Stainless steel flake:

This pigment is available in both dry and paste forms. When used in paints, the films possess exceptional hardness and very good corrosion-resisting properties. It has high opacity and is used in solutions where corrosive or chemical attack is likely to be severe.

Bronze powders:

This term covers a range of alloys of copper and zinc containing a small quantity of aluminum. The paler and brighter shades are marketed under the name 'gold powder'.

Zinc:

This is marketed as a blue-grey powder under the name Zinc Dust containing 95 to 97 percent metallic Zinc. The balance is zinc oxide formed by oxidation of the finely divided metal.

Manufacture of zinc dust:

Metallic zinc (Spelter) is vaporized and the vapour is led into large condensers, under the conditions prevailing, the metal condenses as a dust, which is removed by suitable method. By rigid control of conditions the particle size distribution can be controlled to within fairly narrow limits.

Properties of zinc dust:

Zinc dust is supplied in two grades known as Standard and Superfine. These compare as follows:

	Standard	Superfine
Specific gravity	7.1	
Average particle size range	5-9	2.25-3.0

The particles are spherical in shape. The pigment has very good opacity but very low tinting strength. It is very reactive.

CHAPTER-5

FINISHING OF LEATHER

The surface of leather or the grain was treated in ancient times with a protective season. The modern finishing however has been developed in the last thirty years to a high performance technology with respect to the chemical composition and to the methods of application.

Generally 'Finishing' is defined as the up gradation or treatment of the leather surface with finishes and season to impart the special properties desired of leather as commercial product.

FINISHING MAY IMPROVE THE QUALITIES OF LEATHER IN SO FAR AS:

- a) Levelness of color on the skin.
- b) Uniformity of shade from skin to skin and pack to pack.
- c) Changing the color to that, which is required.
- d) Imparting color or pattern to un-dyed leather.
- e) Adding a transparent film through which the natural appearance of the leather may be viewed.
- f) Adding a transparent color film to the leather.
- g) Covering the leather with an opaque film in order to obliterate all defects.
- h) After the surface of the materials splits.
- i) Improve the scuff resistance of the leather.
- j) Improve the water resistance of the leather, i.e. the finish should not discolor or swell and hence protect the leather and retain its good appearance.
- k) Give a leather of optimum cutting value.
- l) Seal the leather surface so that it remains clean.
- m) Render the leather light fast.
- n) Render the leather heat fast.

- o) Render the leather fast to alkalis.
- p) Render the leather fast to acids.
- q) Render the leather resistance to a light pull up on lasting.

**FINISHING WHICH BEST OF THESE QUALITIES TO
LEATHERS MUST THEMSELVES HAVE THE QUALITIES OF:**

- 1) Remaining in its original condition of gloss or matt for long periods.
- 2) Not make a film on the leather, which is too plastic like in appearance.
- 3) Not spoil the feel or handle of the leather.
- 4) The finish should not craze or be easily removed.
- 5) It should be resistant to the adhesives used in the manufacture of leather goods i.e. solvents adhesives.
- 6) It must adhere to the leather in damp or wet conditions e.g. moulded leather skin boots and gloves etc.
- 7) It should resist dry cleaning fluids.
- 8) Resist heat and not tack.
- 9) Have resistance to cold crack.
- 10) Allow the leather to be washed.
- 11) The finish should not take up color from nearby articles or impart color to it.

It will be concluded that all leathers do not require all the above properties and it must be stressed that all the above properties can not be achieved the use of one finish only.

The number of coats of finish applied to a leather and the way in which they are applied is very important sometimes more important than the actual constituents of the finish. Most leather should be dyed a slightly darken shade then that they are intended to be finished.

PROPERTIES OF THE FINISH FILM:

An ideal finish film of the leather must deserve the following properties:

- Excellent flexibility and stretchiness
- Good adhesion
- Good holding power
- Fine glossing property.
- Abrasive resistance and fastness
- Waterproof ness and water vapor permeability

CHARCTERISTICS OF AN IDEAL FINISH FILM:

FLEXIBILITY AND STRETCHINESS:

Leather is a flexible material with certain degree of stretchiness. If the films to the leather surface dose 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.

ADHESION:

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

HOLDING POWER:

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

GLOSS:

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

ABRASIVE RESISTANCE AND FASTNESS:

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

WATER PROOFNESS AND WATER VAPOR PERMEABILITY:

The film should repel water so that it dose not spoil the leathery appearance of the finished leather at the same time, the film should hide all the defects in the leather.

THICKNESS:

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

RESISTANCE TO ACID, ALKALI AND CHEMICALS:

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

THEORY OF FINISH FILM FORMATION

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

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

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

In molecules there may be several dipoles but the overall dipole moment of the molecules is the resultant of all the dipole moments in it. For simplicity let us consider two different arrangements of equal and opposite charges at the corners of a square as shown in figure A and B-

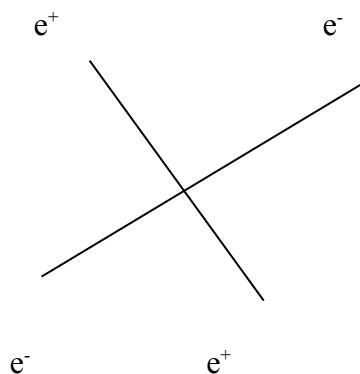


Fig-A

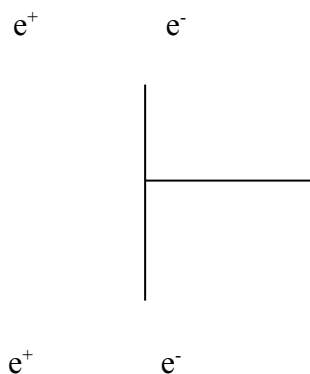


Fig-B

In fig-A the centers of action of both the positive and negative charges are at the point “0” and therefore the dipole moment is zero. But in fig-B the centers of action of both the positive and negative charges are L and M respectively. The whole system electrically is thus a rod LM of length S, one end of which is negatively charged with an intensity $2e$ and the other end positively with the same intensity. The molecules with definite dipole moments are called polar molecules whereas non-polar molecules have no dipole moments.

Of course, dipole moments can be induced on many polar molecules are separated from each other; the molecules become non-polar again. This is induction effect.

There is another effect called the dispersion effect by which non-polar molecules may gain polarity. This type of secondary valence force arises from the temporary relative displacements of the nuclei and electrons during the vibration of several parts of molecule with respect to one another.

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

- Polar molecule
- Intermolecular space
- This is called orientation effect.

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

LEATHER FINISHING SYSTEM

In general, the finishing of leather is done by application of the finishing materials in three layers, which can be termed as (i) Ground of bottom layer, (ii) top or final layer. The functions of these three layers are quite different and as follows-

(i) Ground or bottom layer of Base Coat:

This layer would form the foundation of the finish and control many of the key properties including adhesion, flexibility, filling and tightness of the grain, concerning of the leather surface defects and general uniformity.

Generally, solution of a suitable film forming material, which may or may not be colored with both dyestuffs and pigments, is used. The solution used for the bottom layer should have low acidity or alkalinity with P^H values within 6 to 7. The main

objects for the successive intermediate and top layers and to provide better adhesions between leather surface and the intermediate layer.

(ii) Intermediate or Middle layer:

This is the layer just above the ground coat and it represents the major portion of the film thickness. The film forming materials used in the intermediate layer should have strong affinity for pigment particles, materials used in ground coats. In protein-finished leather, the casein of the base coat is modified by the addition of albumins, which in resin finishing a harder resin or resin mixture is used.

(iii) Top layer:

The main objects of this layer are:

- i) To give required degree of gloss.
- ii) To protect the middle layer from scratch, frictional damages and abrasion and also from other damages due to sweat, acids, alkalis and other injurious materials.
- iii) To make the finish film waterproof, and
- iv) To produce very good feel and attractive appearance. The materials used for top must be very hard to make the leather smooth after planting, better resilient and round when bent with grain side out.

The technique of finishing leather differs from tannery to tannery, country to country. In many tanneries top coat is not applied separately and they use more binders in the season for the middle coat. The seasoning coat is generally applied by hand spray after the middle coat, but some times it is often on clear cut difference between the before mentioned various coats and amalgamation of various coats is being wide used now-a-days for ease of application and saving in time.

TYPES OF LEATHER FINISHES

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

- 1) Water type finishes.
- 2) Solvent type finishes.
- 3) Emulsion type finishes.

1) Water type finishes:

This may be based on pigment, protection binders, such as casein, shellac, gelatin, egg, and blood albumin, waxes and mucilaginous substances like decoration of linseed. These finishes are mainly used for glazed finishers, which are required to be glazed by glazing machine.

The binders in the finish are intended to hold the pigments or dyes in suspension and bound firmly on the leather surface. Softness, glazing properties and 'handle' are contributed by water soluble plasticizers, waxes and mucilaginous matters.

Recently water type finishes based on pigment or dyes and resin dispersion are increasingly used to achieve especial effect on the finished leather. The use such finishes produced may improvement over the conventional protein based finishes such as better adhesion and flexibility of the finish, improved filling and sealing properties and greater uniformity of the flesh.

2) Solvent type Finishes:

In contrast to water type finishes solvent-based finishes contain as a binder polyurethane or collodion (Nitro-cellulose). These finishes are dissolved in organic solvents such as butyl acetate, cyclohexanone, etc. These finishes are widely used for finishing based on vinyl resin instead of nitro cellulose have shown improved

resistance to flexing and better flexibility at low temperature. They have been successful used on upholstery leather, case leather, case leather and certain military where low temperature flexibility is necessary.

3) Emulsion type finishes:

Emulsion type finishes consist of nitrocellulose or resins. Such emulsions are being widely used to confer combining properties of water and lacquer finish. Laquire emulsion top coat for upper, garment and glove leather are gaining wide acceptance.

FILM FORMING / COATING TECHNOLOGY:

The coating applied in leather technology may be divided into four broad classifications:

1. Lacquer systems
2. Drying oil systems
3. Condensations systems and
4. Latex systems

Leather finishing, as applied in practical methods, may be the result of several of theses coating systems. The systems differ from one another in their mechanism of film formation and in the chemical nature of materials involved.

Lacquer systems:

The formation of a film in a lacquer system is the evaporation of the solvent containing a film-forming material. A simple example of this is the dissolving of shellac in alcohol and applying this to a surface, nitro cellulose dissolved in an organic solvent is also an example of this type of coating. This type of high-gloss lacquer is commonly used in household decorative enamels.

Drying oil Systems:

The second basic group of film-forming materials is the drying oils. Into this classification fall the nature drying oil, such as linseed and tung and also any material which will undergo polymerization, upon drying. This is different from a lacquer in that the setting up of the film is not simply a deposition of a high molecular weight material; rather it is chemical reaction- taking place between the dissolved film forming material and atmospheric oxygen. In the drying oils the film forming materials (a binder) is an organic chemical having a high degree of instauration. As the oil absorbs oxygen from the air, the unsaturated material is oxidized and reactive portions of the fatty acid molecule develop which can than polymerize with other fat molecules to form a continuous film on the surface.

Condensations systems:

In condensation systems the formation of the film is due to a chemical reaction between the various components of the finish after application. The reaction may form a plastic or polymer in water between two molecules. Such systems are usually heat-activated and may be baked, glazed, or hot pressed. Condensation of polymerization is used in the leather industry though protein-aldehyde reactions and with other resin systems. In this kind of finish the reactive components are usually mixed shortly before application, due to the limited pot life of the components.

Latex systems:

In a latex system the binder is emulsified water, when the latex is applied, the water evaporates, or sinks into the leather, and eventually a phase inversion takes place. A continuous layer of the binder spreads, on the surface of the material being coated and becomes a continuous film. Latex systems have their advantage in easy of application. The flammability and toxicity of organic solvents are largely avoided; the film can be diluted with water, enabling thin films to be applied

Through modern techniques for forming co-polymers, a wide variety of different lattices can be made which have a broad spectrum of properties. The versatility, low cost and ease of application of such systems have led to their wide spread use in the leather industry. The latex system and dispersions of resins in an emulsion form are by far the largest and most widely used method of preparation in leather finishes today.

CLASSIFICATION OF FINISHES:

According to the finishing materials:

I

- 1) Casein Finish
- 2) Resin binder or polymer finish
- 3) Nitro-cellulose finish
- 4) Polyurethane finish

According to the finishing technique:

- 1) Glazed finish
- 2) Glazed/ plate finish
- 3) Plate finish
- 4) Embossed finish
- 5) Spray finish
- 6) Curtain coating finish

According to the finishing effect:

- 1) Aniline finish
- 2) Semi-aniline finish
- 3) Opaque finish
- 4) Easy care finish
- 5) Antique finish
- 6) Fancy finish
- 7) Two-tone finish

CHAPTER 5

PRODUCTION PROCEDURE OF LEATHER (PROCESS INFORMATION)

EXPERIMENTAL PROCEDURE:

Raw Materials:

Wet salted goat skin good selection)-two pieces

Trimming: By hand knife.

Take wet salted weight. (All % based on this salted weight).

Name of Operation	% of Chemicals use	Time	Analytical Checking
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Pre-Soaking:

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:

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	

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

Painting:

6.0%	Lime (CaO)
3.0%	Sodium sulfide (Na ₂ S)
0.20%	Wetting agent
Water required making a paste	

Apply the paste on the flesh side of the goat skin and pile up flesh to flesh manner for 4 to 6 hours or over night in a flat bed. Then unhairing by hand knife.

Liming: (in bowl/ drums/paddles)

300 %	Water at N.T.
4.0 %	Lime
3.0 %	Sodium Sulfide
1.0 %	Liming Auxiliary (Erhavit MB/ Colapel-DL)
0.3 %	Wetting agent (LD-600/Lisapol)
0.2 %	Preservatives (Busan-40L/Aracite-DA)

run for 30 minutes. **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 Operat % 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 37°C

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)

	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	Run for 0'+30'+30'+90' min

Leave Over Night

Nex day add 0.5% hypo run for 30'

P^H=2.8-2.9

Drain half of the pickle bath.**Chrome Tanning**

Add to the pickle bath

4.0%	Basic chrome powder	run for 30 min
Add 4.0%	Basic chrome powder	
0.8%	Sodium formate	Run for 60 min
1.0%	Remsol OCS	

Check the penetration

+ 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: (CRUST)

Samming: Samming is done by machine.

Shaving: Shaving is done by machine (Thickness-0.7-0.8 mm).
Take shaved weight (All % based on this shaved weight).

Acid Wash:

150 %	Water at N.T.	
0.3 %	Oxalic acid / Acetic acid.	
0.4 %	Tergolix W 01	Run-30

Drain, Rinse well. P^H 3.2-3.3

Rechroming:

100%	Water at normal temperature	
1%	Catalix GS	Run for 15 min
4.0%	Basic chrome powder	
4%	Chrome Syntan	
1.0%	Sodium formate	Run for 60 min
Add 1.0%	Granofin A	Run for 30 min
Add 2.0 %	Varnatan AKM	
Add 1.0%	Sodium bicarbonate	Run for 90 min
	Check p ^H – 3.8 to 3.9.	

Retanning

	100%	water at 45°	
	4%	Tergotan ESN	Run for 30 min
	1.0%	Derminol SE	Run for 10 min
Add	4%	Vernatan R7	Run for 20 min
	4.0%	mimosa	
	2%	Quibracho	

	4%	Tanicor PG	
	4%	Coranol OT	
	2%	Dye	Run for 75 min
Add	50%	Water at 50 C	
	4%	Derminol ASN	
	4%	Derminol SE	
	2%	Derminol CST	Run for 60 min
Add	0.5%	Formic acid (1: 10 dilution)	Run for (15+15+15) min
		drain, horse up overnight	

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 70°C / 75 kg pressure.

Then it was ready for finishing.

FINISHING:

Base Coat:

Ground UP	100 parts
Water	100 parts

1X Spray, Plane plate at 80⁰ C/50 lb/1 sec.

Season Coat:

Melio Resin 776	100 parts
Melio Resin 820	100 parts
Wax 185	50 parts
Melio Top 286N	50 parts
P.P.E pigment (Tan)	80 parts
Melio Promul 54 A	40 parts
Melio Promul 39A	20 parts
Water	560 parts

Spray 2X, Sand Blast at 80⁰ C/100 lb/1 sec.

Again 2X spray.

Top Coat:**For Sample 1**

Melio EW348	200 parts
Water	200 parts
Ultra metallic copper	30 parts
Aqualen AKU	5 parts

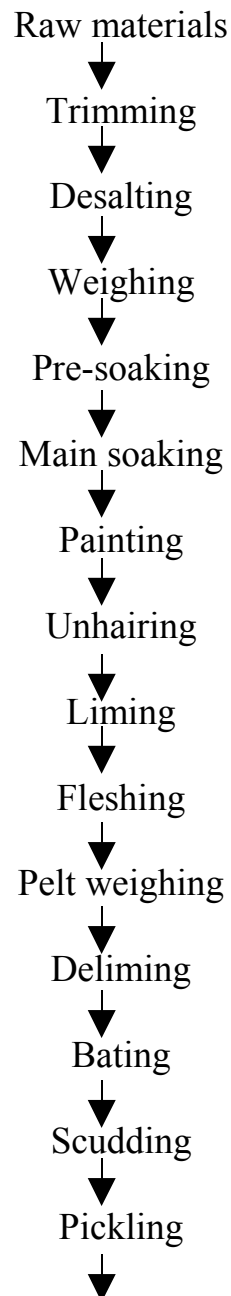
Spray 2X, roto press at 100⁰ C/50 lb/ normal speed.

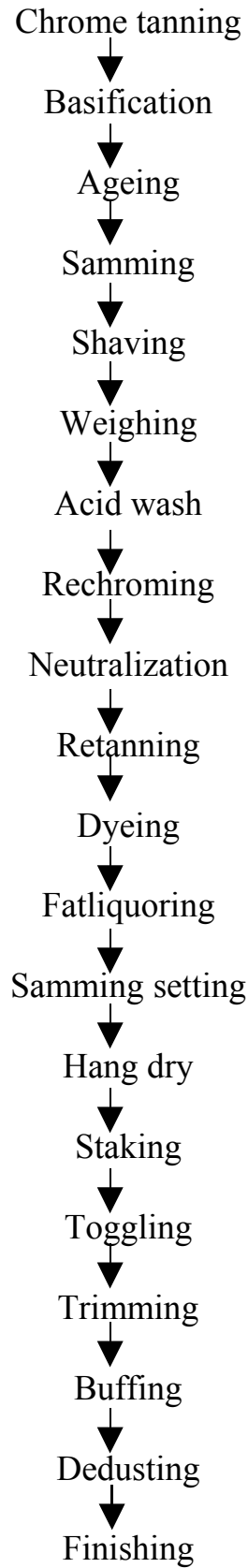
Top coat:

For Sample 2

Melio EW348	200 parts
Water	200 parts
Ultra metallic Bronze	30 parts
Aqualen AKU	5 parts

Spray 2X, roto press at 100⁰ C/50 lb/ normal speed.

FLOW CHART OF WORKING:



CHAPTER -6

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. Chromitan B** : 33% Basic chromium sulphate
BASF

9. Cartaflex GS liq : Cation-active fat liquor

Properties

- Appearance : Creamish white pour-able liquid
- Chemical Character : Weakly cationic-active fatty acid condensation product
- pH of a 10 % solution : 4.0 to 5.0
- Active ingredients : 25 % to 27 %
- Stability to : Very good to acids, electrolytes, hard water, Chrome.
(Clariant)

10. Vernatan AKM p : Auxiliary tanning agent for neutralization

Properties

Appearance	: Pale cream coloured powder
Chemical Character	: Aromatic condensation product, buffering & complex active compounds
Solubility	: Readily soluble in water
pH of a 1 % solution	: 6.5 – 7.5 (Clariant)

11. Vernatan R7 p : Tanning cum filling agent for the retannage of all types of leathers

Properties

Appearance	: Pale brown coloured powder
Chemical Character	: Nitrogen containing polymeric amino resin
Solubility	: Partially soluble in water and gives a fine dispersion
pH of a 1 % solution	: 8.5 – 9.5 (Clariant)

12. CoralonOT Powder Dispersing and leveling agent

Properties

Appearance	: light brown powder
Chemical character	: condensed naphthalene sulphonates
Ionic character	: anionic
Active substance	: min.92%
pH of a 5% solution	: 6.5- 8.0
Acid value	: nil (Clariant)

13. Tergolix W-01-IN Liq : Soaking Agent

Properties

Appearance	: Clear, Pale Yellow liquid
Chemical Character	: Blend of organic substances
Ionic Character	: Nonionic
Dry content	: approx. 40 %
pH of a 10% solution	: 8 – 10 (Clariant)

14. Melio Promul AP-39.A

Solids content	: approx. 19 %
pH value	: approx. 8,5

Composition:

Melio Promul AP-39.A is an aqueous aromatic PU dispersion.
(Clariant)

15. Melio Resin A-820

Solids content	:	approx. 24,0 %
pH value	:	approx. 8,5

Composition:

Melio Resin A-820 is a compact binder based on selected polymers and filling agents. (Clariant)

16. Melio Resin A-776

Solids content	:	approx. 22,0 %
pH value	:	approx. 8,5

Composition:

Melio Resin A-Impregnation and adhesion binder
(Clariant)

17. Melio Promul 54.A

Solids content : approx. 20,0 %
pH value : approx. 8,5

Composition:

Melio promul 54. A-is a adhesion binder
(Clariant)

18. Melio EW-348.B

Solids content : approx. 17,0 %
pH value : approx. 8,5

Composition:

Melio EW-348 NC-emulsion lacquer, multiple use
(Clariant)

19. PPE Pigments

Composition:

The PPE products are a range of aqueous pigment dispersions for leather finishing.
They are dispersed in a minimum amount of anionic casein solution to maintain the
Suspension of the finely ground pigments over long storage times.
(Clariant)

COSTING

I took two pieces of goat skin. By using metallic pigment lower grade can be upgrade. The costing of manufacturing fashionable ladies shoe upper is described bellow:

(per square feet)

(including all cost)

Raw material----	Tk 50.00
Wet blue -----	Tk 8.00
Crust -----	Tk 14.00
Finishing -----	Tk 12.0
Total =	Tk 84.00

SAMPLE ATTACHEDMENT

SAMPLE 1:

Copper

SAMPLE 2 :

Broze

Conclusion & Recommendation

Modern worldwide leather market is now a days very fond of quality leather. Finished leather is also an intermediate product. Which serves as a raw material for finished leather is therefore, fashion driven, requiring more responsiveness to the market, whereas crust leather is more a commodity type product. Since 1990-91, Bangladesh has started exporting footwear and other leather goods. Bangladesh currently exports leather footwear to Europe and Japan. As production capacity in finished leather and leather goods is developed in Bangladesh, new jobs will be acquired, and markets will be accessed. Therefore, the availability of goat skin, the international demand for it as well as the quality has intended me to develop a recipe for the production quality leather using organometallic compounds.

Finishing with metal pigment give more covering. Lower grade can be upgrade by using metallic pigment.

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