INTRODUCTION

Can you remind me the modules you have covered previously in sequence?

Post tanning operation, in this context, includes after tanning wet end physical and chemical sub operations such as siding, splitting/if no pelt splitting/, Sam/setting, wet shaving, neutralization, retanning, dyeing, fatliquoring and fixation. Dyeing can be straight or dried crust dyeing. It also includes drying processes as it is the automatic sub operation after drum operation, though the latter will be dealt at another module. It is the first stage at which enormous product diversification starts as per customers' demand and the tanner's know-how, skill and experience are tested.

I .PHYSICAL PROCESSES

1. SAM/SETTING

1.1) Definition: Sammying *is dewatering of leather (eg, wet blue, retanned leather)* ***mechanically*** *by pressure as part of wet end operation.*

*Whereas****, setting out*** *is flattening and slight stretching of leather with reversely moving bladed rollers. The latter is one of the mechanical mechanisms to achieve better area yield.*

Usually in modern tanneries these two operations are done simultaneously by through feed ***Sam/setting*** *machine.*

1.1.2) purposes or objectives of Sam/setting:

Sammying is to:

- *Bring the moisture content of the leather into suitable range of working condition. If the leather is too wet /dump/or too soft/less resilient/, it will be dragged and torn by cylinder of the shaving machine/the subsequent operation/.On the other hand, if it is too dry/hard or horny/, it will not be pliable enough to lie snuggly against the guiding bolster of the shaving machine and also be difficult to wet back.*
- *Slightly reduce the water content of wet blue and reduce the weight and transportation costs, especially if the product is to be sold at this process stage.*

Setting out is to:

- *Avoid creasing/pleating/of leather so that we can achieve area yield not only by flattening by blunt blades but also by avoiding/reducing/tearing during shaving .It has also some drying/sammying effect.*

N.B*: Do not allow over drying (dried chrome tanned skins can not easily wet back and take up dyes or fatliquors unevenly)*

1.1.3) process variables:

In our case, the subject of process variable refers to considering the extreme cases of a given variable and its influence on the leather processing or the ultimate leather quality and quantity.

What else is required over and above the simple function of removing as much water as possible by sammying at fastest production?

Primarily the leather must not be damaged. Thus, the range of moisture content before shaving operation should be seriously considered .The recommended range is 45-50%. Pleating during introduction to the machine can affect quality and causes area loses and hence setting is required.

Friction on the leather surface caused by speed differences of machine conveyors/in the case of through feed/and excessive local pressure / in the case of simple motor driven machine/brings about grain damage. ***Hence both speed and pressure variables, as well as moisture level, as process variables should be inspected.***

Besides, Sammying needs to be uniform throughout machine area and hence leather area. Related to this, to avoid point pressure, but still be sufficient to expel the water, there must be enough pressure zones or they must be as wide as feasible. (The wideness can also increase rate of production)

1.1.4) practice:

At least we can have two types /generations /of Sam/setting machines.

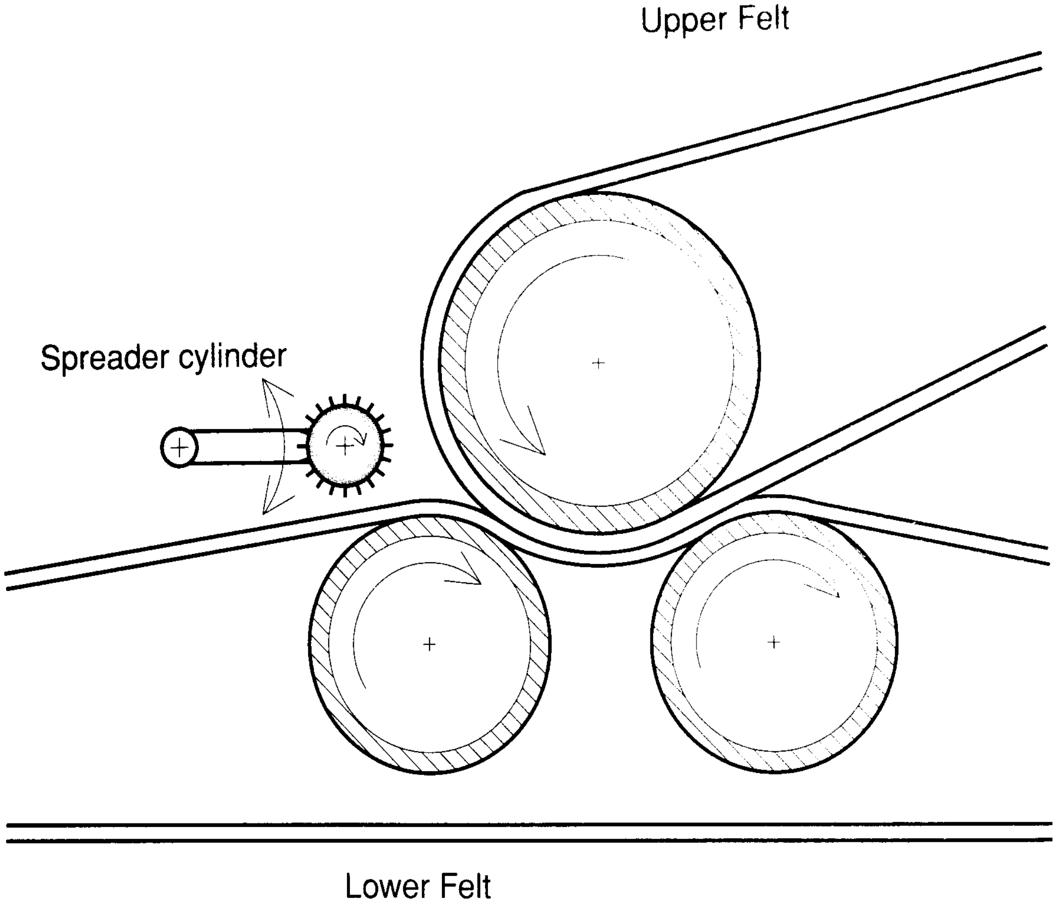
i) Simple motor driven mangle: *This machine/motor/generates mechanical pressure by driving of gears and transferring the gear motion to the squeezing water-proofed felted rollers simply by pressing of the foot treadle of the feed roller. This pressure is then used to press/squeeze out water from a wet skin that passes through two rollers which are wrapped by the felts. The practice of sammying by this machine is becoming obsolete due to the problem of point pressure and capacity limitation.*

Besides, it lacks setting out effect.

ii) Through feed Sam/setting machine: *In this case, the pressure is produced by hydraulic effect. The configuration of this type of machine is in such a way that top and bottom pairs of rollers are held by the PVC feeding conveyor, the smooth surface of which helps the operators to spread out and facilitates the spreading action of the bladed spreader roller .Hence, when the leather is held and transported by the feeding conveyor through the pressure rollers and spreading rollers ,the leather is not only sammed but also well flattened. Note that in this type*

of machine, the top and bottom pairs of rollers are driven from the same source, so speed differential may not occur .e.g., Bauce through feed machine.
***N.B**.Recently, Bergi Company has developed a sammying/drying machine employing a heated roller and a felt with a large contact area against it, especially for retanned leather.*

Diagram for through-feed Sam/setting machine



1.1.5) Process control:

Day to day works control of Sam/setting process variables is necessary in order to achieve consistent results of quality and quantity. In this duty, the drying or effectiveness of water reduction is mainly a function of the pressure between the rollers and the feed speed, in other words the pressing time. Thus, we have at least three aspects to control:

- *The relatively uniform moisture content/level of the sammed leather through out the area,*

- *Flatness or crease free leather and*
- *Pressure and speed adjustment of the Sam/setting machine.*

N.B: *The moisture content of leather can be measured using any oven from a laboratory or using any ready made moisture meter especially for semi dried or dried leather. Pressure is adjusted according to the type of input to be processed (sammed/set) and the type of machine to be used. But the consistency of the pressure applied is controlled by reading the pressure gauge installed. Besides, the rate of production is inspected by following up of the conveyor and operators speed.*

WET BLUE SPLITTING

One of the mechanical sub-activities practiced in post-tanning operations is splitting of hide, if it was not done at lime pelt stage.

Do you remember the actions of cambering and decambering activities and the relevant advantages while lime splitting? Splitting why? What are the three main layers of skins*?*

As you may know, in most cases, lime splitting is an environmentally better option than blue splitting as the former allows:

- *The grain and the split layers to take different routes of tannage as per the requirement for end uses*
- *The split which is not usable to leather making but to use it for the manufacture of gelatin or collagen castings for food stuffs*
- *To reduce the consumption of inputs/chemicals, water etc./ and improve drum capacity by avoiding non leather making rubbishes*
- *To shorten process time due to the reduction of overall thickness that in turn facilitates penetration of pretanning and tanning chemicals, like those chemicals having weak penetration power as CO_2 for deliming purpose.*
- *Reduces waste, especially tanned solid waste and*
- *Better area yield due to maximum relaxation of the grain surface, especially for spready upholstery. But a tanned hide is a little more stiff and wrinkled*

But there are cases where wet blue splitting is more advantageous than lime spitting. These technical reasons or the strict specification of the final product can include:

- Accuracy and ease of handle i.e. tanned and sammed/set wet blues are more comfortable to handle and reduce pelt damage and thickness variation while splitting than the limed pelt and the former helps to split the leather to more uniform and accurate thickness. E.g. pelt splitting provides a maximum precision of ±0.25mm, wet blue splitting provides a precision±0.15mm, but shaving provides a precision of as high as ±0.05mm.
- Resolving the other disadvantages/limitations of lime splitting like:

- ✓ If there is no means to split at lime stage or the material at hand is already tanned blue
- ✓ To maximize the use of split/ in area yield, thickness, accuracy etc./
- ✓ Preference to leather types that need to be firmer or needs only weak liming and open-up or where swelling and high water penetration at liming stage are not recommended, e.g. for firm shoe upper.

1.3) SHAVING:

1.3.1) Definition: Shaving *of leather, as one of the wet end operations, is simply considered as the removal of flesh and loosely attached structures such as adipose tissue remains as well as thickness adjustment into a salable form according to the would be leather type and the customers demand.*

1.3.2) purpose of shaving:

Shaving is required (after sammying/setting and siding to the moisture content of about 45-50%)

- ❖ *To bring the leather to a uniform thickness throughout the skin area in a precise manner (and with greater accuracy than can be obtained by splitting operation) as commercial leather should be of uniform thickness.*
- ❖ *To remove the loosely attached tissues and fibers that reduce the aesthetic appeal of the flesh side leather and to remove flesh offal remains, if any.*
- ❖ *To intensify surface dyeing by exposing the inner fiber especially for suede.*

1.3.3) process variables:

In a tannery, the mechanical operations such as sammying, splitting and shaving can result in substantial losses in usable cutting value if the related variables with those processes are not closely monitored and controlled. The main reason for the diminishing of the usable cutting area is the noncompliance to thickness specifications. But this specification cannot be achieved by controlling of shaving alone. Because, if wet blue splitting is poorly controlled and heavy shaving is required or splitting is widely nonuniform or gashed partly, the shaving operation doesn't always lend you the degree of thickness correction you desired. As it is said above, too wet/soft/ or too dry/horny/leather especially around neck and shank areas can result in area loss. Thus these parameters or variables should also be controlled before shaving operations.

The other variable to be considered is the proportion of hide thickness or substance to the degree of shaving required. If you are desired to get a lower thickness from relatively thicker hides/skins/, you may lose a lot of leather making fibers as shaving dust and the remaining grain part is easily vulnerable to tear. Here you will affect *not only the leather quality/physical strength/but also the environment with heavy shave dust load.*

1.3.4) PRACTICE:

Although a shaving machine has a lot of parts, the cutting blades/spiral knife blade/, repeller/guard fan/, the feed roller/bolster/, the pedal/treadles/, the safety guard and the adjustment board/buttons/are our interest. Knowing these parts and their relevant functions can make easier the practical activity of these sub operations.

The shaving machine cylinder is fitted with spiral blades of steel. The spiral form of the blade aids us not only for cutting/scraping but also for spreading/widening out of the skin; and the leather movement is controlled by the operator. The blade revolves at higher speed/up to 1500RPM/ and is kept sharp continually by a grinder in a much the same way as with the fleshing machine. The feed roller is moved by pressing the treadle/pedal/. Thus, an operator feeds at a time a portion of the skin/hide between the feed roller and the shaving cylinder with the flesh side facing the shaving cylinder or blade followed by pressing the pedal. Before that, by using the adjustment board, the appropriate/predetermined/ and accurate setting is done so that the feed roller is brought up against the cutting cylinder and is held away from the cylinder. Then the flesh side of the skin is moved against the sharp revolving knife blade and shaving is done. While shaving is proceeding the repeller is revolving against the direction of the blade revolution and prevents the wrapping up of shaved skins. This helps prevent skin damage. The common thickness ranges for some products can include:

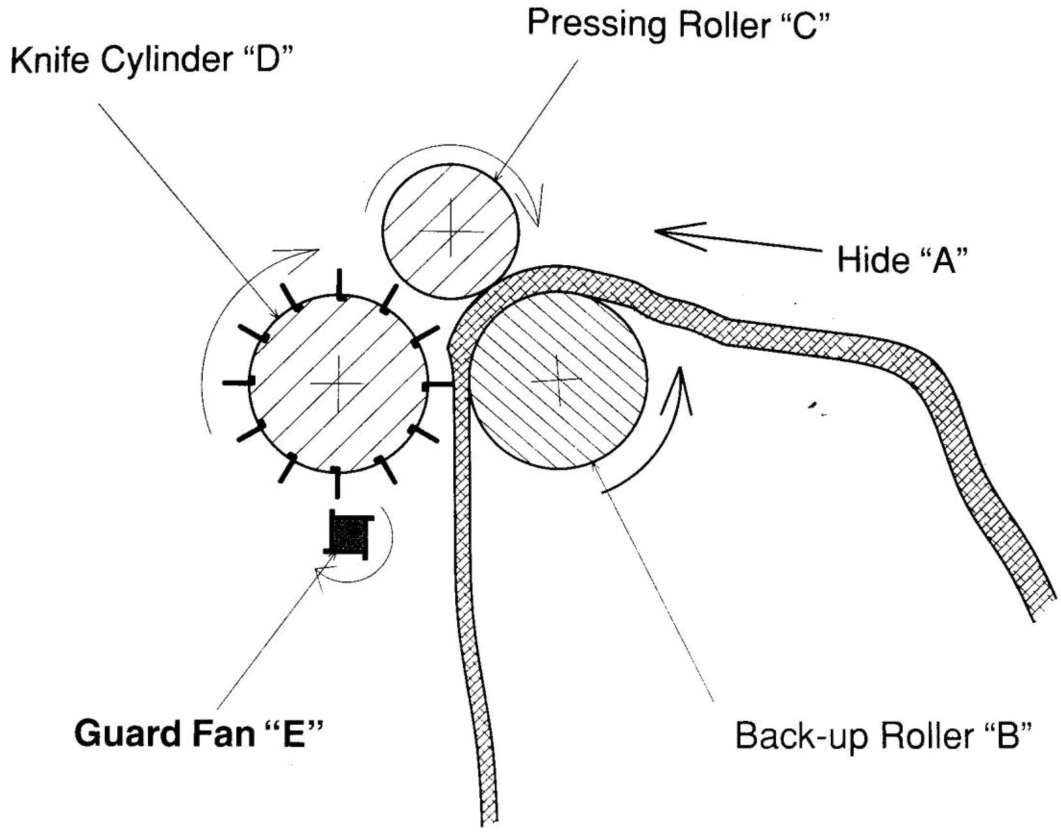
Garmen**t***: 0.6-0.9mm*
Upper-a) skin*: 0.9-1.1mm*
  b) Hide*: 1.2-2.2mm*
Lining-a) skin*: 0.3-1.0mm*
  b) Hide*: 0.9-1.2mm*
Dress Glove-a) ladies*: 0.3-0.45mm*
  b) Men*: 0.55-0.65mm*
Upholstery*: 1.2-1.4mm*

After the shaving operation to the required thickness, the next process is shaking off and if requires trimming so as to avoid the shave dusts, as other wise, which will affect the weight and the smoothness of the grain while vacuum drying.

The shaved hides/skins are then weighed and this weight shall be the base for chemical offer during the subsequent chemical/drum processes. But in some cases area and moisture content of the skins can be the base for chemical addition.

N.B: *Make sure that before starting work the blade is covered by the safety guard.*

Diagram for Shaving Machine



Q: **How do you shave/feed specially skins which may have easily damageable or horny backbones while shaving?**

1.3.5) process control:

Here again inspecting of related parameters or possible process variables is a key to achieve quality products. Controlling of the process of Shaving is just to avoid the possible quality defects and to achieve the required productivity. Thus the main quality aspects to be controlled in this process include:

- ✓ *Moisture and crease control before starting work/both issues can be the cause of tearing or chattering of skins/*
- ✓ *Thickness control/this is the main objective of this operation as salable leather must be of uniform thickness through out the area and the given customer order/*
- ✓ *Machine adjustment/m\c setting needs control/*
- ✓ *Aesthetic appeal of the shaved leather should be inspected /loosely attached flesh and fibers should be removed/.*
- ✓ *Continual grinding from end to end/to avoid chattering/*

***N.B**: Thickness measuring can be done manually using graduated and calibrated thickness measuring gauge or using electronics/computerized/thickness measuring instrument, eg, GERR. The latter is especially used for dried leather.*

II. ***CHEMICAL /DRUM/PROCESSES:***

Introduction

In this sub section we will raise some basic chemistry concepts such as charges, ions, anions, cations, bonds, chemical reactions, hydrolysis, neutralizations etc. that help us to the whole idea of the course. Thus, let's touch these ideas in some detail as bridge cases.

Type of bonds:

1) **Covalent*:***

Two types;

Normal covalent bond*: occurring by electron sharing from both bonding atoms.eg.in CO_2, disulphide linkage,--S—S--, ester linkage,--CO—O--, peptide bridge,--CO—NH—etc.*

Coordinate/dative/or complex bond*: occurring by unshared electrons or it is one sided donation and acceptance.eg, inNH_4^+, complex formation using between some transition metals and ligands etc.*

2) **Ionic bond***: Occurred by complete electron transfer from one atom to another. E.g. NaCl is formed by complete electron transfer from Na/highly electro positive atom/to Cl/highly electro negative or electron affinitive atom/.The so called* ***'salt bridge bond'*** *is an ionic linkage between oppositely charged side chains or groups e.g. sulphonic acid group with amine group of the protein collagen (RSO_3H^-----$H3N^+R$. (This is due to electrostatic or opposite charge attraction).*

3) **Hydrogen bond***: Hydrogen atom, higher electropositive atom, can be covalently bonded with the highly electronegative atoms such as F, O and N. The resulting bond is relatively highly polar. This bond type is called hydrogen bond. This type of bond is common in compounds having alcohol/hydroxyl groups/, carboxyl groups, amine groups in protein molecule etc.*

4) **Vanderwaals force***: Molecular attraction for (either intra or inter molecular attraction).It occurs due to:*

- *The difference in dipole moment (electrostatic force)*
- *The induced dipole, i.e, due to the polarization of one molecule by the dipole of the surrounding molecules or geometric structure.*
- *London dispersion force—which is due to an instantaneous unsymmetrical distribution of electrons around the atomic nucleus even*

in the very inert atoms like helium.Hence, temporary dipole can be created.

***N.B**: Vanderwaals force is the combination of the above three effects.*

Type of chemical reactions:

1) ***Neutralization Reaction**: Acid –base reaction where the acidic effect is neutralized or avoided by the treatment of base or vice Vera. (One of the definitions of acid is that it is a chemical group that can donate or generate proton/H^+/at least indirectly/during hydrolysis/ to other chemical group. Similarly, a base is a chemical that is capable of donating hydroxyl/OH^-/group or can accept proton. The level or concentration of proton or hydroxyl group is expressed as P^H.) There are different types of neutralization reactions.*

***Hydrolysis reaction**: The reaction of a salt of acidic or basic ion with water molecules either to produce acidic or basic group (H_3O^+ or OH^-) or media. Thus, let's consider the following five cases:*

A. *The activity of* **the salt of strong acid and strong base** *in water: eg, NaCl, i.e., $NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O$*

=>Practically the hydrated Na^+ ion has little tendency to donate a proton (H^+) to water, i.e, Na atom is more stable to stay in the form of Na^+ ion than NaOH (i.e, by releasing H^+ and by trapping OH^-if it were possible) .Besides, Cl^- ion has also little tendency to receive a proton from water (i.e, Cl^- more stable than HCl in water).

=>that is why we always get a complete dissociation of NaOH or HCl in water into Na^+, Cl^- , and H_2O

=>The solution of NaCl remains neutral.

***i. Related to this, describe how NaCl salts prevent acid swelling**.*

B. *The* **salt of strong acid and weak bas***e. e.g., NH_4Cl*

$$NH_4Cl + H_2O \rightarrow NH_4^+ + Cl^- + H_2O \rightarrow NH_3 + H_3O^+ + Cl^-$$

- ⇨ *NH_4^+ is fairly strong acid to donate or release proton in aqueous media. That is, NH_3 is more stable than NH_4^+in water. Whereas $Cl^-$is very weak base as mentioned above (don't want to receive H^+)*
- ⇨ *The resulting solution will have excess H^+ produced.*
- ⇨ *The total media becomes acidic.*

***ii. Do you remember how you delime your pelt by NH_4Cl salt**?*

C. *The* **salt of weak acid and strong** *base, e.g, NaHCO3:*

$$NaHCO_3 + H_2O \rightarrow Na^+ + HCO_3^- + H_2O \rightarrow Na^+ + H_2CO_3 + OH^-$$

- *As mentioned above Na^+ doesn't want to be the cause for release of H^+ as it doesn't want to form NaOH*
- *But $HCO_3^-$is relatively a strong base as it loves to accept H^+ (i.e, the dissociation power of carbonic acid is lower or it wants to exist in neutral H_2CO_3 form.*

- *Due to the free existence of OH^-ion, the resultant solution becomes alkaline/basic/in nature.*

iii. Do you remember how you basify the chrome tanned media/leather and liquor*/?*

D. The ***salt of weak acid or weak*** *base, e.g., NH_4HCO_3:*

The following conditions can occur;

- *If $K_{acid}=K_{base}$, then the solution becomes neutral.*
- *If $K_{acid} > K_{base}$, then the solution becomes slightly acidic.*
- *If $K_{acid} < K_{base}$, then the solution becomes slightly basic, where K is dissociation constant of acid or base.*

iv. How could NH_4HCO_3 be used for neutralization of chrome tanned leather*?*

E. Hydrolysis by heavy metals: *Hydrolysis can also occur between water and metal salts or metal ions which form precipitation in water.E.g:*

I) $Cr^{3+}+3H_2O \rightarrow Cr(OH)_3\downarrow+3H^+$

II)$Al^{3+}+3H_2O \rightarrow Al(OH)_3\downarrow+3H^+$.=>The presence of these ions can increase the acidity of a given media in which they exist,e.g, in wet blue or wet white processing and Al is more hydrolysable than Cr.

v. Explain the interference of these ions, especially if they exist freely, in retanning, dyeing and fatliquoring media before neutralization*?*

2) Complex reaction or coordinate compound formation*:*

This type of bonding or reaction occurs as a result of the availability of empty bonding orbitals especially on the" d" or "f" orbital of some metals like chromium, aluminum, cobalt, zirconium etc; and the capacity of some nonmetal groups/ligands/ to donate electrons. This type of reaction is also called secondary valence reaction.

=>In geometrical position, the central metal ion accepts electron pairs from the available ligands into the available empty metal orbitals.

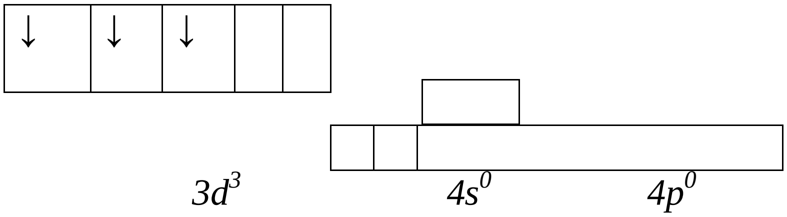
E.g.: the ground state electron configuration of chromium atom is $^{24}Cr:1s^22s^22p^63s^23p^63d^54s^1$.

=>The outer electron configuration is $3d^54s^1$

As we know the primary valence number of chromium is 3. Thus these 3 electrons can be consumed for ***normal ionic bond*** *or ionic reaction by complete electron transfer .Hence, the chemical structure of chromium that participates for coordinate reaction is Cr^{3+}.*

=>The outer electron configuration of Cr^{3+} ready for coordinate reaction shall be$3d^34s^0$.

=>orbital representation of Cr^{3+}:



=>The two 3d orbitals, the one 4s orbital and the three 4p orbitals are available unoccupied to form six hybrid orbitals (d^2sp^3) *(i.e., orbitals blended together having equivalent energy level). But the rest three 3d orbitals containing three unpaired electrons couldn't have the same energy level as the blended orbitals.*

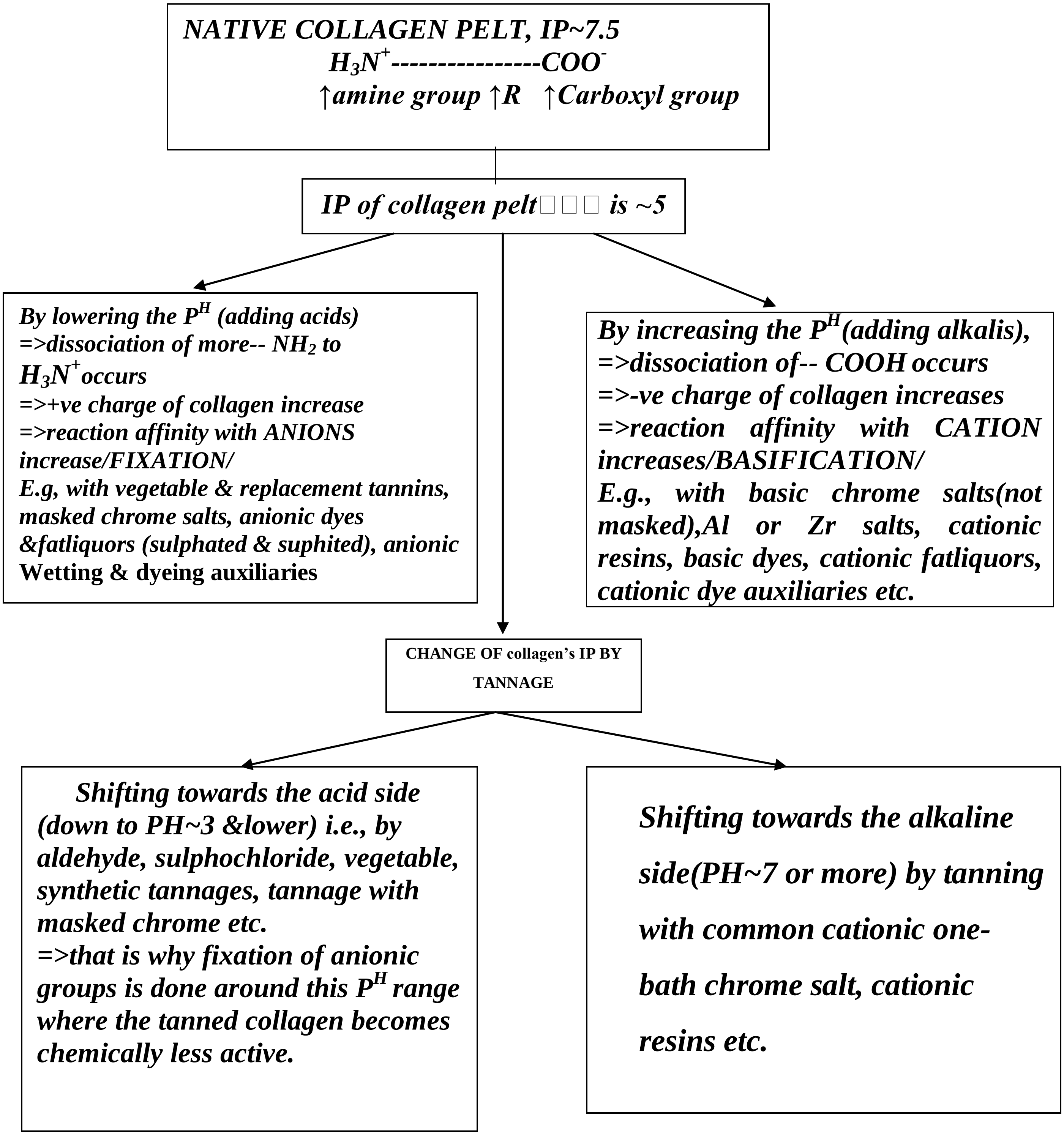
=>But the six blended orbitals can accept six pairs of electrons from the ligands, e.g, OH^-, H_2O, *sulphate* ($SO4^{--}$), *formate* ($HCOO^{--}$),*cyanide*(CN^{--}) *etc. approaching and forms coordinating (one sided electron donation)or complex compound as:*

=> $[Cr\ (CN)_6]Cl_3$.

vi. When we say that chrome, aluminum or zirconium tanning is occurred, what is the specific ligand to donate these electrons*?*

3) *Other types of reactions include addition, displacemet, precipitation, redox etc.reactions.*

RELATIONS OF CHARGES AND RETANNAGE



NATIVE COLLAGEN PELT, IP~7.5

H_3N^+----------------COO^-

↑amine group ↑R ↑Carboxyl group

IP of collagen pelt□□□ is ~5

By lowering the P^H (adding acids)
=>dissociation of more-- NH_2 to H_3N^+ occurs
=>+ve charge of collagen increase
=>reaction affinity with ANIONS increase/FIXATION/
E.g, with vegetable & replacement tannins, masked chrome salts, anionic dyes &fatliquors (sulphated & suphited), anionic **Wetting & dyeing auxiliaries**

By increasing the P^H(adding alkalis),
=>dissociation of-- COOH occurs
=>-ve charge of collagen increases
=>reaction affinity with CATION increases/BASIFICATION/
E.g., with basic chrome salts(not masked),Al or Zr salts, cationic resins, basic dyes, cationic fatliquors, cationic dye auxiliaries etc.

CHANGE OF collagen's IP BY TANNAGE

Shifting towards the acid side (down to PH~3 &lower) i.e., by aldehyde, sulphochloride, vegetable, synthetic tannages, tannage with masked chrome etc.
=>that is why fixation of anionic groups is done around this P^H range where the tanned collagen becomes chemically less active.

Shifting towards the alkaline side(PH~7 or more) by tanning with common cationic one-bath chrome salt, cationic resins etc.

Q: If tannage of collagens by cationic tanning agents, like with basic chrome, is possible at higher P^H why so pickling is important?

=>By tannage, the IP of normal pelt collagen (IP~5) can be CHANGED either to 3 or 7 according to the type of tanning agents used and their charges.

Iso-electric Point is the PH with the net charge zero of collagen, i.e.; the number of both charges (amines and carboxyl groups) and dissociative groups are equal.

=>IP is the most important magnitude to describe binding and modification processes.

=> With the binding of any kinds of chemical compounds (tanning or retanning agents), always the magnitude of charges at the fiber /collagen/will be changed.

E.g.1) If collagen made react with a polyacrylate or any anionic agent, then the amine groups/ positive charges of the collagen/can be consumed/reduced/

=>The collagen will be loaded with more anionic carboxylic groups which lead to an excess of anionic charges.

=>The IP of the whole system is shifted to the side where the charge exchange can be achieved by diminishing of the negative charges by lowering the dissociation, i.e., in the more acidic region of the PH scale. Change of IP (decrease or increase) is not dependent on bond type, but of charge type.

=>Addition of cations lifts IP, while addition of anions drops IP.

=>By washing of retanned chrome leather (part of neutralization process) anionic compounds are removed.

=>this leads to increment of cationic charges

=>IP shall increase.

E.g. 2) Acid dyes are applied below IP of the leather in the normal acidic P^H range (<7) .For basic chromed leather, the IP~7 and for anionic retanned leather IP~4.

=>For pure chrome leather (with no any other retannage &which doesn't really exist any more), the acidification doesn't need (or not strong, if any)

N.B: The affinity based on the charge interactions is usually very strong for low molecular weight chemicals, e.g., dyes. But these dyes stripped of easily from leather with alkaline floats.

Besides, as the molecular size increases forces other than charge interactions come into play.

2. NEUTRALIZING AGENTS AND NEUTRALIZATION

2.1) Wetting back, Washing and Pre-Neutralization Retanning Processes:

2.1.1) Definitions:

Wetting back is the process of rehydration or remoisturizing (to about 67%) of a relatively dewatered wet blues after mechanical operations or possible light /heat / exposure.

Washing, here, refers to the removal of surface contaminants with plain water or together with nonionic amphoteric dispersing agents, or in case of pastel /white shades together with weak acids such as acetic or oxalic acids which can remove unbound chromes, chrome stains from long stored wet blues, and assist grease dispersing from greasy skins like sheep and pig origins.

Pre-Neutralization Retanning processes, in this context, refer to activities such as rechroming with chrome and other mineral tanning agents, aldehyde tanning, pre-dyeing and pre-fatliquoring and treatment of leather with cationic resins etc. before the main alkaline neutralization, but of course after washing, according to the type of the ultimate leather we plan to produce and the chemical nature (ionic nature) of the retanning materials. ***Retanning in this context refers to all chemical processes accomplished in post tanning operations like rechroming, dyeing fatliquoring etc.***

2.1.2) Purposes:

Wetting back is to:

- ❖ get uniform /leveled dyeing, good penetration of retanning and fatliquoring agents

Washing is to:

- ❖ . Remove collagen bound and some free acids found or reside on the surface of the leather.
- ❖ Remove the unfixed chrome and the acid groups attached to it.
- ❖ optimize the economy of alkaline salts consumption and time
- ❖ Reduce the acid and unbound chrome that adversely affects the chemical processes carried out before neutralization, especially if we use anionic dyes and fatliquors at this stage.

Pre-Neutralization Retanning process is to:

- ❖ Get fine and tight grain as well as level and deeper dyeing by using mineral syntan complexes based on Cr, Al or Zr (mainly called rechroming). Rechroming is also used for leveling of wet blues come from different batches or sources.
- ❖ Get desired soft handle and perspiration resistant leather (aldehyde tanning).
- ❖ Render the leather a lubricating effect so that it will not be affected in the subsequent mechanical drumming (pre-fatliquoring).
- ❖ To get more intense and through dyed leather

2.1.3) Process Variables:

Level of **wetting back** depends on the initial moisture content of the leather, its thickness, the mechanical drumming, load weight, skin quality/fiber density/or firmness, float length, type and amount of wetting auxiliaries used ,temperature and time.

Thus, to develop a consistent recipe, one should consider the above listed variables. Particularly the initial moisture content of the shaved leather should be considered seriously as it affects not only wetting back but also neutralizing, retanning, dyeing and fatliquoring process as the weight will be the base for these operations. That is, if we fail to use consistent moisture content, we will also miss the consistency of color shade, leather fullness or softness from batch to batch. Of course, some tanners use adjusted 70%moisture of leather as a reference calculated based on actual moisture content and actual leather weight as an input.

$$\left(\frac{100-actual\ MC}{100-70}\right) * Actual\,Wt.$$

MC and Wt represent moisture content and weight of shaved leather respectively.

Then, after wetting back, **washing** can be done (mostly twice) until the surface becomes clean and grease free .Besides, P^H , temperature, weight and float level and time are important variables to be considered for processing of the required pre-neutralization retanning sub operations or pre-neutralization retanning processes .

2.1.4) Practice:

Usually, wetting back is done by using 250-300% water @~40ºc in the presence of nonionic or amphoteric dispersing agents (~0.3-0.5% per shaved weight) and run for about one hour or even for overnight according to the level of initial moisture content and type of leather to be processed. Of course, if wetting back is to be done instantly, (say in 40-60 minutes) a mechanical action of 8-16RPM can be used starting from the slower speed. As it is mentioned above, percentage is based on direct shaved weight or adjusted to 70% moisture content. After this, draining and washing will follow. Washing can be done by 300% plain water only @~40ºc for about 10-15 minutes using 16 RPM about twice for full shade leathers. But for white or pastel shades washing should be done by the help of some organic acids (0.2-0.3% acetic or oxalic) which can remove chrome and other stains and also improve the grain character. Now the P^H should be between 3.0-3.2 as it serves as the starting media for pre –neutralization retanning sub operations, before main alkaline neutralization. In addition, if the skins to be processed are greasy nature (like pig or sheepskins),together with acid wash, 0.2-0.5% nonionic dispersant or fatliquor having dispersing and filling effects can be used. If the latter is used the percentage can be increased up to 3% and should actually be electrolyte stable.

Thus, leathers for white or pastel colors greatly benefit from a light acid wash if they are to be subsequently retanned with light fast syntans, dyes and fatliquors.

As we will see in detail, the process sequence of chemical offering for post tanning operations, after wetting back, for medium and dark colors of ordinary firmer leather, especially for corrected grain is in the order of neutralization, washing, retanning (syntans and vegetable), dyeing, fatliquoring and fixation.

But for the leather of high quality, light colors (white/ pastel) and softie types, which needs non astringent retannage with say, mineral syntan complex salts, the sequence can be different. Thus, the acid washed leather can be retanned /rechromed with 3-5% mineral salts for ~60-90 minutes, basified gradually by about 0.5% NaCOOH and/or synthetic neutralizing agent followed by addition of 1-1.5% $NaHCO_3$ (diluted 1:10@~33ºC)to achieve a P^H of ~5.0-5.5.Then washing will follow with warm water (40-45ºC) at least twice before the main retanning, dyeing and fatliquoring sub operations. Ofcourse, before addition of dye, light retanning agents (replacement syntans, aldehydes, resins etc) which will assist in the production of mellow handles, full and level dyeing can be offered. If the retanning materials particularly the resins are cationic, they should be offered before neutralization.

E.g1: Classical box calf/bouncing leather/ and side upper leather, especially black and leather of darker color after wetting back and plain water washing , retan by formate masked chrome @P^H ~3.3-3.5 (i.e., no acid wash)for about one hour, raise the P^H to ~4.5 by $NaHCO_3$,dye with the 2/3 portion of the total offer then, retan by resin /replacement tannins/, fatliquor and acidify to a PH of ~3.5-3.6 and finally top dye (the rest 1/3 portion) and top fatliquor/cationic / followed by cationic fixing agent

E.g2: In the production of chrome nappa type or softy upper, aldehyde (glutaraldehyde) and acrylic polymers are much favored as retanning agents. Here, the shaved and acid washed leathers are first retanned with 1-2%glutaraldehyde (diluted 1:10@30ºC) and ~1% acid stable or /and dispersing electrolyte stable fatliquor (emulsified 1:10@~50ºC), process in 100-150% float length for ~30-40ºC followed by retanning with mineral syntans (2-5%) that consolidates fiber strength, reduce grain looseness and produces short and tight nap required, especially for suede. After one hour, raise the P^H of the bath to ~4.3-4.7 with NaCOOH or synthetic neutralizing agents followed by 2-4% acrylic resins (if necessary) for ~30 minutes. Subsequently, the P^H of the float is raised to the neutralization level (5.0-6.3) using NaCOOH, light fast retanning /neutralizing syntan and some $NaHCO_3$. Finally the leather is washed at least twice or more by water of 250-300% @45-50ºC and then dyed and fatliquored in the usual manner.

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2.1.5) Process Control:

- After wetting back check the pliability of the wet skin and moisture level or water uptake
- After washing check the cleanness of the skin surface, wash liquor and P^H of the liquor especially after acid wash (3.0-3.2)
- Check that the skin surface is grease free
- Check that the skin surface is stain free

- Check that time of wetting back and washing temperature and mechanical action are optimum.
- In pre-neutralization chemical sub operations, control the compatibility of dyes, fatliquors and syntans with the media or skin's ionic nature.
- Monitor and control the emulsion and exhaustion of fatliquors, the levelness and penetration of dyes and syntans, the temperature, float length and time.

2.2) CHEMICAL/ALKALINE/ NEUTRALIZATION

2.2.1) **Definition**:

Chemical neutralization is relatively a more thorough deacidification of mineral tanned leather with mild neutralizing salts than the simple surface flooding off of the free acids, unbound basic chromes and acids attached with them. If we need our ultimate leather to be softer, level dyed, well lubricated, inner fibers are full and round, relatively complete neutralization is a must.

2.2.2) **Purposes:**

- To remove collagen bound and some free acids which still reside on the skin surface (even after washing) and which are found in the inner fibers.
- To remove unfixed chrome and the acid groups associated with it.
- To reduce the acids and unbound chromes that adversely affect the uniformity of the main processes of dyeing, retanning and fatliquoring etc. as we usually use anionic nature of such chemicals.
- To improve the aesthetic value of the ultimate leather, i.e, the physical properties of leather such as grain character, surface feel, fullness, strength and dye take up can be adversely affected if the acids are still there.

=>the excessive positive charge must be removed for smooth reaction with any anionic substances to come.
=>To make the users and the leather itself safe from acid damage or rot.
=>To improve the quality and character of the final leather.

These mild neutralizing salts not only neutralize the free acids and basic chromes from the leather but also replace or substitute the aquo and sulphato groups /ligands/ in the collagen-chromium complexes. That is, there will also be reaction between the anions of the neutralizing agents and the chromium in the leather by the introduction of the fairly complex organic groups into a chromium compound in displacement or substitution of the acidity (sulphuric) in the leather.

=>This improves the physical properties and processing behaviors of the leather (feel, grain character, level dyeing, improved take up of fats and tannins). These mild alkaline salts give anions that able to enter into the complex of chrome tanning compounds displaying masking effects. The anions such as acetates, formates, lactates, phthalates, adipates, diglycolates etc. have very mild alkalinity on the grain. In addition, they can modify (reduce) the affinity of the leather towards the anions of the dyes, synthetic or natural tannins, anionic emulsifiers etc. This results in deep penetration and even or uniform distribution of these chemicals.

Table 1: Selected Commercial Mild Neutralizing Salts and Their Properties

Product	**P^H(diluted 1:10)**	**Properties**	**Remark**
Soda ash(Na_2CO_3)	10.8-11.2	Danger of excessive neutralization, because of superficial action and have detanning effect	Seldom used, except for some type of suede
Sodium bicarbonate($NaHCO_3$)	7.8-8.1	Good penetrative power. Danger of excessive neutralization only when large amounts are used. Don't dissolve above 35ºC, because otherwise soda formation.	Don't use more than 2% based on shaved weight
Borax($Na_2B_4O_7.10H_2O$)	9.0-9.2	Danger of excessive neutralization is similar to use of soda. Acts somewhat milder at the beginning but on the prolonged treatment the alkaline effect can be higher than that of soda.	Don't use for overnight neutralization
Ammonium bicarbonate(NH_4HCO_3)	7.5-7.8	Particularly penetrative neutralizing agent. Danger of excessive neutralization can't be excluded completely.	Very suitable for leather of denser texture and uniform &deep neutralization across each thickness,as glove
Sodium sulphite(Na_2SO_3)	7.8-8.0	Mild neutralizing agent with uniform penetrative power	Don't use for pastel shades as it has greenish effects
Sodium thiosulphate($Na_2S_2O_3$)	6.5-7.0	Has poor neutralizing power. Thus used in large amounts. Besides, it can lighten leather colors by deposition of	Mainly used for white and light colors, as golf glove

		sulphur(bleaching out)	
Sodium acetate(CH_3COONa)	8.0-8.2	Mild neutralizing agent with bleaching effect towards blue	Very suitable for white/pastel shade /Al tanned leather/
Sodium formate(HCOONa)	8.5-8.7	Rapidly penetrative and mild neutralizing agent. No excessive neutralization even if large amounts are used	Mostly used in conjunction with $NaHCO_3$
Calcium formate($(HCOO)_2Ca$)	6.5-7.5	Mild neutralizing agent. No excessive neutralization. But there exists interference by formation of $CaSO_4$	May produce $CaSO_4$ stain
Tanigan PAK-S(Bayer synthetic product)	6.5-7.0	Strong neutralizing and buffering synthetic salt. It has also retanning effect	Use in conjunction with HCOONa &$NaHCO_3$
Neutrigan(BASF synthetic product)	7.5-8.0	Mild neutralizing agent with masking and buffering effect. No excessive neutralization problem.	Use in conjunction with HCOONa &$NaHCO_3$

N.B: All neutralizing agents mentioned above and other plain alkalis like caustic soda can remove collagen bound acids fairly quickly, raise the P^H of the leather and reduce the positive charge of the chrome tanned leather. But it is always important to be selective than using any alkalis at random, especially the strong ones. Why?

As described above, during neutralization, there may be exchange of ligands. What do you think then about the status of basicity?

2.2.3) Process Variables:

a. Alkalinity of Neutralizing Salts:

Higher acidity of tanned collagen (whether it be free, bound with collagen or the basic chrome itself) impedes the subsequent processes such as deep penetration, even dyeing, emulsion of fats and selective deposition of organic retanning materials, if especially anionic species, in and on the leather. These problems can occur if the P^H of the media is usually less than 4.3.

On the contrary, if we use high alkaline media or if we neutralize with plain alkalis like soda ash or caustic soda that results in sudden P^H rise, detanning effect can result. That is, the collagen—chrome complex is sensitive to rush P^H change (especially to P^H higher than 5.0—5.2) and to a higher P^H even if gradual P^H change in the presence of buffering agents.

Thus, if we treat chrome tanned leather with some plain alkali, as the P^H of the leather rises, the free acids and the radicals outside the chrome complex are neutralized. In parallel, the acido groups ($SO4^{--}$or $HCOO^{-}$) inside the chrome complex are started to be **replaced by the hydroxo** (OH^{-}) groups. **Can you explain the electrochemical series of difference ligands**?

But don't forget that the tanning effect of the chrome salt depends up on the optimum proportion of the hydroxo groups in relation to the acido groups in chrome compounds, which is known as basicity figure. But if the P^{H} rises still higher (because we have stronger base), the bond between collagen—chromium acid complex is affected due to the rapture of the bond which results in detanning or chrome precipitation in the form of $Cr(OH)_3$, due to the replacement reaction.

Can chrome salts having basicity greater than 58% have good tanning effect?

Thus,

Over neutralization due to high concentration of OH^{-}(and hence higher P^{H}) can result in detanning in the neutralization bath.

Due to higher replacement of acid radicals like acetate, formate, or sulphate by hydroxyl groups, the leather character can change (becomes hard, loose or empty, coarse and brittle or weak grain).

E.G: Neutralization of wet blue especially by soda or borax particularly for soft nappa type can over neutralize the outer layer leaving the inner zone least affected which in turn result in zonal difference in retanning, dyeing and fatliquoring, and hence affects the fullness, softness, levelness etc. of the final leather.

b) Temperature:

If the temperature of the neutralizing bath is above some limits, say above 35ºc,the neutralizing salts shall be over-activated (E.g. $NaHCO_3$ can be changed into Na_2CO_3)and hence results in superficial and over-neutralization .Cold neutralization doesn't help the process effectually as the solubility of the neutralizing salt, especially the organic base, is reduced. Practically, the temperature range of 33--40ºc is important and especially at the higher extreme range, hydrolysis of chrome salt is increased and hence accelerating diffusion of acids formed by the hydrolysis. Besides, the neutralizing salts(formate, acetate, phthalate, glycolate etc.) which involve no precipitation with chrome solution penetrate into the chrome-leather complex faster (within 30 minutes) and attain equilibrium at a P^{H} of about 4.5—5.0. But as mentioned above, this elevated temperature is only suitable for aliphatic and aromatic complexing or neutralizing agents, not for borax, soda ash or ammonium bicarbonates which should be <35ºas otherwise causes chrome precipitation or over neutralization.

c) Chemicals:

Generally, simple acid radicals or plain alkalis with less buffering and masking capacity tend to break down the chrome complexes. On the contrary, too much masking or chrome complexing and hence excessive stability can pose/create other difficulties such a reduction in affinity for dyes, vegetable and synthetic retanning agents , difficulties in exhaustion of fatliquors and ultimately production of loose and spongy leather with higher water absorption which in turn resulting in difficulty of finishing .

Hence, it is recommended to use a combination of radicals that give stable chrome complex, mild alkalinity and optimum masking and buffering:

E.G:

- Organic neutralizing salt/ formate +$NaHCO_3$
- Organic neutralizing salt/formate +NH_4CO_3
- Organic neutralizing salt/formate +synthetic neutralizing agent +$NaHCO_3$ etc.

Note also that those anions of monocarboxylic acids (acetate, formate etc.) can form stable complexes and have good masking effect; but relatively with less filling effect.

However, anions of polycarboxylic acids (phthalates, diglycolates) have both filling and masking effects. Besides, neutralized synthetic tanning agents , either naphthalene base or based on highly aggregated aromatic sulpho-acid condensation products are used for neutralizing, buffering and filling agents as they have tanning effects as well as grain tightening and dye leveling power.
N.B: These neutralized syntans or salts act as neutralizing agents as the possible CARRIED OVER strong acid (H_2SO_4) from chrome leather is consumed by the syntans to release the weaker tanning sulphonic acid with the by-product of Na_2SO_4; Na^+ comes from the neutralized syntan salt, H^+ goes to the amine group of collagen to form__NH_3^+ and then the anion group sulphones will react to __NH_3^+ of the collagen, and as result, the overall acidity of the leather is reduced or consumed, hence neutralization.

How do buffering work?

d) Float Length and Water Type:

It is extremely important to see that during the course of neutralization no objectionable precipitation of chrome salts may take place in order to prevent the coarsening of the grain, especially on the looser parts of the leather. (**Too long** float, hard water, alkalis etc. which form precipitates should be avoided).

Note that for usual drum neutralization, very long float must be avoided in order to prevent the possible chrome precipitation and the float is to be confined within 150—170%, calculated on shaved weight. **How does chrome precipitation occur as a result of long float**? Hint: Deal the diffusion rate of OH^- to leather and amount of hydrolysis expected while float level goes up.
What will happen to the process if the float is too short?

2.2.4 Practice

Let's see two basic neutralizing practices or procedures for chrome tanned leather based on the intensity of neutralization we need.

a) **For Box Calf and Side Leather**: Box side or calf refers to pure chrome tanned bouncing and firm leather with minimum amount of fatliquoring; bouncing or elastic effect is mainly due to high chrome content. For neutralization of box and side upper type of firm leather, the P^H range of 4.3—5.0 can be enough. Especially the product of side upper type is usually dark shades (black or brown) and corrected grain in type. Thus, after wetting back and washing (sometimes use acid wash if you need to rechrome), use 0.5—1.0% neutralizing salts of organic base at float length of 150—170% @~35ºc and run for ~10 minutes followed by offering about 0.5% of synthetic neutralizing and retanning agents and run for an other 10 minutes with about 16 RPM. Then, based on the resulted P^H level, use 0.7—1.4% $NaHCO_3$ (dilute 1:10@~33ºc) and run for about 40—50 minutes based on the thickness and fiber texture of leather being processed. After checking the final neutralization level, wash thoroughly (twice or more) to avoid the salts created during neutralization, as otherwise can interfere in the subsequent processes. Then you can carry on the next process.

b) **For Suede, Softie Nappa, Pastel Shades etc.:** Here neutralization is expected to be relatively thorough, uniform and complete (but still not refer to the true neutralization to the P^H =7 nor to the P^H=6.5—7.5, which is the IP of the cationic chrome tanned leather).

Thus, here, after wetting back, washing and pre-neutralization retanning processes as desired or required, the final neutralization P^H for the subsequent process is recommended to be risen to 5.0—6.5. It is so because, here, dyeing is expected to be fully penetrated, leather be soft by thorough and uniform distribution of fatliquors, be full and round by uniform and selective distribution of retanning materials. But care must be taken not to raise the P^H too high as otherwise coarsening of the leather grain and looseness of the final leather can face/Due to detanning and poor fixation of retanning, dyeing and fatliquoring agents as a result of over masking etc./

Thus, as usual use about 150—170% float length @~ 33__38ºc with the chemical offer of 1.0—2.0% organic base neutralizing salt (usually NaCOOH) followed by 10 minute run with RPM of 16, 1.0—1.5% synthetic neutralizing agent of another offer followed by 10 minute run and finalize by the last offer of 1.0—1.5% of $NaHCO_3$ or NH_4HCO_3 followed by 45—90 minute run depending on the type of product we desire and the fiber texture and thickness of the input. Then, check the neutralization level, wash thoroughly (at least three times) and proceed the upcoming process.

2.2.5 Process Control

- ✓ Check always the temperature of the main float of neutralization before and after processing, and the temperature of the water used to chemical diluting with alcoholic or mercuric thermometer.
- ✓ Check always the P^H of the neutralizing bath with P^H-meter or P^H-paper. But as the latter is less effective and less legible in the neutralization media containing organic dispersing or wetting agents and fatliquors, it is recommended to use the former type for such media.
- ✓ Control the float amount both visually and with the predetermined or pre-graduated volume measuring vats before commencing neutralization process.
- ✓ After processing, cut off a small piece of leather from a section of denser texture (usually from neck area).Then let a 0.1% indicator solution of bromo cresol green /BCG/ (dissolved in 50% alcohol), drip on to the cross section.

  Interpretation: If the color of the cut shows **pure blue**, the P^H of the cross-section is expected to be about **5.5** and above and this range of neutralization is suitable for products such as softie nappa garments, gloves, suede, upholstery and some pastel shades.

  - If the color of the cut shows **bluish –green**, the P^H is expected to be about **5.0** with intermediate range of neutralization which is especially suitable for box side upper type.
  - If the color of the cut indicates **pure green or yellowish green**, the PH is about **4.0** and neutralization is not good, and needs corrective measure.

Chemical preparation: Always prior to adding to a drum, weigh it properly, dilute it 1:10@~33ºc, especially $NaHCO_3$ and NH_4HCO_3 and add slowly (to the drum) through the axle pipe (not through door) while the drum is running as otherwise, uniformity of dyeing can be influenced negatively. Still, salts of organic and synthetic neutralizing agents can be offered in powder form.

2.2.6 **Observable Defects on the Leather Due to Neutralization Errors**:

- **Inadequate Deacidification** : Results in the middle zone of the cross section remain unneutralized .Thus, clearly the following problems are observed in the process or on the leather:
  - ✓ Astringent retanning agents diffuse only with difficulty into this middle zone (You can have a look at a white streak on the leather, especially in dyeing).
  - ✓ Fat emulsions crack in this zone and cause smudging/staining and fat stain
  - ✓ In the leather the free acid migrates into the outer zone, causing corrosion at metal parts of final products. Fatty spew may also occur to a greater extent.
- **Over Neutralization and over masking**: Results in detanning of the grain zone and thus result in loose grain, strawy, brittle grain or in unfavorable cases even crackiness of the grain. Furthermore, it may lead to uneven, pale and thin dyeing.

How do you recommend about the amount of ammonia to be offered while dyeing of some type of products?

3.0 RETANNING AGENTS AND RETANNING PROCESS

3.1 Definition: *Any second tannage following the first tannage is considered as retannage or retanning regardless of the fact that the first tannage is only a slight pretannage. Of course, this is generally done to influence (usually positively) the physical and chemical properties or behaviors of the ultimate leather or to get any desired character of the final leather.*

***E.g.1**: Strong filling influence thickness. But if the filling level is beyond the required level for the different products, then the fiber density in a given cross section is reduced; this in turn reduces the tensile and tear strength, the elasticity of the leather. This is usually undesired character for very soft leather like garment and dress glove.*

***2.** Feel (softness or resilience) can be changed*

***3**. Heat resistance (especially for shoe upper during molding) can be changed.*

***4**. Alkaline resistance, perspiration, light reaction etc. can be influenced.*

=>Retannage is a subsequent treatment with the various tanning agents, following the main tanning process, in order to give the leather special, optimum properties for use.

=>Retannage is a stage where combination tannage is practiced. For instance primary chrome tanned leather can be further tanned /retanned/ with additional mineral tanning agents, vegetable tannins, replacement tannins, white tannins, aldehyde tannins and/or resin tannins.

Through this, any desired character of leather can be achieved.

=>It is a way of tuning of the universal or versatile semi-processed products/wet blues, wet white or wet browns/ into a specifically desired product.

3.2 purposes

Most of the purposes of retannage are derived from the customers' or producers' interest for the characters of leather to be imparted. Thus the main purposes are to

- ✓ *Improve the handle and feel of the leather, softer or firmer as desired by the customer or market /chrome syntans, polymer resins, aldehydes /*
- ✓ *Change the color of the chrome tanned leather for white leathers and pastel shades /Al, Zr tannins, aldehydes white or light fast replacement Syntans, especially dihydroxynaphthalene sulphonics).*
- ✓ *Improve the buffing properties for corrected leathers, suede and nubuck (Al/Zr syntans, dispersed resins and vegetable tannins).*
- ✓ *Improve embossability(vegetable tannins, syntans)*
- ✓ *Adjust the dyeing properties (dispersing syntans i.e. naphthalene sulphonic compounds)*

- ✓ *Produce crust leathers with the right properties for fast and level spray dyeing or aniline finish (i.e. to get fine grain by using less astringent synthetic tannins)*
- ✓ *Improve certain specific properties like perspiration resistance, fastness to washing, thermal conductivity, flammability/aldehyde tannins, synthetic tannins/*
- ✓ *Support water resistance / high molecular polymer resins, chrome stearate etc./*

List of Retanning Materials:

1. **Chrome salts**: *Preferably with higher basisity and /or masked for better exhaustion or other mineral tanning agents based on Al, Zr, Ti salts*
2. **Auxiliary Syntans***: Naphthalene sulphonic acid formaldehyde condensation products, with high dispersing but with little tanning power and can reduce the color strength of dye.*
3. **Syntans as Replacement Tannins**: *Phenolic syntans ranging from light tanning power but high dispersing effect to medium tanning power and less dispersing effect, depending on molecular size.*
4. **Syntans as Replacement tannins**: *Based on dihydroxy diphenyl sulphone, white syntans with high tanning power and a strong bleaching and/ or covering effect on chrome leather surface due to its higher molecular size and hence strong surface reaction*
5. **Chrome Containing Syntans**:
   a) *Simple mixture of aromatic compound with chrome salt*
   b) *Chrome complexes with aromatic sulphones*

6. Vegetable Extracts: *Mainly catecohol type like wattle, quebracho chestnut or other extracts including hydrolysable tans like the old sumac with low astringency and good light fastness properties. Quebracho is more preferable to greater fullness with firmness especially if it is used as a semi soluble extracts; and mimosa and softened chestnut for giving fullness without seriously affecting the flexibility.*

7. Glutaraldehyde, Dialdehyde Starch, and Simple Formaldehyde:

8. Resins (Dicyandiamide, Melamine and urea): *As dispersed resins for practically **selective filling agents**, in contrast to vegetable and synthetic replacement tannins, deposited on the parts of the leather that are less dense such as flanks and belly areas.*

9. Polymer Resins: ***The common*** a*crylic and methacrylic resins, the strongest growing group of retanning agents today with a lot of important properties.*

10. Resins Based on Oligomer Polyurethane Dispersions: $H_2N\text{-}CO\text{-}O\text{-}C_2H_5$; *with a lot of important properties, except being expensive*

11. Fillers Based on:

- *Protein compounds dispersed or combined with Syntans or acrylic resins:*
- *based on starch and other organic materials*
- *inorganic materials like kaolin, Na_3PO_4*

12. Special products with filling, lubricating and water proofing properties: ***e.g. high molecular acrylic resins***

Some specific objectives achieved by retanning:

1. Chrome Tanned Wet Blue Leather:

Retanned With:	Improvement Achieved/objectives
Vegetable and /or replacement syntans	*Filling , firmness, non elasticity, handle*
White tanning agents	*Tan or light color, fineness of grain, surface cover, handle*
Chrome tanning agents/rechroming	*Dyeing properties, grain tightness and strength, heat resistance/no color change in exposing to heat, say while lasting*
Polymer tanning agents	*Softness, fluffy handle, filling, chrome fixation, thermosetting property, dry drumming, good light fastness, grain tightness or roundness without firming of the leather*
Aluminum/zirconium	*Fiber texture or density, fineness of grain, shade brilliance*
Dispersed resins	*Selective filling of bellies and flanks, firmness of grain, heat resistance, embossability, buffing properties*
Glutaraldehyde	*Fine grain, resistance to perspiration, dry washable, alkaline resistance, softness, draping effect, dry drumming, better water vapor permeability etc.*

N.B. *Vegetable tannins and replacement syntans can play most of the rolls of dispersed resins but the formers are not selective and they can't help to get* ***UNIFORM FULLNESS*** *or thickness as per required.*

2. Vegetable/Synthetic Tanned Wet Brown Leather:

Retanned With:	**Improvement Achieved/objectives**
Vegetable and syntans	Area yield, tan color, levelness of color
Chrome tanning agents	Temperature resistance, dyeing properties
Bleach-tanning or white synthetic tanning agents/ e.g. Tanigan BL-1	Tan color, fixation
Resin tanning agents	Filling, alkali and heat resistance
Aluminum/zirconium	Buffing, dyeing properties, tan color

3. Aluminum Tanned Wet White Leather:

Retanned With:	**Improvement Achieved/objectives**
Glutaraldehyde	Resistance to perspiration, softness, fineness of grain and draping effect
Polymer tanning agents	Softness, handle, filling

Thus, as a summary, the leather properties, which can be improved or influenced as objectives or desires, by the retannage can include:

- **Fullness**
- Grain tightness/roundness
- Grain fineness and smoothness
- Softness
- Fat distribution, e.g. by aldehyde tannins
- Leather color, degree of whiteness
- Dyeing properties, levelness of dyeing
- Light fastness
- Dry drumming properties/grain break/
- Embossing properties/print retention/
- Buffing properties/short and strong nap, fuzzy or velvety feel/
- Physical properties/ tensile, tear strength etc./
- Water resistance
- Chemical or analytical results as required/chrome content, ash content etc/. E.g. *relatively low chrome content for dress glove and high chrome content for suede*.

Practical Retannage: Practically the work of retannage is mainly applied for chrome tanned leather. The main character of leather is determined by the first tanning operation; but the retannages are adjustments to that.

As a summary, there are three main types of results, depending on the final crust required /after retannage/:

1. *RETANNAGE FOR FILLING* of the looser structure of wet blues by vegetable tannins, replacement syntans, and resin tanning agents as selective filling effect. This leather is also designed to have good tightness, buffing, emmbosability and finishing properties. This is mainly applied for corrected grain leathers, which are the lowest quality of the wet blue selection. E.g. different types of smoothes, embossed leathers etc. say from VI or R or scrap grade or split leather.
2. *RETANNAGE FOR SOFTNESS AND AN ATTRACTIVE LOOK*: The full grain selection has to have the good grain and cutting value. Here it is important to retain the natural or elegant appearance with a good grain break, full color shades from dyeing stage and an attractive feel from a full handle, even in the belly area or flanks. *Retannage for softness and an attractive look* are often more important than the character of tightness or firmness. E.g. full grain ranges/ aniline, glove, waxy, softie nappa/, say from grade I, II, III, or IV or TR/tannery run or table run/
3. *RETANNAGE FOR UNIVERSAL CRUST WITH MEDIUM PROPERTIES*: A compromise of the above towo or universal or versatile so that there can be further sorting in the crust stage to optimize quality value and profit for the tannery. That is, this class of crust leather can be either full grain or corrected grain as condition allows. It is a valuable option to have a versatile retannage (as MEDIUM fullness, and tightness, MEDIUM softness and feel), suitable for finishing as either full grain or corrected grain. E.g. Universal/ natural/ crust leather say from IV or V grade, say for nubuck or full grain with slight print as kiss print.

N.B:

- A tight grain is no longer in sufficient demand by the market. Rather, softy full grain and nappa type leather is in great demand today. Even a slightly looser grain is often desired so that the leathers will have good dry drumming /milling/ properties and at the same time the leathers obtain an attractive grain pattern or break. Similarly great demands are made on the fineness of the grain, the dyeing properties or the levelness of the dyeing.
- Though grain tightness is still important today for corrected grain leathers, they have also to be considerably softer than the classical corrected grain sides of the sixties. But here, the dyeing properties are less important for this type of leather, as the shade and intensity of the color is usually obtained in the course of the finishing operations.

Q: Do you think that the softness property is required only for full grain leather? If so, how do you reconcile the quality problem that we face nowadays?

3.3 **Process Variables**

A) **Effect of the Sequence of Chemical Addition**

Generally **the golden rule** of tanners recommends us to follow:

1) **Hydrophilic & small size molecules** are always offered first; and **hydrophobic & large** molecules then to follow.

2) **Less astringent** chemicals are always added to a retanning/tanning process prior to the offer of high affinity chemicals.

Evidently, in retanning, the products which are offered first on the chrome leather, determines or changes the properties of the leather surface. Products with the same surface charge (as the leather) which are added first can not change the surface to any significant effect, but penetrates into deeper layers of the leather. In general, the main retanning materials such as vegetable tans, replacement syntans, oil tans, etc. are less astringent or less influential comparing to dyestuff & fatliquors. This is the reason why the retanning sub operation is often done prior to dyeing and fatliquoring. Then, these retanning products occupy the **optimum** binding sites on the neutralized leather surface and protect the leather from over loading by those astringent products (dyes, fatliquors & polymer resins) to be added later on.

For safe retanning process (based on the charges of leather and retanning materials):

- ✓ Mineral tans & aldehydes are offered to retanning processes before neutralization. In addition dispersed resins can be offered later after only a slight neutralization (p^H~4.2). These chemicals show good penetration but reduced fixation at this lower p^H.
- ✓ Vegetable tans, replacement syntans, polymer resins and some type of buffered and masked dispersed resins are offered to the retanning media after the main neutralization. Otherwise, these groups of chemicals faces reduced penetration but fast fixation at the lower range of p^H ($p^H<4$). But the reverse occurs at around the p^H range of the main neutralization (pH~5.0/6.0). In addition, as polymer resins are larger in molecular size and less reactive than others in the group, offer them separately some minutes prior, as otherwise they compete for the same reaction sites and may fail, although it seems contrary to the above general rule especially concerning molecular size.

N.B.: If we apply those groups of chemicals like cationic retanning materials, anionic dyestuff & fatliquors in wrong order, there can be chemical incompatibility or precipitation of each other and the ultimate desired character of the leather can not be achieved. Thus, surface charge consideration is important for penetration and levelness of retanning, dyeing and fatliquoring materials.

B) Effects of the Temperature

Still considering the penetration level, low working temperatures help the re-tanning materials to penetrate deeper into the leather, while higher temperatures improve surface binding. This is generally related to the fact that "a rise in temperature of 10^{o}c increases a reaction velocity by 200-300% "due to the improvement of molecular kinetics. It works also for dyeing and fatliquoring.

Thus, once the working temperature for retannage has been fixed (for penetration~25-30^{o}c and for fixation 40-50^{o}c), it must be strictly adhered to it if consistent results are to be obtained.

C) Effects of float length/concentration/

The retanning materials penetrate more deeply into the interior of the leather if they are applied in short floats /high concentration/ which results in strong diffusion rate due to high potential gradient difference/ than they do in long float. Penetration is important because retanning materials should not be bound too superficially in order to prevent grain distortion, case hardening and drawn grain. Thus, modern retanning processes should work with relatively short floats/100—150% based on shaved weight /, if possible. But if we reduce the float further, the following undesired effects may occur:

- Chafe marks
- Entangling of skins and then tearing
- Untimely temperature development
- Non uniform penetration.

d) Effects of the Running Time

The longer the running time the more completely the retanning materials are taken up /exhaustion/ and more deeply and uniform they penetrate into the leather (usually in 30—40 minutes); keeping the above variables and the type of drum used optimum. But exceptionally longer running time may however lead to chafe marks and loose grain.

Gener ally the art of tanning/retanning is related to control the rate of penetration and fixation to achieve the required distribution of tannins in the skin. That is why controlling the above mentioned process variables is a must.

3.4. Representative Retanning Practice

Retannage practice can be conventional or compact type. In our case we shall see the former.

***As it is mentioned, post tanning operation is the stage where product diversification is common and h ence it is impossible to show all the retanning practices in a single recipe*. Thus, let's see only some representative recipes as follows.**

1) Heavy Shoe Upper Leathers With Corrected Grain (Thickness ~1.8mm):

- ✓ The aim of retannage in this type of product is not only to fill up the interfibrilar spaces of the leather parts mainly in the bellies and flanks but also in the grain layer so as to improve buffing and thickness (By retannage we can increase thickness by about 0.1—0.2mm).

N.B: If we need further increment of thickness by retannage, the grain may crack.

The majority of these types of leathers are rather firm and only light neutralization is required. For these types of products dispersed resins, vegetable tannins and replacement syntans are the preferable retanning agents. The model recipe can be presented as follows.

Model Recipe for Retanning Of Wet Blue for Corrected Grain (T~1.8mm, WBS):
% calculated Based on shaved weight WBS

PROCESS	CHEMICAL	%	T,ºC	TIME	PH
After neutralization and washing					**~4.7**
Float adjustment	water	**100**	**30--40**		
retanning	Dispersed resin/p/	**2--3**		**15'**	
	Dispersing/replacement syntan/p/	**2--5**			
	Vegetable tannins/p/	**4--6**		**40--50'**	
Then Check exhaustion Proceed the next processes					

2) Retanning of skin garment (Especially from Sheep WB T~0.8mm):

Practically for all light leathers like nappa garment from calf, goat, lamb or sheep, filling is not the purpose of retanning. Rather, here, retanning has to provide leveling but even more importantly softening effects which are required. The softening effect is normally achieved in two ways: Primarily, by using the softening retanning agents like chrome containing syntans (chrome complexes with aromatic syntans) and mainly by using polymer resins of the acrylic bases. As described below in the recipe, good exhaustion of polymer resin is achieved at relatively hot media and poorly exhaust liquor shows milky appearance and needs further running time.

Secondly, retanning can improve the fatliquor distribution which also helps the mellowing/softening/ effects.

Glutaraldehyde is also recommended for softening of leather without much filling effect and is also suitable as a retanning for washable garment leathers as well as its perspiration resistance effect.

Model Recipe for Retanning Of Wet Blue for Garment Leather (T~0.8mm):
% calculated Based on shaved weight wet blue

PROCESS	**CHEMICAL**	**%**	**T,ºC**	**TIME**	**PH**
After pre-Neutralization processes, neutralization and washing					**~5.5**
Float adjustment	water	**150**	**40--50**		
retanning	polymer resin /diluted 1:5@~50ºc/	**4--5**		**25'--30'**	
	Replacement syntan/p/, especially white base/ in 2 portions	**3--6**			
	Vegetable tannins/p/	**0--2**		**30--40'**	
Then Check exhaustion and Proceed the next processes					**~5.3**

3. Retanning of Softy Shoe Uppers:

For many years now the trend has clearly been going towards soft leathers not only for boots but also for most types of shoes like softie full grain, floater and nappa upper. Since most soft leathers should still show a fine and tight grain, neutralization should be carried out under safe conditions and a buffering system as well as a retannage with buffering syntans and/or buffering fillers is recommended. The success of many of the new polymer resins is due to the possibility of controlling the filling effect very efficiently and achieving good softness without too much fatliquor. Here the polymers refer not only acrylic base but also protein ones or the mix. The right polymer resins also guarantee a fine grain, good dyeability and high stability to ageing with good fastness to light. Aldehyde tannins also play very important roles in achieving some specific leather properties as mentioned earlier.

Model Recipe for Retanning Of Wet Blue for Softie Upper Leather (T~1.4mm, WBS):

% calculated Based on shaved weight WBS

PROCESS	**CHEMICAL**	**%**	**T,ºC**	**TIME**	**PH**
After pre-neutralization processes, neutralization and washing					**~5.5**
Float adjustment	water	**150**	**40--50**		
Retanning	dispersed resin/p/(if not offered before)	**1--2**		**20'**	
	Polymer resin /diluted 1:5@~50º/	**4--5**		**20'**	

	Vegetable tannins/p/	**0--2**			
	Replacement syntan/p/	**0--2**			
	Protein base polymer	**2--4**		**30--40'**	**~5.3**
Then Check exhaustion					
Proceed the next processes					

4. Retanning of White Leather from Wet blue:

It would be a great advantage if the wet blue could be produced specifically for this purpose so that the color of the chrome tanned leather is bluish and not green or worst of all even olive which is much more difficult to cover by retannage with a white syntan. For this reason:

- ✓ *use masked chrome rather than simple basic chrome*
- ✓ *avoid neutralizing agents that aggravate greenish color*
- ✓ *wash the shaved WBS using bleaching acids like acetic acids before neutralization*
- ✓ *use chelating agents to trap any iron atoms that causes greenish stain (small amount of EDTA or oxalic acid)*
- ✓ *use a well covering white syntans /up to 3 different installments /*
- ✓ *use a small amount of red dyestuff /0.005—0.01%/ with one of the portions of the white syntans to kill the green tint*
- ✓ *Acidify between different portions to improve surface fixation and surface coverage.*
- ✓ *Use white pigments /e.g.TiO_2/ at the retanning stage*. To prevent preferential absorption of pigment at drum stage by the flesh side it is important to add it after fatliquoring. If we use pigments at post tannage or drum level, it can be well fixed by acrylic polymer resins.

Q: Explain how pigments are bound to leather surface.

Model Recipe for Retanning Of Wet Blue for White Retanning Leather (T~1.4mm, WBS):
% calculated Based on shaved weight WBS

PROCESS	**CHEMICAL**	**%**	**T,ºC**	**TIME**	**PH**
After pre-neutralization processes, neutralization and washing					**~4.8**
Float adjustment	water	**150**	**40--50**		
Retanning1	White syntans/diluted/	**4**		**30'**	
	White syntans/diluted/	**4**		**30'**	
	Neutral syntan /p/(dispersing agent)	**3**		**45'**	
Fixation1	**Formic acid/diluted 1:10 cold/**	**1**		**20'**	**~4**
wash	**water**	**200**	**50**	**10'**	
Retanning2	**Float, water**	**150—200**	**45**		
	White syntans/liq/	**2**			
	White pigment/dil/	**2**			
	Red dye/dil/ **N.B. Fatliquoring is also used here**	**0.008**		**60'**	
Fixation2	**Formic acid**	**1**		**15'**	**~3.5**
	Cationic fatliquor	**0.5—2.0**		**30'**	**~3.2**
Then Check exhaustion					
Proceed the next processes					

5. Retanning of Lining Leather:

Lining leather faces too much perspiration effects. Thus vegetable tannins /which have higher water absorption properties/ and aldehyde tannins/which have higher perspiration resistant property/ are two ideal retanning chemicals if you need to produce high quality lining leather. Mellowing/ velvety or ladies touch/ with polymer resins is sometimes important as the product has direct contact with our skin. But practically this type of product is processed from lower grade input and even low production cost and there is no such serious cares are kept in processing it.

N.B. Fixation should be strong to reduce substances removable by washing or different exposure to wetting.

Model Recipe for Retanning Of Wet Blue for Lining Leather (T~0.9mm, WBS):
% calculated Based on shaved weight WBS

PROCESS	**CHEMICAL**	**%**	**T,ºC**	**TIME**	**PH**
After pre-neutralization processes, neutralization and washing					**~5.2**
Float adjustment	water	**150**	**40**		
Retanning	polymer resin/dilute 1:5@~50ºc/	**2--3**		**25'**	
	Replacement syntan/p/,white base	**~3**			
	Vegetable tannins/p/	**~5**		**50'**	**4.7**
Then Check exhaustion					
Proceed the next processes					

6. Retanning of Vegetable Tanned Leather/Heavy Tanned Leather/:

For vegetable tanned leathers such as sole, bag and belt, retannage is not common or not much important. This is so because, the main purpose of retannage for these types of products, filling, is mainly achieved by the vegetable tannin itself during the first tannage. But only slight adjustment of properties such as weight (by adding lead polyphosphates and magnesium/barium sulphates) and bleaching process is done. Here bleaching refers to changing the bright brown vegetable tanned into uniform light and pale brown or tan color. Hence bleaching can be done by:

1) *Treating the leather with previously bleached vegetable tans, e.g., Quebracho by sodium methabisulphite ($NaHSO_3$~3%)*
2) *P^H reduction(from original P^H ~4 to P^H ~3 using organic weak acids such as formic, acetic or oxalic) ~0.5%; followed by washing*
3) *The combination of the above two methods (i.e., bleached vegetable tans followed by sequestering acids like oxalic one)*
4) *Direct use of $NaHSO_3$ ~0.3%*
5) *Naphthalene base bleaching agents (2—3%). They are bleaching syntans that give more uniform and reliable bleaching effect. E.g. Tanigan Bl-1 of BayerAG It is offered to the retanning drum, dipped or in acidification in the C-RFP process.*

Q: ***Design a reasonable model retanning recipes for suede, split nubuck and glove leather.***

3.5 Process control

As usual to get the required penetration and fixation, the ranges of different process variables should always be controlled or monitored.

Thus check/control:

1) The float level of the retanning media before starting operation both visually and using measuring devices.
2) the P^H of the float before and after the process
3) the temperature of the float before and after the process
4) the dilution/emulsification/ level of some chemicals like polymer resins
5) the running time and speed
6) finally the exhaustion of retanning liquors

Special Notes:

1) **Polyacrylics as Tanning Agents:** They are Polyacrylic acids or polymethacrylates and a certain number are esterfied (alcohol +acid) but with small /low number/ of ester groups and the molecular weight go up to 100,000; even at these numbers they can't form film. But still it is too difficult to make it penetrate well to the leather thickness. Thus during retanning/tanning it is always recommended to use smaller sizes of this type of product. Besides, they can't be considered as tanning agents as they can't enhance shrinkage temperature.

   However**,** they are **valuable** retanning agents as they fill leather grains without causing any coarsening on the grain /fine and smooth grain/.

If you need firmer grain or more binding, select the polymer having methyl group called Meta acrylics.

On mixed applications with poly phenol anionic Syntans or vegetable tans, both will be competitors for the same reaction sites. But the polyacrylates are as large as vegetable or syntans or even larger.

=>They can't have equal chances to bind in comparison to the smaller molecules, which have in addition, strong aromatic binding forces.

=>It is advisable to add the polyacrylates into the retanning media some minutes **prior** to the other syntans.

2) The main difference between the tanned and raw hides is that the latter is easily hardened and stiffened to become horny and difficult to wet back after drying than the former. This is due to the dehydration of mechanically and chemically bound water and the restructuring or internal reaction of fibers or gelatinizing or gluing effect. That is, water, in its presence, gives softness and firmness to raw hide/skin and the required flexibility as there is sticking of fibers.

But by tanning, the tannins play the role of water dehydrated by filling the gaps/spaces/ and preventing the restructuring or sticking of fibers.

In case of vegetable tannage, the polyphenol acidic groups can displace the bound water in the basic and peptide groups to form hydrogen bond or ionic groups due to dipole moment. But the leather may not be soft or flexible or even harder or temper due to:

- quality of tannins used (due to its strong filling action)
- The power of vegetable tannins to form aggregate formation (solidity power) between tannins those fixed with fibers

=> Fatliquoring is a solution for this agenda

Tabular Summary of Tanning/Retanning Materials and Their Usages/Leather Character Improved/:

parameter	Vegetable tan	Chrome tan	Al/Zr tan	Oil tan	Aldehyde tan	Synthetic tan	Dispersed resin tan	Polymer resin tan	Others/if any
Tanning material sources	Water extracts of barks, wood, leaves, fruits and root of plants	Chrome sulphates/ chloride	Al sulphates, chlorides or alum Zr salts	Code liver oil	Formal-aldehyde, glutar-aldehyde, dialedhyde	Auxiliary, replacement, (including white tannins**)**	Urea, melamine, dicyandiamide with aldehyde	Acrylic, methacrylic, acriolite	Organic/ proteins, starch/& inorganic filling agents
Quantity used	As per the amount of property we need &type of product	**ditto**	**ditto**	**ditto**	**ditto**	**ditto**	**ditto**	**ditto**	**ditto**
Effect of P^H of tan liquor	Low P^H/<3.2/ gives faster and greater tan fixation and poor penetration	Low P^H /<3/reduces speed & degree of tan fixation & have higher penetration	Ditto to chrome	Not very P^H sensitive	Low P^H reduces fixation, mild alkaline P^H facilitates fixation even @low concentration	Usually low P^H gives faster and greater tan fixation as vegetable tan	Low P^H reduce speed and degree of tan fixation & have higher penetration /most resins are cationic/	Ditto to vegetable tannins	It depends
I^P of wet leather & ionic charge @P^H~5	**~4** anionic	**~7** cationic	**~7.5** cationic	**~3—4** anionic	~3—4 anionic	**~2.5—3** anionic	**~7** cationic	**~3-4** anionic	it depends
Handle Property of leather	Relatively dense, firm or solid	Soft or resilient	Usually very soft	very soft and stretching	soft and spongy character if the amount is too much	as required, usually like vegetable tans	firm grain but denser/fuller than vegetable tans	soft, thermosetting, heat resistant with good cohesive force power	firm and full using inorganic for vegetable tanned &organic base for chrome tanned
weight yield of	gives high	low yield	low yield	low yield	low yield	generally low	low yield	low yield	gives

leather	weight of leather per unit of raw skin					yield			high weight per unit area
color after tannage	pale brown and darkens in daylight	pale green or blue and little change in daylight	white, little change in daylight	dully yellow, bleaches in sunlight	white and goes whiter in sunlight	generally paler than vegetable tans but may also darken in sunlight except the white replacement ones	light fast	light fast	generally has no effect
removal of tan by water	washes out very slowly	doesn't wash out	can be washed out	doesn't wash out but very water absorbent	doesn't wash out but very water absorbent	usually similar to vegetable tan but doesn't wash out	doesn't wash out	doesn't wash out	can be washed out
characteristic uses	Shoe sole, bag , belt, book binding, straps parchment	shoe upper, gloving, clothing, lining etc	glove, white leather, suede etc	washable leather	washable leather, gloves, clothing white leather etc.	white leather, specialty leather, upper, clothing	uppers, corrected leathers	white leather, clothing leather, soft leather	vegetable leather
type of bond	hydrogen bond, Vander waals force, or dipoles	Coordinative(dative) bonds	coordinative	normal covalent bond like in aldehyde	normal covalent bond	hydrogen bond, Vander waals, or salt bridge	with methyl groups like aldehyde	they may not have bonding as they can't improve shrinkage temperature	they may not have bonding site

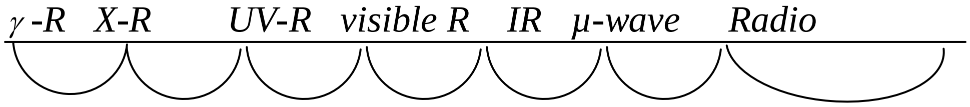
N.B:

- Aldehyde tannage can improve dye leveling, dispersing of fatliquor and other acidic group retanning materials(vegetable and synthetic tannins) as the aldehyde can reduce the effect of basic groups (i.e. amine groups by reacting with these groups).
- Dispersed resins are mainly cationic and hence you are not recommended to use simultaneously with vegetable or syntans so as to prevent mutual precipitation on the float or on the grain. Take care also for the amount used for this dispersed resin as it causes grain crack.

4.0 DYESTUFFS AND DYEING PROCESS

INTRODUCTION

The concept of dye and dyeing is directly related to the concept of light and color. As you know, "white light "or simply light energy is one region of the different electromagnetic radiations (γ-rays, x-rays, UV, visible/light rays/, IR, µ-waves and radio waves) with a standard or proportional mixture of electromagnetic waves of wave length between 400—750nm that can be detected by human eyes. This region is also called visible region of EMR waves. Diagrammatically:



=>Energy and frequency is decreasing to the right
=>Wave length is increasing to the right

In the order of writing above, the types of transitions occurred by each EMR are nuclear (for both γ-R and X-R), inter shells, outer shell, molecular vibration, molecular rotation and NMR effects.

Specifically the visible region can also be split into seven main color regions /rainbow colors/. Viz. **VIBGYOR** colors.

Visible Color Regions in the Human Eyes as Per the Wave Length Range:

Range of Wave Lengths (nm)	Absorbed color by a Body	Reflected complementary color by a Body and Sensed by Eyes
400-435	violet	Yellow-green
435-480	blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	green	Purple
560-580	Yellow-green	Violet
580-595	yellow	Blue
595-605	orange	Green-blue
605-750	red	Blue-green

Thus, selective absorption in the visible region is necessary for the formation of color. For instance, the violet-blue portion of the white light is absorbed from a body, the remainder of the color (green and red-orange) is reflected; as a result the body appears YELLOW.

WHAT IS COLOR?

- It is simply a reflected or composite reflected light rays.

- It is a byproduct of the EMR interaction with matters i.e. when the valence electrons of an atom or a molecule absorbs EMR in the visible light region and emits it latter on, color is observed in the process of fluorescence/return of excited electron to the ground state/, called emission or reflection.

Q: Explain the difference between light emission and reflection, if any.

- It is a sensation registered by the eyes when they see certain reflected or subtracted light spectrum from a certain body or object. Thus, this body can be considered as a colored object at least temporarily and it is characterized by its ability to absorb visible light and latter on it emits out. In fact, it is for this reason that it appears to be colored. Otherwise, it is colorless. That colored object is so called colored because it carries some coloring matters called colorants.

To see colors, light source/visible light/, an object to be seen/carrying colorants/ and an observer/eyes/ should exist**.**

Group of Colorants

A	B
- Organic	-inorganic
-E.g. dyes	-e.g. inorganic pigments
- Soluble in the given solvent (Water or organic)	- insoluble in any solvent
-have strong affinity to a given Substrate, like collagen fibers	- inert/poor affinity to a given substrate
-Structurally complex	-structurally simple salts or oxides

4.1 DEFINITION OF DYES: Dyes are complex, natural or synthetic, inorganic or organic solvent soluble, colored organic compounds having the property of imparting their permanent color to other substances such as collagen, wool, cotton fibers etc**.**

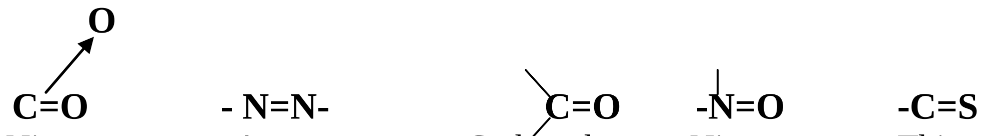
From the definition one can recognize that every colored compound can't be called a dye, like beet roots. Thus, specifically, for a colored compound to be called a dye, it must be**:**

- organic compounds=>not inorganic, unlike pigments
- colored compounds=>not colorless or white, unlike pigments
- capable to fix chemically by itself to other fibers permanently=>not as easily washable as beet root nor physically coated as paint/pigment
- complex and larger in molecular size so that it can be inert or fast to be resistant for the action of light, solvent, abrasion etc.=> not as simple as picric acid.
- natural origin, e.g., wood log dye or synthetic dye, e.g., mauve or aniline dye synthesized by Perkins from coal tar or petrochemicals
- Soluble in a given solvent /aqueous or organic solvents**/=>**not insoluble**.**

4.2 CHEMICAL STRUCTURE OF DYES:

It is discovered that the **unsaturation** of molecules is important for producing colored compounds and the reduction of unsaturation always resulted in the formation of colorless products**.** Thus,

I) the color of organic compounds is mainly due to the presence of groups of unsaturation /groups with multiple bonds is more appropriate terms/ which is called **chromophores** /Greek **chromo=color**, **phorein=to bear**/. Some of the chromophores include**:**



$C=O \rightarrow O$	$-N=N-$	$>C=O$	$-N=O$	$-C=S$
Nitro	Azo	Carbonyl	Nitroso	Thiocarbonyl

Thus, chromophore is any isolated functional group which exhibits absorption of light near UV or visible region. Note also that compounds containing the chromophoric groups are named as **chromogens**. E.g., benzene ring compounds with chromophores.

II) The intensity of a color increases with the increase of the number of chromophores in a chromogen. The effect is particularly marked if the chromophores are conjugated bonds. Thus a single double bond, **-`C=C`-** , chromophore is not sufficient to produce color but if a number of them are present in conjugate form, persistent color may develop.

Example: $CH_3(CH_2=CH_2)_6CH_3$ and
CH_3 $(CH_2=CH_2)_{12}CH_3$ are yellow and red respectively.

III) Certain groups which by themselves fail to produce color have important effect on the color of the chromagens**.** These groups are termed as **auxiochromes (Greek auxien=to increase or intensify)** and can increase the absorption power of the chromophores**.** They are acidic or basic in nature.

E.g.:	**-OH**	**-OR**	**$-NH_2$**	**-NHR**	**$-NR_2$**	**-X**
	Hydroxyl	alkoxy	amino	alkylamono		halogen

N.B1: The presence of auxiochromes are not only to help the intensity of the color of chromogen but also imparts substantivity to the color on the other substrate (i.e. increases solubility and affinity to the substrates), thus making the chromogen a dye**.**

N.B2: When auxiochromes, especially anions, are attached to chromagen containing chromophore, absorption shifts to a longer wave length called **bathochromic** effect which is the most occurring case in dyeing**.** There are some cationic auxiochromes whose absorption effect shifts from longer to shorter wave lengths called **hypsochromic** effect.

For instance,

- Both naphthalene and naphtols are colorless. But 2, 4-dinitronaphtalene is pale yellow and 2, 4-dinitro-1-naphtol is orange red. See that: nirto groups introduce color to naphthalene and it is therefore chromophore. The hydroxyl group by itself can't make the compound colorful, e.g. see in naphtol. But –OH group deepens the color of chromogen, 2,4-dinitronaphtalene from pale yellow to orange red**.**
- **Azobenzene (C6H5-N=N-C6H5)** is a chromogen having azo chromophore. But still it is almost colorless. Whereas, if you introduce the amino **(-NH_2**) group, you can make a yellow color due to the effect of the auxiochrome **–NH_2**.

N.B: Unfortunately, all the above examples can't be considered as dyes as all molecules are **simple and fugitive i.e. they have poor fastness to different chemical and physical encounters.**

Conclusion:

- the color of organic compounds are explained due to the presence of three types of groups:
    - unsaturated conjugated bonds in the molecules/chromagens
    - chromophores
    - auxiochromes
- The greater the number of chromophores, preferably in conjugate form, the deeper it will be its color

4.3 Leather Dyeing and Its Purposes

As mentioned above dyes can impart colors to some substrates such as collagen fibers, cotton and wools. Thus dyeing of leather is the process of imparting color to the leather fibbers. Nowadays, many types of leathers, except some heavy leathers and some corrected leathers, are drum or spray dyed.

Dyeing of leathers has several purposes, if properly done.

E.g.:

1. To improve its appearance or **aesthetic appeal**, as color or dye can enhance the beauty of leather or divert the psychological tendency / choice of the users towards some color of the leather/ and then you can make your products competent in the market**.**
2. To make the leather **adaptable to fashion** style. For instance, aniline dyed leather has elegant appearance and long lasting fashion in the leather market than heavy pigmented finish**.**
3. Dyeing is one of the well known **value adding** process steps in leather processing. The marginal price markup after dyeing is clearly higher than the intrinsic cost incurred due to dye consumption

4. To fulfill leather properties and customer requirements, i.e. **color properties** rank equally with different leather properties such as feel, break, temper etc. factors by which most leather types are evaluated /inspected by customers as quality parameters**.**
5. To **upgrade** leather by covering of defects**.**

4.4 Classification of Dyestuffs:

Dyes may be classified according to the **method/properties/ of their application** to the substrate/collagen fibers or on the basis of their **chemical structure**. Whereas, the former is of immense importance in industry to the dyers; while the latter is chemists/scientists' issue and will not be dealt in this module.

4.4.1 Classification According to Application: That is, it is based on the behavior of dyestuffs such as penetration, intensity of shade, fixation or reaction or affinity etc.towards various natural and synthetic fibers in different acidic or basic medium. Leather dyestuffs, according to the color index, approximately about 1000 are in use in the world industry of which (from commercial available dyes):

- **acid dyes comprise~70%**
- **direct dyes comprise ~18%**
- **Mordant dyes comprise~6% and**
- **Miscellaneous dyes /such as basic dyes vat dyes etc. /comprise~6%.**

N.B: Vat dyes are insoluble in water media and made soluble by application of excess sodium sulphite first in a vat and hence called vat dye. Thus, it is not common to use this type of dye in leather dyeing**.**

From acid dyes:

- ✓ azo dyes comprise ~40%
- ✓ Metal complex dyes comprise ~26%
- ✓ Anthraquinone dyes comprise ~3%
- ✓ Unknown dyes comprise ~25% and
- ✓ Other dyes comprise ~6%

All acid dye types are anionic or slightly amphoteric or nonionic types. The acid dyes can also be further split into**:**

a. Simple Acid Dyes: Dyes containing sulphonic acids or carboxylic acid groups of anionic species. It is acid dyes because it must be used in acidic media (mordanting by external acids, usually formic) to fix it with the substrate/fibers, or to reduce the affinities or solubilities of dye molecules so that they will react with fibers. Chemically, they are not real acid; rather they are salts of a form $\mathbf{R1SO_3Na}$. They are simple because they are relatively highly water soluble due to the presence of the sulphone groups; their molecular weights are relatively smaller (between 400—800g/mol), becomes anionic in solution a**s:**

$$R1\text{-}SO_3Na + H_2O \rightarrow R1\text{-}SO_3^- + Na^+$$

For this type of dye, addition of neutral sodium salt (**NaCl** as an example) can inhibit the ionization of this dye.

=>Common salt can play the role of even /level dyeing.

=>Generally, the purpose of mordanting is to dampen/reduce the affinity of dyes towards the leather fibers when we need levelness or in other extreme towards the dyeing floats while fixing it. E.g. for chrome leather vegetable tannins are good mordant of the subsequent acid/direct dyes.

=>Heavy metal ions like Mg^{2+}, Ca^{2+}, Cr^{3+} etc. can react with anionic groups of this dye and causes precipitation as

$$2R1\text{-}SO_3^- + M^{2+} \rightarrow (R1\text{-}SO3^-)_2M\downarrow$$

=>Use only soft water and in a media free from such heavy metals to avoid the possible risk**.**

=>Acid dyes can be used with any anionic dyes or tannins but never with cationic ones**.**

ADVANTAGES: Good dyeing /brilliance/ and penetrative

DISADVANTAGES: Poor in light fastness, wetting, perspiration and washing**.**

To reduce the problems, use these simple acid dyes together with direct dyes or use it in the first/bottom dyeing/for penetration purpose followed by cationic dyes for fixation /top dyeing**/.**

b. Substantive/Direct Dyes/: almost all are azo-type dyes. They are related to simple acid dye types in that they are also weakly anionic and contain sulphonic and /or carboxylic acid groups. It can be represented as RSO_3Na.

As different from simple acid dyes, direct dyes are higher molecular compounds i.e. R>>R1, exists in the form of dispersed state, dyeing can be done without acid addition, or acid mordanting, hence direct dyes. Thus, direct dyes can react with fibers by vander waals force, H-bond and/or ionic bonds without external acid addition. Rather they are not stable to extreme acidic media.

As their chromophores are plentiful and higher molecular size, they are used for intensified dyeing and with good coating or covering properties and have corrective power for surface defects. Thus, they are mainly used in dark shades like black and brown leather dyeing. These groups of dyes have also strong combination and fastness powers as well as tanning/ filling effect due to their larger molecules and larger number of chromophores**.**

But they can’t be preferred for fine and aniline grain finish as they need higher temperature/even up to boiling/ to make them soluble and hence make the grain rough and less soft**.**

=>Chrome leather can be bottom dyed with simple acid dyes and topped with direct or basic dyes**.**

c. Special Leather Dyes/Pre-metallized Dyes/: The idea of producing pre-metallized dyes was derived from a mordant dye. A mordant is any substance /in our case metals like

Cr, Co etc. / which can be fixed to a fiber that can be dyed later to produce colors on fabric fast to washing. Thus metallic mordants like salts of Al, Cr, Fe, Sn, Cu etc. are used with acid dyes**.**

Q: Explain how rechroming or Al/Zr retanning can improve dyeing properties.

Strictly speaking, the term mordant dye / or chrome dye/, is reserved for such dyes as it can form coordination or chelate complexes with metal ions. The process of mordant dyeing consists of /reaction in situ/: impregnating the fiber with the mordant in the presence of wetting agent, and then soaking of the mordanted fabric into the solution of the acidic dye follows**.**

=> The process is known as pre-metaliizing.

=>Mordants combine with acidic/carboxylic group of the collagen fibers primarily and then with the acid group of the dyes forming insoluble color lakes fast to light and washing. **Lakes** are chelate compounds formed by the metal ions and the dye molecules. There is also **afrer-metalling** in that the mordant is added after the fabric has been soaked with dye and bath has been fully exhausted.

Q: Can you explain how basic chrome powder uses as fixing agent, by metal coupling process?

But nowadays, **1:1**or **1:2 metal to dye** complexes are readily available in the market which can dye fibers directly, not alternatively. They are also known as the real Premetallized dyes**.**

Properties of 1:1 Metal complex Dyes:

They possess good light fastness, washing properties, good leveling and penetration capacity. But rich/deep shades can't be achieved with it. Mainly applicable for garment, upholstery, glove leather and any pastel shades, not for suede leather that need deeper shades.

=>It is ideal for pastel shades as it imparts dull shade to leather**.**

Caution! Combination with other dyes or complexing substances/metals/ should be avoided as demetallization/substitution/ may occur**.**

Properties of 1:2 Metal Complex Dyes:

In these types of dyes two dyestuff molecules are bound as ligands to a single metallic central atom. It is more anionic compared to the 1:1 complex dye and hence more P^H sensitive to fixation, like other acid dyes. These dyes are relatively more complex in nature and higher in molecular sizes**.**

=>One can achieve strong surface shade/due to higher molecular size/ than by 1:1 complex dye**.**

=>They are very fast to light, wetting and perspiration/less fugitive**/.**

=>Their leveling and penetration capacity is considerably reduced**.**

These dyes are further subdivided into dyes which are **free of sulphone --groups** and **with sulphone- groups**. Thus, if the solublizing group is not present in the molecule, the product will be soluble only in organic solvents or in combination of organic solvents and surface active agents and it is particularly used for spray dyeing. But generally, when dyeing is performed in dye bath, they are used as covering and full dyeing purposes**.**

d. Basic Dyes/Cationic Dyes/: Dyes containing amino or amino substituted groups and can react with the acid groups of collagen or tannins. Basic dyes are cationic in nature as the molecules are positively charged. Hence they have no affinity to chrome and aluminum tanned leather /except for those highly masked/. Rather, they have strong affinity to vegetable and anionic synthetic tanned leather. Thus it can precipitate with oppositely charged anionic dyes, vegetable tannins, syntans, fatliquors, hard water/containing $SO4^{--}$, Cl^- etc/ ions. It has a general formula of $\mathbf{R\text{-}NH_3^+Cl^-}$. Basic dyes can produce brilliant and richest color and full shades especially on vegetable tanned leather and also mineral tanned leather which have already been predyed with anionic dyes. They have also strong perspiration resistance. But shades dyed with basic dyes have poor light and rub fastness, poor penetration and hence bronzing effect. Due to their high affinity for vegetable and synthetic tanned leather, basic dyes can't produce a level shade and minor grain faults in the leathers are accentuated by being concentrated on the faulty portions much deeper than the rest of the grain. (This is due to that as more tannins and syntans can highly reside on that defected open structure parts). If you need to top dye leather of vegetable, synthetic or any anionic treated leather, the bath should first be exhausted or fixed before basic dyes are offered and the temporary water hardness should be avoided. They are mostly used as separate intermediate dyes in the so called sandwich dyeing/anionic-acid-basic-anionic-acid/. As most of them are fugitive to light, they are not used extensively in leather dyeing especially for leather of exterior wear such as gloves, garments upholstery etc; unlike suede leather.

e. Reactive/Active/Dyes: It is reactive because this type of dye can form primary valence bond or covalent bond with collagen fibers/substrates. They have not yet gained importance for dyeing of leather because**:**

- ✓ they are costly
- ✓ Covalent reaction is usually occurred at higher P^H of about 8 or alkaline range. But as the color fastness and especially the wet rub fastness are higher for reactive dyes compared to ordinary acid dyes and basic dyes, they can be potentially selective in the future**.**

The main shade names of commercially available dyes often include suffix letters like**:**

- **B**=bluish, **O**=orange**, R=**reddish**, Y or G(**Gelb in German)**=**yellowish to indicate the observable tints
- Higher intensity by repeating the letters that indicate the shade. E.g. **RR** to show deep red or very reddish and **N**=pale/light shade, **M**=medium shade, **C**= deep or conc. Shade, **L**= good levelness and **P**= penetrative
- Light fastness, wash fastness etc. by **F** and **WF** respectively
- Acid dye, Cationic dye, Direct dye etc. by **S** (sauer in German), **K** and **D** respectively.

4.5 Properties of Dyestuffs

Properties or quality effectiveness of dyes are usually graded by numerical systems by the dyestuff manufacturers as**:**

5= very good 3=satisfactory 1=very poor

4=good 2=poor

These dyestuff properties are generally grouped into two**:** dyeing behavior and fastness behavior.

Dyeing Behavior: Some dyeing behaviors of dyestuff are tested at the laboratory stage or by dyeing substrates**.**

For instance:

1. **Homogeneity:** it is the measure of chemical purity or the percentage level of **identical dye molecules**; it is not the measure of any non dye impurities. Thus homogeneous dyestuffs contain one single product as main constituents and 5% maximum one or more other dyestuffs. Homogeneity can be tested by **blow or capillary tes**t method**.**
2. **Solubility:** Anionic dyes are more soluble than cationic ones. Usually solubility is checked at **20ºc** and **60ºc** by distilled water**.**
3. **Levelness:** Evenness or **uniformity of dyeing** on the leather surface on a piece or across different pieces**.** It can be affected by the method of process used**.**
4. **Penetration:** It depends on constitution of the dyes /molecular size, charge type etc. / and the pretreatment of the substrate. This property is mainly important for suede, gloving and clothing leather**.**
5. **Exhaustion:** Level of uptake of dyes by the substrate from the dye bath. One can check visually using white paper or filter paper. Good exhaustion is especially important in view of the high price dye types**.**

Fastness Behavior: Fastness refers the fact that the fixed dyes should not come out when the leather is dry rubbed, wet rubbed, washed with water, alkali, acid solution, or when contact with sweat or similar solution/ perspiration/; or the color of the dye fixed should not fade out when the leather comes in contact with sun light, dust, air, different other gases etc. Evidently, fastness properties mainly depend on both strength of bonding and inertness of the fixed dye**.** The degree of fastness is presented in numbers by the help of standard scale called **grey-scale.**

4.6 Process variables for dyeing

The minimum quality requirements of dyeing for high quality leather include:

- Perfect levelness of shade
- Maximum depth of shade achieved with minimum amount of dye/exhaustion/ or up-takes
- Good covering of defects
- High color fastness
- Complete penetration and distribution

To achieve these quality issues, we have to control the following influencing factors called ***process variables.***

1. Neutralization & Neutralization P^H

a. **Uniform** neutralization is essential (over-neutralization& inadequate neutralization should be avoided). Neutralization to a minimum of **$P^H \approx 5.5$** prevents surface occlusion of the acidic dyes**.**

b. Increasing the P^H value improves penetration in dyeing & retanning agents, but reduces the absorption of anionic dyes

c. Addition of **masking** products also improves penetration of dyes & retanning agents & absorption rate of dyes**.**

=>Inadequate neutralization causes poor leveling of dyes

=>Addition of NH_3 solution to the dye bath (to increase the $P^H \approx 8$) can enhance leveling and penetration of the color especially when we use hight affinity acid dyes. But raising the P^H too high can reduce the firmness of the grain, like over-neutralization**.**

2. Retanning Agents

a. Purely chrome tanned leather has the highest affinity for anionic dyes (followed by other mineral tanning agents)

b. Self replacement syntans, white syntans & polymer tanning agents reduce the affinity but give level & bleached shads for anionic dyes)

c. Cationic resin can intensify (deepen) the dyeing

d. Aldehyde tannage can give us level & pastel shades due to reduction of cationic groups of the substrate /by consumption of amine groups of the collagen by aldehydes)

=>Any retanning can change the absorption behavior and fixation of anionic dyes to either end

=>High degree of mineral tanning can result in poor level of dye but deep shade (for anionic dye)

=>High vegetable, synthetic or polymer tanning agents can result in highly leveled but poor intensity or deepness of shade (for anionic dyes)

=>The higher percentage of /the addition of/ syntan or vegetable tannins, the lower dye up take will be (due to the increasing saturation of the fiber surfaces by the anionic tanning agents).

3. Fat liquoring Agents

a. Highly **sulphited or sulpho__chlorinated** fatliquors can reduce the up take or absorption properties & /or cause stripping of dye (if fatliquoring is done in the dye bath)

b. Depending on the kind & amount of **emulsifying components**, improved penetration & levelness of shade can be achieved with reduced depth of shade

On the contrary, practically if fatliquoring is done after dyeing, the deepness of the shade increases

=>in dyeing of suede, the main fatliquoring is done after dyeing process

=> Intensity of shade should be evaluated, under constant fat content, order of addition & uniform distribution (by emulsifiers or dispersing agents)

4. Dyeing Auxiliaries (On Dyestuff Affinity

a. Some dyeing auxiliaries are to help level & uniform dyeing (e.g. naphthalene sulphonic acids or non ionic surface active agents derived from polyglycolic ethers by reducing the rapid fixation power of anionic dyestuffs & tan stuffs)

=>No superficial fixation will occur

b. And others to deepen the shade and to increase dye build –up capacity of anionic retanned chrome leather (these are cationic amine groups of dicyandiamide condensates and Cr or Al salts)

c. Color build –up (deepening) can also be improved by several installments dyestuff offering than a single shot irrespective of the total amount

=> Anionic or nonionic products have a leveling effect on anionic dyes but a fixing effect on cationic dyes

=> Cationic products have a leveling effect on cationic dyes but a fixing effect on anionic dyes

5. Choice of Dyes

Dyes that are used together in a dyeing formulation must be compatible (i.e. Combinable without being affected each other or precipitation)

Otherwise, unleveled shades & poor fastness will result**.**

=>Compatibility /combinability/ is mainly dependent on

- Chemical structure /charge difference of different dyes/
- Absorption rate of dyes /molecular size of dyes & dyes-to-collagen charge difference/
- Build-up properties of dyes /level of chromospheres & auxiochromes on the dye/
- Kind of retannage (vegetable or synthetic tanned leather & mineral tanned leathers versus anionic & cationic dyes & the resultant levelness & color intensity)

E.g. Aluminum retannage of chrome tanned leather can increase brilliance but vegetable or synthetic retannage can decrease brilliancy but can increase levelness for anionic dyeing)

=>Improvements may be achieved by applying dyeing auxiliaries

6. Addition of dyes

a. Addition in paste form or particularly in dissolved form is essential especially for high quality and uniform aniline dyeing

b. Addition of dyes in powder from (after pasting or mixing well for several dyes) can help penetration in the cost of levelness

c. Addition of dyes in several portions can increase the depth and levelness of shade

N.B: Normally pasting refers to dissolving a dye in **a little cold water** until thoroughly wetted and then further dissolving it **@ ~90**$^{O}{}_{C}$ in 1:10 or 1:20 ratio of dye to water**.**

=>As a result, the Secondary valence force of attraction between molecules decreases**.**

=> Aggregation of dye molecules decreases**.**

=> Solution can be formed /the higher temperature, the lower the aggregate of dye molecules will be. The lower the aggregate of dye molecules, the higher penetration of the dye and the lower surface fixation will be**/**

7. Float length

¶ High float length promotes distribution & levelness of dyes and auxiliaries, particularly if,

- ✓ affinity of dyes or auxiliaries is higher
- ✓ chamber dyeing vessels are used

- ✓ we need to dye leather with small percentage offer (pale shade) i.e. it is difficult to get uniform shade by small offer than bulk, especially in short float)

¶ **Short float** length is favored if,

- ✓ Levelness of dye is less important
- ✓ We have best auxiliaries &/or less affinity dyes
- ✓ We need deep shade (due to temperature increment) with a given dyestuff concentration
- ✓ Good penetration is required

8. Temperature

Chemical reactions are less complete and slower at low temperature.

The same is true with respect to uptake & fixation of dye. In addition, many dyestuffs form aggregates in aqueous solution at room temperature that possess little affinity for leather.

=>The dye penetrates further but fixation is too low at the surface.

=>By heating the media latter, the aggregates distribute & fixation with fibers can occur

=>No surface staining, but better leveling of shade results.

But dye offered to leather under high affinity condition (heat), will fix on the surface superficially.

=>Uneven dyeing can occur

Thus, the optimum procedure is to maintain a low temperature (~30$^{O}{}_{C}$) at the beginning of the dyeing process and a high temperature (>50 $^{O}{}_{C}$) towards the end of the dyeing process to fix the dyes.

9. Mechanical Action

- ✓ High mechanical action can improve **penetration** of dyes which is a necessary condition for **level dyeing**. Low mechanical action may improve intensity if the required temperature is achieved.
- ✓ Even with less than **0.5%** offer of a dye having a high affinity can give a deeper shade in the presence of higher agitation (**16-20 RPM**)
- ✓ Besides, to achieve a well leveled dyeing, especially on the start phase, immediately after adding the dye to the dye bath, there should be a rapid mix or strong mechanical action (here not to develop heat or T^{O})

10. Amount of Dyes offer (to the surface of a substrate)

- ✓ The level & distribution of small amount of dye offer is much more difficult than with larger offer.

=> The intensity of shade obtained depends on

  - ➢ the concentration of dye in the dye bath and
  - ➢ float level

- ✓ With a higher offer of dye, both shade intensity & levelness increase. But with higher offer (to the surface), bleeding of dyes during washing (that is the indication of poor fastens) can occur.

  =>Optimum offer is required not only for cost reduction but also for quality requirement

11. Fixing Agents

Acidification of the dye bath **lowers** the solubility of the dyestuff which then starts to bind to the substrate (collagen) than staying in the liquor.

- ✓ Dyes with lower P^H dependency are fixed irreversibly i.e. when other dyes are offered portion wise for the 2nd step; the previous dyes shall not be leached out**.**
- ✓ Formic acids are often preferred for acidification because of its high volatility on drying. But if we prefer other less volatile acids like sulphuric, the leather will stay longer at this lower P^H & hence chrome and other materials including dye may leach out.
  a. Addition of formic acid can be in :
     - ➢ One portion only if dye is extensively absorbed /exhausted/
     - ➢ Several portions if dye is still available in the dye bath to get levelness

  b. Running time after addition of formic acid depends on thickens & P^H valve of leather. If running time is too short, poor fixation & unsatisfactory levelness of shade will result (~ 15 minutes after the last portion offer)

  c. Fixation with cationic products (e.g. **Selafix WS from TFL**) should be used in fresh bath; i.e. the fixing bath should contain least amount of dyes, as other wise, the fastness to wet & dry rubbing is impaired

  d. Basic chromes can be used for fixation, too, by metal coupling method.

4.7 Dyeing Practice

Generally we can categorize dyeing practice into the following groups**:**

1. Dyeing of Vegetable Tanned leather:

E.g. for bag leather, fancy leathers, shoe lining etc.

- The leather at P^H ~ 5.0 is warmed to $45^O{}_C$ & floated to ~ 200%
- Dyestuff is weighed out (usually 0.5% of anionic for tan color) pasted, & dissolved in sufficient hot water to make less aggregate
- Add slowly to the agitated dye bath
- If you need level dye, add in several portions
- Running time ~ 40 minutes or more if you need better penetration
- The dye bath can exhaust by itself if the dyestuff is in small offer or use formic acid (dilute 1:10) & run for 20 minutes & check the P^H to be 3.7-3.8. Usually the common estimate of the amount of acid offer is ½ of the percentage of dye offer.
- If you need to get strong or deep shades the amount of anionic dye shall be > 3 % & topping with 0.5 % basic dye may be necessary
- Here to be safe, drain the anionic dye media & proceed with a fresh bath for topping ; but the result may show poor light fastness
- So, as an alternative to topping, retan the leather with cationic mineral tanning agents (Cr, Al, Zr) and /or with cationic resins by following the steps :
  - ~ 2% anionic dyes …… run 30’
  - Acid exhaustion …….. run 20’
  - Cationic retan (~ 1 %) run 10’ or 2%basic chrome run ~run 40’
  - 1 % anionic dyes run ~ 20’ and finally fix by acids

=>This method gives better light fastness than cationic dye topping**.**

2. Dyeing of Chrome Tanned Leather:

a. from Wet Blue

- After retanning or in the retanning media main dyeing can be done**.**

i) **Pale shade:** For pale shade **0.25—0.5%** dye is enough /based on shaved weight/. Then dyeing can be started at~30--40ºc with a float length of~300% for ~45 minutes at a speed of ~16 RPM.

  - Around the end of the process the temperature is raised to ~ $55^{O}{}_{C}$ and acid fixation is done
  - If you are processing thicker hides (>1.6 mm) & you need penetrated dyeing, you have to control both neutralization P^{H} & the type of anionic dyes (that can easily penetrate)

ii) Full shade; For full shade keeping other things the same, the dye offer can extend up to 10% depending on the level of fullness of the shade & the float can be 150-200%

b. From Dried chrome leather (crust)

- Here the crust has to be thoroughly wetted back in drum with about 400-600% float based on shaved crust weight in the presence of surfactants (~ 1%) at ~$50^{O}{}_{C}$ with ~16 RPM for about 60 minutes or overnight (but latter with low speed or stationary**)**

- Then using ~1.5% NH_3 solution (to~7.5=P^{H}) &~ 300-500% float at ~$30^{O}{}_{C,}$ dyeing will start with ~16 RPM**.**

Mostly Crust dyeing is important for suede, glove, garment or other full shade leather types, because by drying, the affinity of leather to dye can be reduced & hence good penetration & leveling can be achieved**.**

Especially for the suede products, the dye offer is too much that can extend from 10-28 % based on dry weight, or area if the leather thickness is thinner (to get better color consistency)

=> Thus longer drumming (60-120 minutes), portion wise addition of both dyes & acids, and dye intensifying cationic groups are important**.**

- In addition sandwich (topping) can be used for leather that don’t need strong care to fastness properties e.g. shoe suede.

3. Methods of Dyeing

Nowadays, the common dyeing methods include**:**

1/ Drum dyeing/drum, mixer and chambered dyeing machines/

They are used for

- ✓ **dyeing in hot float:** most frequently used methods for processing deep shade and drum used to not only to keep or maintain the temperature but also develop heat as mechanical action and its different parts as pegs and shelves (You can’t do this by paddle**/.** Usually its speed is ~ 16 – 20 RPM during dyeing**.**
- ✓ **Dyeing without float:** helps to accelerate penetration /in short time before temperature development, <25^{0}C/ and hence good levelness**.**

- ✓ **Dyeing in steps (sandwich dyeing i.e. anionic dye – cationic dye – anionic dye/.** By this method**,**
  - ➢ Depth of shade can be improved**.**
  - ➢ One can use acid or cationic auxiliaries to improve shade, levelness and fastness at each step (or between two dyes additions**/**
- ✓ **Effect dyeing:** producing cloudy, patchy or marbled dyeing with two- or multi--tone effects by creating penetration difference of dyes or media variation or manual knitting of skins**.**

2/ **Spray Dyeing (using spray Gun):** only grain side spray**.**
It is an application of dyes to crusted leather by means of compressed air**.** It is common to aniline leather finish together with surfactants/penetrating agents/, organic solvents and binders. The dyestuff type is usually the larger molecular size of Premetallized **1:2** complexes to give leather bright and natural appearance that can't be achieved by pigments**.**

3/ There are other dyeing methods like paddle, curtain, tray dyeing etc but are not common for leather dyeing because of different reasons**.**

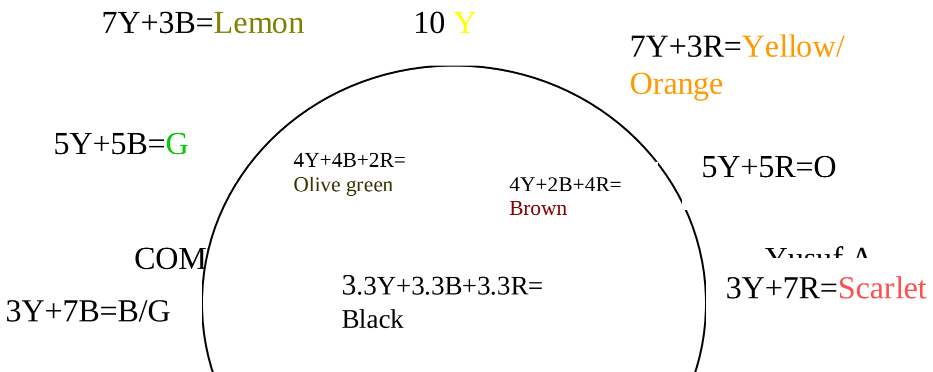
4. Color Matching

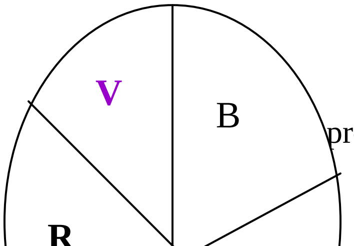
- It is the adjustment of color depth and shades according to the sample requested by customers or designers or who forecast color fashions.
- Knowledge of color is essential to develop the skill of color matching.
- Color is the composite reflected/emitted light out of the total visible light spectra. Out of these elements of spectra, yellow, blue and red are called primary colors for dyes, pigments or paints. **=>Any other colors are the blend /mix/of those primary colors.** They are so because they are the base for the formation of any other colors but either of it can't be formed purely by any combination**.**

- In order to see colors, light, reflecting object and observer should exit**.**
- In the color triangles, colors opposite one another are called complementary colors. Complementary colors are part of reflected light spectrums except those parts of light spectrums that are absorbed and vice versa**.**

=>Dyeing of leather is a process of treating it with substances /dyes/ capable of absorbing some fraction(s) of light in the color spectrum and emitting/reflecting, or transmitting/absorbing of the rest as viewed on the treated leather.

Let's see diagrammatically (as e.g.)





From the region,

R + B = V
R + Y = O
B + Y = G
R+Y+B=WHITE=> all are reflected.
R+Y+B=BLACK=>all are absorbed

Note that the symbol'**+**' mean a composite reflection at a time, except for black which is total absorption**.**

From color experience or from the above mix,

R is opposite to **G** or there is wider wave length difference **=>** the latter can kill the former or vice versa, due to that while one is reflected the other is absorbed.

Y is opposite to **V =>** the latter can kill the former or vice versa

B is opposite to **O =>** the latter can kill the former or vice versa

Color matching can be done based on these facts/principles.

🟨	🟦	🟥	🟩	🟧	🟪	⬛	■	🟫	■	■	■	■	■	■	■	■	■
yellow	blue	red	green	orange	violet	black	Grey 50%	brown	tan	Navy blue	Olive green	pink	indigo	rose	lime	cyan	magenta

E.g. If the brown we have is too orange, then add to it a little blue

If the brown we have is too red, then add to it a little green

If the blue we have is too green, then add to it a little red

NB:1. Any two colors (one primary and the other secondary), which when mixed can produce white are called complementary colors**.**

2. Orange, green and violet colors are the best examples of the secondary colors produced by equal proportions of the respective primary colors; while brown, navy blue and olive colors are the best examples of tertiary colors produced by the proportion of **4R+4Y+2B, 4B+4R+2Y *and* 4Y+4B+2R** respectively**.**

3. *"*To approach the theoretical primaries, the red should be quite bluish (magenta); yellow should be slightly greenish and blue should be cyan*"*

=>If such primaries could be procured, it can be possible to produce any color by combining two or three of the primaries in various proportions; and equal proportions of those three dyes could only give black shade (if all colors are totally absorbed) but if only partial but equal proportions are absorbed and hence other equal proportions are reflected, the resultant color is grey).

Thus, no commercial dyes or pigments meet the requirement of pure basic/primary colors of R, Y and B /. It is theoretical or work only for light spectrums in vacuum.

In order to satisfactorily match a particular color on leather the dyer should adopt the following steps: (It is seldom possible to match a given shade by using a single dye)

a) Critically compare and contrast the depth and shade of the sample to be color matched with the color of shade cards of the dyes you have in the stock and short list those you assume best fit for the purpose.

b) Select the appropriate dye mix with proportions that suit the nature of tannage and the type of leather to be dyed. The dyes mix should have **compatibility** (equivalent amount and nature of charges) otherwise the expected color from the mix may not be achieved. Besides the nature of tannage affects the strength of the shade expected**.**

c) Decide on those dyes, which in combination, will produce the required depth and shade effect taking into account such properties of the selected dyes as level dyeing, fastness, exhaustion and, of course, penetration. E.g. If we plan to get a brown color using the formulation 4y + 2B + 4R, and if Y and B have poor penetration power than R, then the resultant color on **surface** will be 4Y + 2B which is **blue-yellow,** not brown, and **reddish inside**)**.**

d) Having determined the above steps, one can combine the dyes in appropriate proportions quantitatively that will produce the color required on the leather and start to test color matching at small scale level.

Practically,

1/ the majority of the brown shades can be matched by combining, in various proportions, a yellow brown, a red brown and a dark brown dyestuff types available in the market**.**

2/ If suitable dark browns are not available in the stock, matching trials may be restored by adding blue, black (only a little) and green or grey as shading dye to obtain the desired brown**.**

3/ Pastel colors are shaded or dulled by adding grey or better, by adding a little dark brown than black**.**

Although color matching can be done by the aid of computers, in the field of leather, we still have to depend on the experience and personal skill and judgment of the dyer due to:

- tanned leather are not always white (don’t lend themselves to rigid instrumental instruction)
- Various tannage we use can influence coloring and complicate matters in respect to penetration, uniformity, depth, brilliance etc**.**

After color matching process, color assessment/uniformity, depth and shade/ called **dye trial** should be done. But it should not be done:

- In a room with colored wall as reflections from the wall may sill the color or undertone which then actually influence in your vision to the color of the product (use grey wall)

- Under wet stage or before appropriate crusting as different dyeing methods and crust preparations (like staking or shaving) can influence the existing shade. (wet leather is always darker or deeper in shade than the dried one, may be, due to higher reflecting power of water)
- Under light sources that has tendency to vary in its composition.

N.B:

- Sunlight at mid-day (North light) is an ideal light source for color matching assessment
- Mercury light is too bluish
- Tungsten light is too yellowish
- Xenon light is almost white light which is better than other artificial light sources for color shade assessment

External Factors for color shade Difference for dyed leather:

- Hot & rapid drying give strong shade (especially for vegetable tanned leather)
- Fatliquoring may strengthen or lighten shade according to the order of addition
- Staking or stretching weakens color shade
- Glazing and Hot plating strengthen shade
- Buffing can remove the surface shade (especially if penetration is poor)

5. Terminology of Color Matching

1. Undertone or cast = a perceptible inclination of one color towards an other

E.g. a blue color may have a slight tinge /inclination/ of reddish cast.

=>There may be observable red color on the blue base.

2. Hue It is a general /common/ name for colors but to distinguish one color from another we say red, yellow, blue, green etc.

=>It refers to the specific /predominant/ wave length range of the stimulus

3. Saturation: signifies the level of intensity, depth or vividness of the hue.

a. **Depth /Intensity/:** implies more tinctorial value /color strength/ requiring additional amount of dye for deepening the color /hue/

b. **Shade:** darkness or lightness value of the color.

NB: Deepening of color (intensity) **≠** darkness of color /shade/

↓ ↓

A deep color has more tinctorial strength **≠** a dark shade contains more black dyes

c. **Brightness /Brilliance/=** color lacking blackness or greyness which is the other end of darkness

=> free from dirty color.

E.g. If we match color from **equal** portions of R& Y, we get bright orange color. But if we add **some** blue, we end up with a brown (= dirty) color.

=>In matching colors intended to be **bright**, care should be taken to see that no dye that is complementary (opposite color in the triangle) is offered into the mix.

=>Brightness can be obtained by adding colors **adjacent** to the required color, not the complementary one.

d. **Additive color mixing:** If two or more light sources or rays of different hues are added by being directed to the same white surface/ that can reflect all without being selective/, the color experienced would be different from that elicited by either hue alone. E.g. If yellow & blue lights of equal intensity illuminate the same dress, it will look green (it is not because of selective reflection, but because of wave lengths / hues mixture).

e. **Subtractive color mixing:** It is based on the **selective removal** of wave lengths (hues) or filters from light spectrum to produce a different color.

Common examples are dyes, pigments, inks etc dyed /pigmented on non white surface. Thus, if red dye is applied on a body /non white/ it reflect red while absorbing all other wavelengths, not reflection.

=>Here mixed dyes & pigments are applied & the color result is the results of both **absorption & reflection,** not hues mixture.

4.8 Process control

As usual to get the required quality (or to achieve the set objectives for the leather in general or dyeing in particular) different optimum process parameters should be controlled.

These include:

1. Temperature limits: during dye offer & fixation
2. P^H limits during dye offer & fixation
3. float level
4. Amount of dye /weighing/
5. Ways of addition (powder, paste and/or dissolved)
6. process time
7. Mechanical action
8. Penetration
9. And finally, levelness, depth, covering and fastness

5.0 Fatliquors and fatliquoring process

Introduction

One of the main natural constituents of the raw or untreated skins is oils & fats that make the former flexible, heat resistant and energy source.

But, these natural fats & oils should be removed mechanically (fleshing, scudding) and chemically by degreasing for the following reasons:

i) The Presence of them can accelerate skin degradation/rancidification/in storage of pickle or wet blue

ii) They are not the components of the ultimate leather structure

iii) The fat layers prevent chemical penetration during tanning, retanning, dyeing etc

However, the undesired consequence of removing of these natural fats /oils is that the leather can become stiff after drying, due to sticking/gluing or adhesion of fibers**.**

Thus in order to make the skins or leathers flexible, less stiff or soft after tanning, retanning & dyeing, artificially applying of fats & oils (technically called **fatliquoring** is important**.**

5.1 Definitions:

i) Fatliquors are oils, fats and waxes, synthetic or natural, plus associated products, prepared in some way so that they become **emulsifiable in water** and suitable for use on leather in a water float**.**

- Oils/fats are **esters** of higher fatty acids (**C16--24**) and glycerol. Thus, specifically the ester formed is called **glyceride**. The fatty acids can be saturated or unsaturated. The difference between oils & fats are the formers are unsaturated /drying oils/ and liquid at room temperature, **MP** less than **$20^{O}{}_{C}$** & the latter are less unsaturated solid or viscous and its **MP** is above **$20^{O}{}_{C.}$** But they are similar in chemical structure (because both are esters, except paraffin oils/fats.)
- The unsaturated oils /fats can be hydrolyzed/ oxidized/ by attracting moist air (**O_2**) & hence become rancid (decomposed into smaller fatty acids) with offensive smell
- Waxes are esters of polyhydric /monohydric alcohol of higher molecular weight, not glycerol /with higher fatty acids.

=>The fatty acids used are almost the same as oils & fats but the alcohols completely differ. Waxes are mainly used at finishing stage for filling and plate release than during post tanning operations.

SOURCES OF OILS/FATS/WAXES:

- There are a lot of **natural fatliquors**/fats & oils/ , such as**:**
  - **Vegetables:** e.g. nut oil. Olive oils, coconut fat, carnua wax etc.
  - **Animals:** e.g. neats foot oil, mutton tallow, lecithin oil from egg yolk or protein. Some vegetable oils also contain lecithin which is characterized by the presence of P and N. But the presence of N without P is neats foot oil from protein.
  - **Fish:** e.g. Sperm whale oil, cod liver oil.

Structurally:

i. $(CH_2)3(OH)3 + 3RCOOOH \rightarrow CH_2COOR\text{-}CHCOOR\text{-}CH_2COOR$

↑Glycerol ↑fatty acid ↑ester/oil or fat/

ii. $R'OH + R''COOH \rightarrow R'COOR''$

↑Fatty alcohol ↑fatty acid ↑wax/ester

- **Synthetic oils:** e.g. paraffin waxes, mineral oils, hydrocarbons of acyclic and cyclic petroleum origin treated with chlorine or sulphochlorinated ones. If we become more specific, mineral and synthetic oils are quite different, chemically, from fats and waxes. Synthetic oils are artificial oils, not analogous of natural oils/fats, usually hydrocarbons, chlorinated or sulphochlorinated, distinguishable from mineral oils by the fact that they don't fluoresce under UV rays; and usually detected by the presence of chlorine/copper wire test/. However, mineral oils are obtained from petroleum crude, wholly unsaponifiable or alcohol insoluble aliphatic hydrocarbons/not aromatic as it may cause yellowing in light rays/, before the treatment of them by the associated groups.

- The so called associated products include **sulphate, sulphonate or sulphochlorinate groups.**
  - The bond structure of sulphated groups are represented as**– C- O – S: *splittable***
  - Sulphonated /sulphited/ bond structure as **- C –S – O- : *unsplittable***
  - **Sulphochlorinated bond structure as** $\overset{Cl}{\downarrow}$ **C – S – O-: *unsplittable & with high anionic final group***

=>These groups make the fats/oils **emulsifiable**: Mixable or miscible with water

=>The oils can be dispersed into small droplets /micelles/, giving a white milky or yellowish appearance**,**

=>Thus emulsion is **heterogeneous stable** mixture of two or more liquid substances. This can happen due to the introductions of those groups of sulphates, sulphites, sulphonate or sulphochorinates, by treating the oil/fat with sulfuric acid, sodium meta-bisulphite in the presence of oxygen, and chlorination in the presence of UV light respectively.

ii) Fatliquoring.

- It is a process of coating the surface of fibers (or including the interior fibers for soft leathers) of leather with a thin layer of oil/ fats or **oil-in-water emulsion** of oils**.**
- It is a treatment of leather fibers with fatty substances emulsifiable in water which are introduced into interfibrilar spaces in an aqueous float**.**

5.2 Purposes

The main objectives of fatliquoring processes include**:**

- To give the leather the **desired softness**/ to avoid hardening by drying / & handle i.e. full and round /properties at the same time
- Correction & control of the physical properties (Additional strength) like tensile, tear splits strength & elongation, extensibility /run or stretch/ abrasive resistance.
- Wetting properties or water repelling capacity, water proofness (oils /fats & waxes are generally, water repellent products)
- Permeability to air & water vapor, water absorption & moisture storage capacity by splitting of the fibers
- Resistance of thermal & electrical conductivity & chemical attack
- To make slide fibers one an other as the leather made flexed and avoid breakage in bent
- Reducing of leather density (by splitting or separation of leather fibers)

=> For producing light weight leather => roundness property => fluffy effect

Emulsion Mechanism: Emulsion formation or emulsification is a means of enabling water insoluble materials to be dispersed in water, without readily settlement.

The Classification of Fatliquors *EMULSIONS*

As seen above**,** no emulsion means **Immiscible**; milky appearance means **unstable emulsion** and a slightly yellowish appearance indicates **stable emulsions**.

Natural oils & water are **immiscible** because oil particles are held up together by its own natural cohesive forces which are higher than the adhesive forces that can exert towards water molecules**.**

Definition of Terms:

i. Surface Tension: An attractive property or power of the surface of liquids due to cohesive forces/attractive between similar molecules**/**

=>These forces make the molecules to form surface film

=>It makes molecules difficult to move or pass through the surface than to move them when they are completely submerged**.**

=> Different liquids has different surface tension values

e.g.: Cold water has surface tension ~ 72.8 dyne/ cm
: Ethyl alcohol has surface tension ~ 22.3 ,,
: Mercury has surface tension ~ 465 ,,
: Hot water has surface tension ~ 60 ,,

=>Hot water has good wetting effect than cold water

=>that is why emulsification of oils/fats are done in hot water

ii. Adhesive forces: The attractive forces between different or unlike molecules, e.g. between sulphated fat molecule & water molecule

iii. Surfactants/wetting agents/: chemicals having hydrophobic & hydrophilic ends & that reduce surface tension (reduce cohesive forces) of a given liquid substance

E.g: foaming agents, emulsifiers, dispersants etc.

N.B1: In order to make an oil/fat or fatliquor self-emulsifiable, it is necessary to chemically modify it by attaching a water solublizing group. As it is mentioned, in the case of fatliquors, this is usually sulphate, sulphonic acid or chlorination.

N.B2: In fatliquor, not all the oil molecules are made emulsifiable by this method. If this were the case, the oil would be **soluble** and unable to attach or react with collagen fibers and acts become in effect a detergent or wetting agent.

iv. Mechanism of surface Tension Reduction: In contacting the surfactant molecules & the water surface, the hydrophilic group of the surfactant can be readily attracted/hydrated or solublized / by water molecules found on the surface but the hydrophobic group are not only slightly repelled by water molecule but also attracted by the aggregate organic part of the surfactant.

However, the attractive force component towards water surface is slightly higher and should be higher, due to the degree or amount of associated groups.

=>Part of the surfactant molecule (s) is (are) squeezed into or through the water surface due to that unequal attraction effect.

=>Gradually the surface film of the water start to break

=>Finally the whole molecule (s) submerge (s) in the form of clumped oil droplets /micelles/

=>Miscible Mixture of oils & water or (**oil-in-water emulsions** i.e. the outer phase is water) is formed which is the most required one in fatliquoring process**.**

=>To make leather soft & flaccid the oils/ fats can penetrate into the interfibrilar layers in emulsion form and then, some molecules of fats /oils should be reacted to collagen fibers to achieve non immigrant fats & others will allow not to react but **stay free** so as to get more softness (by using different mix of raw oil & treated oils)

=>In addition to being emulsifiable, to get soft leather, the fats & oils we select should have low surface tension as it can help spread easily over the fiber structures & give excellent stretch & softness. Typical examples of these types are fish oils for garment, glove, etc.

=> Fats & oils with high interfacial or surface tensions give a lower degree of lubrication; for firmer leather, dry handle vegetable oils are typically preferable**.** Here fullness & firmness should accompany with medium softness e.g. upper products.

A high viscosity oils /fats of raw fish, tallow etc fats & waxes have poor penetration.

=> They can remain in the outer surface

=> They give the leather greasy feel & have good solidity, firmness, and filling as well as flexibility properties.

=> They are mainly used in stuffing and as finishing auxiliaries rather than fat-liquoring especially for belting, harness, army upper & other

Vegetable tanned leathers (stuffing is done usually after sammying to reduce the hydrophobic effect)

N.B: After **oil-in-water** emulsion are successfully formed, protective compounds /humectants/ like starch, protein, gums should be added to prevent the re-uniting of dispersed oils in water**.**

Fatliquoring Materials

i. Mineral Oils: paraffin /alkane, alkenes/ hydrocarbons of high molecular weight fatty alcohols, synthesized from petroleum residues, which are mainly sulphochlorinated.

=> They can be made slightly or highly emulsifiable as required**.**

: They are especially used for many uppers

: They are cheap, good lubricants & reduce the danger of fatty spew formation (as they are saturated and can't be decomposed into smaller fatty acid molecules)

: They are abrasion resistant & also used for light fast leather as they are saturated paraffin /alkane**/**

: They are not recommended for leather to be solvent lacquer finished as they cause poor adhesion of solvent based films (e.g. Cellulose)

: They can be made surface and water repellent fatliquor due to their larger Molecular weight or penetrative due to their less reactive nature (of course based on degree of sulphonation). The later can help it to use for dry feel leather

: Due to their poor reactivity it may migrate out to surface

=>They need care especially for dry cleaning process/here also degree of treatment matters)

: Non-splitttable in the type of attachment & hence stable to electrolytes, cationic groups & salts etc

ii. Marine Oils: They are mainly obtained from cod liver oils & sperm whale oils.

- They are widely used for very soft & water proof leathers like clothing & glove.

  => They are powerful lubricants even cause looseness & undesirable stretch.

  However, specifically sperm whale oil can give full & round (not loose) but soft leather**.**

  The reason is that this oil, unlike other fish oils, the alcohol component is **acetyl alcoho**l, **CH_3--(CH_2)15—OH),** not glycerol. Evidently, the former is relatively higher in molecular weight and hence gives soft, round and even better light fastness and free from bad smell of leather, unlike others.
- Though generally fish oils are low priced, due to their high unsaturation they have undesired effect of light reaction /yellowing/

  =>They are not recommended for pastel shades
- Unsaturation leads to oxidation, causes bad smell to leather and high acid value due to decomposition or fat spew formation.

  =>Cares need in selecting and using it.

iii. Vegetable Oils: Mainly obtained from castor, coconut, olive, rice, soybean, palm oils etc.

: They are widely used in producing firm & dry feel leather (i.e. non greasy handle e.g. for suede, white & pale aniline.

(Greasy nap is always undesirable)

iv. Animal oils: They are mainly obtained from land animal parts as lard tallow, skins, neats foot etc.

: Neats foot oil is obtained by boiling the hooves, horns &

Shin-bones of cattle; give stearin ester which has good filling & lubricating powers with medium penetration.

=>It is ideal for high quality upper leathers.

NB: All fatliquoring materials of natural origin mentioned above, except, sperm whale oil, the alcohol group is glycerol. So their difference lies only on the fatty acid group.

Composition of Fat liquor Mixes

Fatliquor consists of aqueous liquid containing oil/fat in a state of fine dispersion. Thus it is found in a **3-phases system:**

a. **The dispersed phase** i.e. the oil which can lubricates the leather (e.g. castor oil, sperm oil, neats foot oil paraffin oil)
b. **The water/ dispersion medium/** i.e. the carrier of the oil droplets into the leather
c. **The emulsifier (S)** which disperses the oil & stabilizes the oil-in water emulsion. They can be anionic, cationic, & nonionic wetting agents/detergents/ as per the type of charge of the oil it self.

Some Analytical Values That Specify the Quality of Fatliquors, oils/fats:

1. Acid value/AV/: It is the proportion of free fatty acids in the oil/fat stock.

: A high acid value of oil /fat indicates a stale oil/fat or stored under improper condition.

=>The existence of high free fatty acids can lead fatty acid spew formation.

2. Iodine value/IV/: It indicates the degree of Unsaturation of the constituent fatty acids in an oil /fat (unsaturated organic compounds can absorb $\mathbf{I_2}$)

E.g.: None drying oils have I-value below 90 %(This type of oil can have only1-double bond).Semi drying oil can have iodine value between 90-140 **%.**

Drying type of oil can have IV above 140%.

=>It can have higher unsaturation =>too much yellowing effect due to oxidation.

=>It is not recommended to use for white & pastel shades or aniline finish.

3. Saponification Value/SV/: The number of **mg** of **KOH** required to neutralize the fatty acids (before esterification) to form soap.

: It is an indication of the size (MWT) of the (fatty acids) in the oil /fat molecule.

: The smaller the SV in a given mass, the higher the MWT of fat/oil e.g. Butter has higher amount of **SV** than tallow.

=> Butter has smaller Mwt than tallow.

4. Ester value=SV-AV: The relative measure of the amount of esters /=oils & fats/present in fatliquor.

5. Acetyl value: The measure of free alcoholic groups present in oils /fats/.

=>It has analogous purposes as Saponification value.

6. Degree of Sulphation /Sulphitation/: Can be expressed as percentage of $\mathbf{SO_3}$ combined with oil, or the percentage of neutral oil present based on dry oil. The greater the degree to which the oil is sulphated, the less will be its lubricating /softening/ effect due to the consequent reduction in neutral /hydrophobic/ oil content.

=> But, the greater the sulphation, the greater the emulsion & its stability.

=> The greater will be its penetration into inner fiber zones.

=> Reduce the oiliness /greasy effect of the grain & flesh, and preferably used for suede.

Look at the following example (based on dry oil):

Approximate % of SO_3	**% Neutral oil**	**Common usage of the oil /fat**
1-2	75-90	Surface oiling of heavy chrome Boots (army shoe), vegetable tanned leather esp. for stuffing => Waxy type
3-4	50-70	General purpose for fat Liquoring soft upper, clothing or Gloving for chrome tanned leather
5—6	30—50	for very soft chrome leather (dressing), garment and Glove blends
6-7	18-30	high emulsion stability, capable of Giving dry surface handle &low lubrication =>For suede and &for admixture with Other oil to increase emulsion stability &penetration

Classification of Fatliquors Based on Chemical Modification & Origin:

1. Soap emulsion: Essentially a saponified fat reacted with an alkali such as soda, potash or ammonia. It is the oldest type of fatliquor with coarser emulsion or dispersion with poor emulsion stability, and hence poor penetration.

=> It is recommended for mainly surface fatliquoring with greasy surface feel**.**

: It is mainly used in P^H range **>3.8** as it is easily broken by acidic chrome leather; don't use below this P^H range**.**

=>Otherwise, the anionic charge on the fatty portion is largely neutralized with the acidity of the leather**.**

=>The greatest problem is that it's very sensitive to acids, salt & hard water and hence less frequently used**.**

2. Sulphated oils: Here the emulsifier is sulphate radical attached to the fatty acid glyceride through **–C-O-SO_3 group (R.O.SO_3 Na)**

=> Although it is less sensitive to acids & hard water, than soap dispersion, still sulphated oils are vulnerable to hydrolysis by mineral acids and salts/e.g. chrome salts/

=>If chrome bathed leather is fatliquored with sulphated oils, there can be precipitation**.**

These types of fatliquors are produced by treating the oil with a given amount of $H_2 SO_4$ under controlled conditions of (low temperatures due to exothermic reaction) & amount of agitation followed by washing off the acid and the oil mixture with a salt solution to remove excess H_2SO_4. Then the sulphated oil is neutralized with Na, K or NH_4 hydroxide until the desired P^H achieved**.**

=>After the process, the product mixture may consist of true fatty oil sulphates (mainly as emulsifier, not as lubricant), neutral fatty oil (mainly for lubricating or softening for lubricating or softening) & fatty acids (undesirable).

Based on degree of sulphation (can make the oil poor, medium or better penetrative) & the type of oil sulphated, it can be used for different leather types especially for firm /upper/leather, as it imparts filling, preserves grain firmness as well as softness**.**

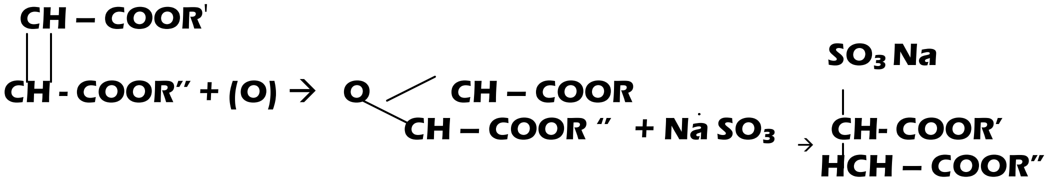
3. Sulphited /Sulphonated/: It is produced by oxidative sulphitation**.**

: The oil (heated to 60-80 ^{O}C) is thoroughly mixed & reacted with a solution of $NaHSO_3$ while the mixture is well aerated**.**

=>The sulphur atom is attached to the fatty acid carbon atom/chain as

(-C-S-bonding) or R-SO_2O-Na.

: I.e. unsaturated oils (e.g. fish oils) + O_2 + $NaHSO_3$ → Sulphonated/sulphited/ oil.



=>Unsaturated fish oils /cod & sperm/ are sulphited & oxidized in this way**.**

=>This type of products not only stable (unsplittable) to any electrolytes (mineral acids, polyelectrolytes like chrome, aluminum & hard water ions like Ca, Mg) but also become light fast as it is oxidized already**.**

=> It can avoid the draw backs existing in sulphated oils mentioned above**.**

=> It can produce more stable, low polarity fine micelles emulsion and becomes more penetrative. Micelles are clumps of oil/fat globules with two different tails, hydrophilic and lipophilic ends.

=>It can be used in pickle, tanning or any retanning bath as it is stable to opposite changes**.**

=> It is preferable for suede (has no surface greasy) & for soft leather (glove, garment, softy as it has better penetration& hence good lubricating effect).

But they don't give the same fullness & roundness unlike sulphated oils which have medium penetration and good filling power**.**

4. Polymer Fatliquors: They are high molecular & viscous acrylic syntan.

=>They give leather retanning & fatliquoring effect at the same time**.**

=>They have also water repellency property, grain tightening & low fogging effect e.g**. Lubritan WP of ROAM+HAAS.**

=> They give higher light fastness, heat resistance with less volatile content**.**

=>They are Important for the manufacturing of automotive leather (as no fogging effect) & garment (where low density is required & resistance to dry cleaning).

5. Solvent Fatliquors: It is based on introducing the oil into the leather with high boiling organic solvent ***like alkyl ethers or acetones.***

=>The solvent will displace the water existing in the leather leaving the solution of the solvent & oil/fat**.**

=>But as the solvent slowly evaporates, the oils remain absorbed deep in fibers.

=> Deep penetration will occur, and gives good softness.

=> It is commonly used in particular for maximum softness, e.g. gloving, clothing softie & milled softies.

6. **Synthetic fatliquors:** They are obtained /produced other than vegetable or animal origins.

=> They are based on saturated mineral oils & others such as long aliphatic alcohols (as wetting & dispersing agent) & fatty amines (**R-CO-NH$_2$**) or amides (as amphoteric dispersing agents) derived from triglycerides.

Most of these oils are modified by sulphation, sulphitation, sulpho-chlorination or ethoxylation.

Comparing with fatliquors based on **natural oils**, the amount required for the same level of softness is smaller.

=>Leather is less loaded with fats/oils to achieve the required softness.

Synthesis Procedure:

E.g. $\text{Mineral oil}+SO_2+Cl_2+h\mu \rightarrow$

$$R\text{-}\overset{Cl}{CH}\text{-}SO_3H$$

=>This makes emulsification & reaction to collagen easy/ possible.

=>Those aliphatic alcohols can dissolve natural fats remaining on the tanned skin & well disperses the fatliquor.

=>Based on the degree of modification (chlorination or sulpho-chlorination) they can form fine emulsion, stable & hence good penetration. **As it is saturated,**

=>It gives good light fatness, doesn't cause any fatty spew, rather can remove any fatty spew due to the presence of dispersing agent alcohol mixture.

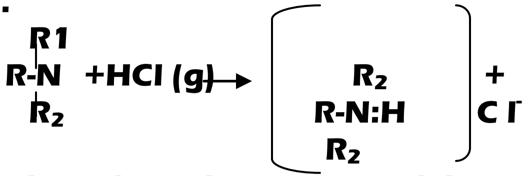
=>It can be used with cationic, anionic, multi charge fatliquors or reaction media.

E.g. paraffin based synthetic products can give leather water proofing, soft & velvety feel for softie leathers.

7. Cationic Fatliquors:

They are fats & oils which are treated with organic bases such as polyamines & then solublized with an acid.

=>When the aqueous solutions of these products ionize the charge on the fatty portion is positive.



$$R\text{-}\underset{R_2}{\overset{R1}{N}} + HCl\,(g) \rightarrow \left[R\text{-}\underset{R_2}{\overset{R_2}{N}}\text{:}H \right]^+ Cl^-$$

=>Such products show strong stability in the presence of acids, and mineral tanning agents.

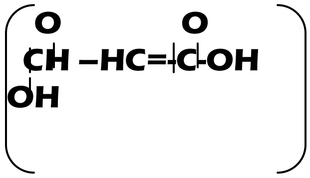
=>It can be used in such P^H media at pre-and /or top fatliquoring where ordinary anionic fatliquors are non-stable.

=> It can give extra surface softening, grain elasticity & break of leather.

8. Fatliquors or other products specifically used for **water barriers:**

i. Silicones: Methyl poly silcoxane 
$-\overset{Me}{Si}-O-\overset{Me}{Si}-O-$

ii. Metal complex oils: chrome or aluminum complex with longer chain fatty acids e.g. Chrome stearate

iii. Succinic acid 
$\left(\overset{O}{\underset{OH}{C}}H-HC=\overset{O}{C}-OH\right)$

The carbonyl group reacts with protein amine & the hydrocarbon chain repel water

5.3 Process variables, Practices and Controls

To ensure that fatliquors give generally uniform & consistent results under varying conditions, we have to follow up some basic variables as guidelines**.**

1. Preparation of fatliquor emulsions: It plays an important role for well exhaustion & penetration of oils.

—- Anionic fat liquors are designed to produce **oil- in- water** dispersion (not the opposite) by adding **oils -to -water** of about 5 fold at~ 55 $^{O}{}_{C}$, not greater than 60 $^{O}{}_{C}$ nor less than 50^{o}c . The amount of water can be up to 10 fold in extreme media like pickle or mineral tanning**.**

——If we use **'water-in-oil´** emulsion, we may face:

***** Coarser emulsion and

* Less stable emulsion

N.B: If the amount of water for emulsion is less than the minimum limit, the reverse (water-in-oil) emulsion may occur & if the temperature is above $60^{O}{}_{C}$ the micelles structure may be disturbed as well as oil charring /decomposition/.

2. Temperature: Fatliquoring temperature for both emulsion & in the drum should be between $50\text{-}60^{O}{}_{C}$ for chrome leathers & at ~45º c for vegetable tanned lathers. Otherwise, the above undesirable conditions can occur.

=>Micelle aggregation disturbance at higher temperature or poor emulsion at lower temperature, especially those fatliquors which poorly or minimally treated by emulsifying chemical groups, can occur**.**

3. Length of Emulsion standing period: The prepared emulsion should be used soon or added to the drum as soon as possible.

- Don't use live steams to emulsify fatliquors, rather, warm the water before adding the oil, then add the oil to the hot water, agitate it well & then use it soon. If you use live steam, there may be local over-heating & hence micelle structure destruction can occur**.**

=>It can less emulsion stability

4. If you use more than one fatliquor: Blend or mix well before emulsifying or don't try to emulsify separately.

5. Water Quality: use soft water as possible

: If you use hard water, don't forget that you are losing ~10-15% of your fatliquor

6. Over emulsion or over stabilization: presence of excessive emulsifies (high degree of sulphation or sulphitation) reduce exhaustion power or wastage of fatliquors can occur as the emulsion will be more active in the emulsion media & hence less reactive to the leather fibers

7. PH Level: For anionic fatliquors (in chrome tanned leather) higher P^H (>5) improves penetration but poor exhaustion; for lower P^H (<4), the reverse occurs i.e. poor penetration but surface fixation exists.

8. Mechanical Action: During fatliquoring, continuous agitation of drum speed ~16 RPM can help emulsion stability and diffused penetration

9. Drumming Duration: It depends on the type of leather, type of fatliquors thickness of leather, amount of fatliquor & the desired fatliquoring effect (surface or soft & dry feel) . But, generally, it takes about 45-60 minutes**.**

10. Float length: A float length of about 150% is used or the dyeing or retanning float can be used after the later processes are well exhausted.

- Shore float facilitates penetration although there may result in uneven fatliquoring.

- Long float helps to get uniform /level/ fatliquoring but with a difficulty of exhaustion**.**

11. **Amount of fatliquors**: Over-fatliquoring can cause undesired effects like looseness and incurring of costs; poor fatliquoring doesn't give the required quality properties like softness, fiber splitting, tensile and tear strength, water proofness, thermal resistance, porosity etc. Besides, a single product type may not give all these desired properties and hence the formulation should include blends of fatliquors **from different origins**.

Generally, the recommended sum of 6-8% fatliquors for normal upper, 8-12% for softie upper, 14-18% for dress glove, 14-16% for nappa garment, 12-14% for upholstery etc. based on wet blue weight may be required. It is also important to know the main type of fatliquor out of the blends as per the properties you desired.

12. Fixation: As it is well known, fatliquoring is mainly the last stage of wet process. Thus, the ultimate fixation or chemically binding of all the used chemicals/retanning, dyeing and fatliquoring agents/ to the substrate /leather is a must.

For this duty, we can use:

- ✓ Light Organic acids/formic, mainly for mineral tanned leathers, oxalic for vegetable tanned leathers/
- ✓ Cationic base materials /unmasked mineral tanning agents, fatliquors, dispersed resins and even dyes/ for anionic treated leather
- ✓ Hot water

Reference Books For the curriculum:

o Gerard John, Possible Defects in leather production , 1996
o J.H, Sharphouse , leather technicians hand Book , 1983
o O, Flaherty, Chemistry and Technology of leather, 1978

- S.S Dutta, An Introduction to the Principle of leather manufacture , 1999
- K.T Sarkar, Theory and Practice of leather manufacture,1991
- The society of leather Technologists and chemists, Leather Technologists Pocket Book 1999

Additional:

- Hand Books of BASF and Bayer AG.
- Asomac, Tanning Engineering

Dr. E. Heidemann, Fundamental of Leather Manufacturing